



# <u>A Study on Online Banking services and its impact on Customers Satisfaction</u> with special reference to Mumbai city

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## **Abstract**

The study has been conducted in order to evaluate and examine the level of satisfaction towards internet banking services. The banking industry has been rapidly developing the use of Internet banking as an efficient and viable tool to create customer value. It is one of the popular services offered by the traditional banks to provide speedier and reliable services to online users . With the rapid development of computer technology as a commercial too Internet banking can be used to attract more customers to perform banking transactions in related banks. However, the main problem of Internet banking faced by the providers is that a large number of the banks' customers are not willing to use the Internet banking services offered. This happened due to the services offered through Internet banking has yet to satisfy their customers. Customer satisfaction is an important factor to help banks to sustain competitive advantages. Therefore, the purpose of this research is to search and examine the factors which influence customer satisfaction towards Internet banking. The purpose of this study is also to observe and analyse the purpose of using internet banking, reasons for chosen internet banking, satisfaction of customers towards internet banking and to find out the problems encountered by the customers. The primary data for this study was compiled through well-structured questionnaire. An attempt was made to study the level of customer's satisfaction with E-banking services in the specified area.

Keywords: Internet Banking, Customers Satisfaction, E-Banking Services.

#### **Introduction**

Banking through electronic channels has gained increasing popularity in recent years. This system, popularly known as 'e-banking', provides alternatives for faster delivery of banking services i.e. offering, supplying and delivering banking products and services to a wide range of customers at their office or home through various electronic delivery channels via electronic devices. It is a generic term encompassing internet banking, telephone banking, mobile banking etc. It provides lot of benefits which add value to customers' satisfaction and to reach out consumers through many routes in terms of better quality of service offerings such as ATMs, telephone, internet and wireless channels which are now available to the consumers to perform their banking transactions in addition to the traditional branch banking and at the same time enables the banks gain more advantage over other competitors.





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Traditional banking involves physical branches that are located around the most populated areas to serve their clients and allow people to complete their transactions and services in person. Whereas, virtual banking or nonbranch bank does not involve any physical action that means going to a bank building, standing in a line and face to face communication. It involves the provision of fully automated banking services (such as ATMs, internet banking etc.) for customers which provides faster access, easier, convenient and secure online shopping and also makes available round the clock irrespective of the customer's location

## Definition

Internet banking, also known as online banking, e-banking or virtual banking, is an electronic payment system that enables customers of a bank or other financial institution to conduct a range of financial transactions through the financial institution's website.

Different types of online financial transactions:

- 1. National Electronic Funds Transfer (NEFT) is a nation-wide payment system facilitating one-to-one funds transfer. Under this Scheme, individuals, firms and corporates can electronically transfer funds from any bank branch to any individual, firm or corporate having an account with any other bank branch in the country participating in the Scheme. Individuals, firms or corporates maintaining accounts with a bank branch can transfer funds using NEFT. Even such individuals who do not have a bank account (walk-in customers) can also deposit cash at the NEFT-enabled branches with instructions to transfer funds using NEFT.
- 2. Real Time Gross Settlement (RTGS) is defined as the continuous (real-time) settlement of funds transfers individually on an order by order basis (without netting). 'Real Time' means the processing of instructions at the time they are received rather than at some later time; 'Gross Settlement' means the settlement of funds transfer instructions occurs individually (on an instruction by instruction basis). Considering that the funds settlement takes place in the books of the Reserve Bank of India, the payments are final and irrevocable. The RTGS system is primarily meant for large value transactions. The minimum amount to be remitted through RTGS is 2 lakh. There is no upper ceiling for RTGS transactions.
- 3. Electronic Clearing System (ECS) is an alternative method for effecting payment transactions in respect of the utility-bill-payments such as telephone bills, electricity bills, insurance premium, card payments and loan repayments, etc., which would obviate the need for issuing and handling paper instruments and thereby facilitate improved customer service by banks / companies / corporations / government departments, etc., collecting / receiving the payments.
- 4. Immediate Payment Service (IMPS) offers an instant, 24X7, interbank electronic fund transfer service through mobile phones. IMPS is an emphatic tool to transfer money instantly within banks across India through mobile, internet and ATM which is not only safe but also economical both in financial and non-financial perspectives.





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## **Review of Literature**

- 1. Dr. M. Abdul Hakeem and Y. Moydheen Sha (2015) in their analysis it was observed that particular age group have used these services, the satisfaction of the customer majorly influenced the convenience, awareness, and responsiveness. In the present technology society, most of the banking customer prefer and switch to e-banking facilities. So the banker may improve their services, loyalty to customers and their retention by increasing awareness of other age groups and concentrating on the factors contributing customer satisfaction.
- 2. A. Samsunisa (2015), The researcher has identified that different age group of customers have different perception toward the e-banking services and the usage level of these banks" customer is different so bank should concentrate on all the age group of customers for betterment of e- banking banks. It has also seen that different occupation group of customers have different perception toward the e-banking services. There are good number of customer in every group like student, service class, business class and professionals, it shows that they all are keen interesting in using the e-banking services.
- 3. Tavishi and Santosh Kumar (2013) in their study "An Empirical Study on Technology Adoption by Indian Banks" studied the factors influencing the customers for the adoption of internet banking and mobile banking in India and hence investigate the influence of perceived usefulness, perceived eases of use and perceived risk on use of internet banking and mobile banking.

## **Objective of the study**

- 1. To know the purpose of using internet banking services.
- 2. To measure the level of satisfaction of customers on Internet banking services.
- 3. To know the Socio-Demographic characteristics of the respondents.

## **Methodology**

The data has been collected from primary as well as secondary sources. The primary data was collected through a structured questionnaire whereas the secondary sources include references to number of journals, magazines and electronic information. A detailed schedule was prepared and analysed on 150 sample respondents.

## Brief sketch about Mumbai

Mumbai is one of the largest and most densely populated cities in the world with total population of 12,442,373 according to 2011 census. It is situated on the western coast of Maharashtra. Mumbai lies between 18°58'30°N latitude to 72°49'33°E longitude. The name 'Mumbai' is derived from 'Mumbai'' – the patron goddess (kuladevata) Mumbadevi of the native Koli community.

## **Data Analysis and Interpretation**

## Table 1: Customer demographic characteristics

<u>Variable</u>	<u>Type</u>	Frequency	Percentage (%)





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Gender	Male	82	54.67%
	Female	68	45.33%
	Total	150	100%
Age	Below 20 yrs	28	18.67%
	21 – 30 yrs	51	34.00%
	31 – 40 yrs	46	30.67%
	41 – 50 yrs	14	9.33%
	Above 50 yrs	11	7.33%
	Total	150	100%
Marital Status	Married	106	70.67%
	Unmarried	44	29.33%
	Total	150	100%
Educational Qualification	Graduate or above	108	72.00%
	Undergraduate	24	16.00%
	Non Metric	15	10.00%
	Diploma holders	03	2.00%
	Other	NIL	0%
	Total	150	100%
Occupation	Student	26	17.33%
	Employee	78	52.00%
	Self Employed	22	14.67%
	Professional	06	4.00%
	Home Maker	14	9.33%
	Retired	04	2.67%
	Total	150	100%
Monthly Income (in Rupees)	Below 15,000	17	11.33%
	15,000 - 30,000	72	48.00%
	30,000 - 50,000	26	17.34%
	50,000 - 1,00,000	27	18.00%
	Above 1,00,000	08	5.33%
	Total	150	100%

## Sources: Primary Data

From the above table it is observed that 54.67% of respondents are male and remaining 45.33% of respondents are female. Out of 150 respondents, a maximum i.e. 34.00% of people belonging to 21-30 yrs age group, followed by 30.67% belonging to 31-40 yrs age group, 18.67% population from below 20 yrs age group, 9.33% of respondents are from 41-50 yrs age group and lastly 7.33% of respondents are belonging to above 50yrs age group. From the sampled data, it is estimated that 70.67% respondents are married and remaining 29.33%





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respondents are unmarried. Out of total 150 respondents, it has been observed that only 72.00% of respondents are graduate or degree holders, 16.00% of respondents are Non-Graduate, 10.00% of respondents are Non-Metric and 2.00% of respondents are diploma holders.

The above table also indicates that from total 150 respondents 52.00% are employees, 17.33% are students, 14.67% are self-employed, 9.33% are Home makers, 4.00% are professionals and 2.67% are retired workers. With regard to monthly income 11.33% of the respondents earn below Rs. 15,000, 48.00% of the respondents earn in the range of Rs. 15,000-30,000, 17.34% of the respondents earn in the range of Rs. 30,000-50,000, 18.00% of respondents earn in the range of Rs. 50,000-1,00,000 and only 5.33% of respondents earn above Rs. 1,00,000.

Purpose	Frequency	Percentage (%)
Bill Payments	150	100%
Balance Enquiry	150	100%
Funds Transfer	141	94.00%
E-ticket Booking	93	62.00%
Retrieving Bank Statement	29	19.33%
Loan repayment	29	19.33%
To Order Cheque Books	21	14.00%
Opening of Term Deposit Account	17	11.33%
Access to Demat Account	09	6.00%
Others	63	42.00%

## Table 2: Purpose of Using Internet Banking

Sources: Primary Data

From the above table, it is observed that 100% of the respondents have availed E-banking service for making their bill payments online and Balance enquiry purpose. 94.00% of the respondents are using online fund transfer services followed by, 62.00% of the respondents are using E-banking services for E-tickets booking, 42.00% of the respondents are benefitted with other online related services. 19.33% of respondents uses E-banking for loan payment and to retrieve their bank statement. 14.00% customers order their cheque books online, 11.33% of the respondents have opened their term deposit accounts online and only 6.00% of the respondents have linked their bank account with demat account.

## Table 3: Classification of Respondents by their Level of Satisfaction with E-Banking

Sr. No.	Level of Customers	No. of	Percentage (%)
	Satisfaction	Respondents	
1	Highly Satisfied	82	54.67%
2	Satisfied	68	45.33%
3	Unsatisfied	NIL	0%
Total		150	100%





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Sources: Primary Data

The above table reveals that 54.67% of respondents are highly satisfied, 45.33% of respondents are satisfied with E-Banking services.

#### **Findings**

- 1. Most of the respondents are in the age group of 21-30 years.
- 2. Majority of the respondents are graduates.
- 3. Majority of the respondents are married.
- 4. Most of the respondents are employees and earning the monthly income of Rs. 15,000-30,000.
- 5. Majority of the respondents are using E-banking services for the purpose of online bill payments, fund transfer, balance enquiry and e-tickets booking.
- 6. Most of the respondents are highly satisfied with E-banking services.

#### **Suggestion**

- 1. Banks should increase their ability to control and manage the various risk elements from etransaction activity.
- 2. Banks should configure security systems and firewalls to the highest security consistent with the level of protection according to the customers requirements.
- 3. Banks should reduce the processing charges for NEFT and RTGS in order to promote more online banking transactions.
- 4. Banks have to educate their employees to give proper training to the customers to use the facilities provided through e-CRM for better usage even for the old aged customers. It can decide best user interface which is very friendly and easy to use, in order to attract more customers.
- 5. The banks should provide proper instructions and personnel assistance on how to use the internet banking to the employees and through them to the customers. The banks are investing heavily on Information technology but unless banks arrange demonstration programs for the customers and train them properly to enjoy all the services.

#### **Conclusion**

The financial sector reforms have brought about significant improvements in the financial strength and the competitiveness of the Indian banking system. The e-banking revolution has fundamentally changed the business of banking by scaling borders and bringing about new opportunities. Therefore, Indian banks need to optionally leverage technology to increase penetration, improve their productivity and efficiency, deliver cost-effective products and services, provide faster, efficient and convenient customer service and thereby, contribute to the overall growth and development of the country. However, hounded by negative issues like identity theft and phishing attacks, banks must be concerned about the attitudes of customers with regard to acceptance of online banking. In years to come, e-banking will not only be acceptable mode of banking but will





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be preferred mode of banking because of the computerization process adopted by banking sector with a vision to reach Indian banking to every citizen.

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# A Statistical Study of Trend of Female Work Participation in India & it's States & Union Territories

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#### ABSTRACT

Studying Female Work Participation Rate is one of the tools to study the trends seen in the level of work participation amongst women. This study is based on Indian Census 2011 data. The paper tries to study the level of female work participation in India and in the different States of India. States are ranked according to their female work participation and inter-state variations are measured. The female work participation of the States is also ranked by their position in the urban and rural region. The researcher also studied the difference in the female work participation and its ranking between the urban and rural population.

Keywords: Female Work Participation, Census, India, Urban, Rural.

#### INTRODUCTION

Female Work Participation is one of the indicators to study the level of progress seen in the female of any country. But it is not always true that a higher level of work participation means that the particular nation is better progressed nation. Higher work participation rate can also be due to bad economic condition of the family, low literacy level and dependency on agricultural income especially in rural areas. So a deeper study is required to draw inferences. But it is one of a major indicator to study the level of work participation by females.

Sunita Sanghi, A Srija, and Shirke Shrinivas Vijay (2015) in their research paper studied the Decline in Rural Female Labour Force Participation in India. They observed that among all the arguments, income effect, education effect and the problem of underestimation, what is left unnoticed is the structural transformation of the economy and its resultant impact on the female labour market in the whole process. With an increase in income levels of the households, a woman no longer prefers working as an unpaid worker or a helper or as a casual worker unless the work is remunerative (as in MGNREGA). However, such opportunities are limited in rural India and as a result women are not finding jobs matching their preference (regular part-time jobs close to their households). Furthermore, with low skill levels, jobs in the non-farm sector are also limited. These factors perhaps have led to the withdrawal of women from the labour force.

Sneha Menon, Dona Tomy, Anita Kumar (2019) in a study under UNDP entitled "Female Work and Labour Force Participation in India- A Meta Study" concluded that "The focus of this report has been to understand the continuing problem of low FLWP for women in India despite massive investments in employment and skill-building initiatives. This analysis reveals that it is not so much the policies that provide employment as ones that facilitate employments, which are the need of the hour.

#### WORK PARTICIPATION RATE - DEFINITION

**Work** is defined as participation in any economically productive activity with or without compensation, wages or profit. Such participation may be physical and/or mental in nature. Work involves not only actual work but also includes effective supervision and direction of work. It even includes part time help or unpaid work on farm, family enterprise or in any other economic activity. All persons engaged in 'work' as defined above are workers.

**Reference period** for determining a person as worker and non-worker is one year preceding the date of enumeration. Those workers who had worked for the major part of the reference period (i.e. 6 months or more) are termed as **Main Workers**. Those workers who had not worked for the major part of the

reference period (i.e. less than 6 months) are termed as **Marginal Workers. Work participation rate** is defined as the percentage of total workers (main and marginal) to total population.

Female Work Participation Rate is the work participation rate **observed in females**.

#### AIM AND OBJECTIVE OF THE STUDY

An attempt is made in this research paper to,

- i. To understand the level of female work participation in India in the year 2011.
- ii. To calculate the level of female work participation in the various States of India
- iii. To study the level of female work participation in rural and urban areas of all States of India.
- iv. To Rank the level of female work participation of the different States of India.
- v. To study the difference in the urban and rural female work participation of different States of India.

#### **RESEARCH METHODOLOGY**

The study has mainly used Census of India 2011 as the data source. The work participation level is calculated in the using the entire population data for India, the different States and for the rural and urban regions.

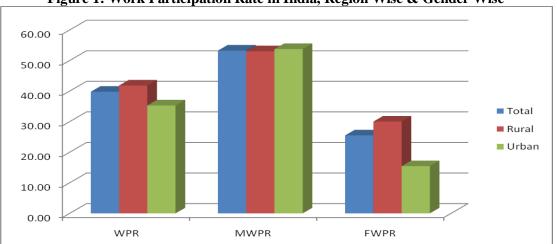
#### WORK PARTICIPATION RATE OF INDIA IN 2011

It was observed that the rate of **work participation of India is 39.80 % only**. The Male work participation rate is 53.26 % and female work participation is only 25.52 %. The female work participation is only 15.44 % in urban areas. In rural areas the level of female participation is better and it is 30.03 percentages.

Residence	Percentage of Work Participation					
	Total Workers	Total Workers Male Workers Female Workers				
Total	39.80	53.26	25.52			
Rural	41.83	53.03	30.03			
Urban	35.31	53.76	15.44			
	C au		•			

 Table 1: Work Participation Rate in India in 2011

Source: Census 2011



#### Figure 1: Work Participation Rate in India, Region Wise & Gender Wise

#### FEMALE WORK PARTICIPATION RATE IN INDIA IN 2011

Below Table gives the Female Work Participation Rate of the Rural, Urban & Total region of India and its other States & Union Territories. Also we have drawn a line graph of the three types of work participation. The overall female work participation is highest in Himachal Pradesh followed very closely by Nagaland and then Manipur.

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Table 1: Female Work Participation Rate (FWPR) in India in Rural, Urban & Total						
State	Name	RURAL FWPR	URBAN FWPR	TOTAL FWPR		
00	India	30.03	15.44	25.52		
01	JAMMU & KASHMIR	20.79	14.46	19.11		
02	HIMACHAL PRADESH	47.40	19.88	44.82		
03	PUNJAB	14.34	13.18	13.91		
04	CHANDIGARH	14.24	16.05	16.00		
05	UTTARAKHAND	32.94	11.29	26.68		
06	HARYANA	20.83	12.11	17.79		
07	NCT OF DELHI	9.72	10.60	10.58		
08	RAJASTHAN	42.68	12.03	35.12		
09	UTTAR PRADESH	18.30	11.28	16.75		
10	BIHAR	20.16	10.44	19.07		
11	SIKKIM	44.63	24.80	39.57		
12	ARUNACHAL PRADESH	39.50	21.31	35.44		
13	NAGALAND	52.26	25.87	44.74		
14	MANIPUR	42.73	33.17	39.88		
15	MIZORAM	41.86	31.05	36.16		
16	TRIPURA	26.28	16.00	23.57		
17	MEGHALAYA	34.97	23.59	32.67		
18	ASSAM	23.69	14.86	22.46		
19	WEST BENGAL	19.35	15.35	18.08		
20	JHARKHAND	34.96	10.07	29.10		
21	ODISHA	29.69	14.12	27.16		
22	CHHATTISGARH	46.29	17.42	39.70		
23	MADHYA PRADESH	39.25	15.14	32.64		
24	GUJARAT	31.95	11.35	23.38		
25	DAMAN & DIU	15.86	14.47	14.89		
26	DADRA & NAGAR HAVELI	33.39	14.66	25.25		
27	MAHARASHTRA	42.52	16.78	31.06		
28	ANDHRA PRADESH	44.65	19.14	36.16		
29	KARNATAKA	38.79	20.81	31.87		
30	GOA	22.64	21.48	21.92		
31	LAKSHADWEEP	12.55	10.51	10.96		
32	KERALA	20.24	16.03	18.23		
33	TAMIL NADU	41.22	21.78	31.80		
34	PUDUCHERRY	21.05	16.06	17.63		
35	ANDAMAN & NICOBAR ISLANDS	17.87	17.71	17.81		

Source : Census 2011

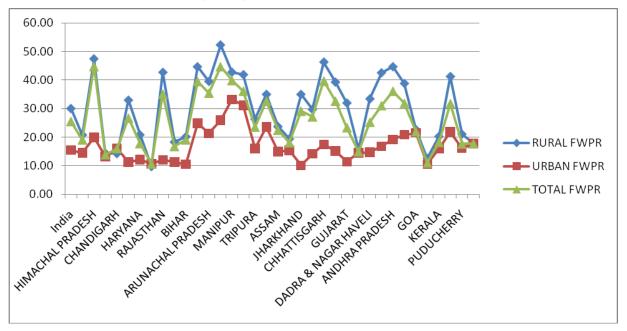


Figure 2: State-wise work participation rate of Total Areas, Urban Areas & Rural Areas

Source : Census 2011

#### RANKING OF FEMALE WORK PARTICIPATION RATE IN INDIA IN 2011

Ranks where found of the female work participation of India and its States & Union Territories. The Ranks are stated in the table below. In Urban areas FWP is highest in north eastern states Manipur followed by Mizoram and Nagaland. Nagaland has highest female WPR in the rural areas. Himachal Pradesh has second best female WPR followed by Chhatisgarh. New Delhi and Lakshadweep FWPR was observed very low in all the three categories. Punjab and Chandigarh also has low FWPR in Rural areas and Bihar in Urban areas.

	Kegion						
		RANK	RANK				
		RURAL	URBAN	RANK TOTAL			
State	Name	FWPR	FWPR	FWPR			
01	JAMMU & KASHMIR	25	24	23			
02	HIMACHAL PRADESH	02	10	01			
03	PUNJAB	32	26	33			
04	CHANDIGARH	33	16	31			
05	UTTARAKHAND	17	30	17			
06	HARYANA	24	27	28			
07	NCT OF DELHI	35	32	35			
08	RAJASTHAN	07	28	09			
09	UTTAR PRADESH	29	31	30			
10	BIHAR	27	34	24			
11	SIKKIM	05	04	05			
12	ARUNACHAL PRADESH	11	08	08			
13	NAGALAND	01	03	02			
14	MANIPUR	06	01	03			
15	MIZORAM	09	02	06			

Table 2: Ranking of Female Work Participation Rate (FWPR) in India in Rural, Urban & Total	
Region	

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16	TRIPURA	20	18	19				
17	MEGHALAYA	14	05	10				
18	ASSAM	21	21	21				
19	WEST BENGAL	28	19	26				
20	JHARKHAND	15	35	15				
21	ODISHA	19	25	16				
22	CHHATTISGARH	03	13	04				
23	MADHYA PRADESH	12	20	11				
24	GUJARAT	18	29	20				
25	DAMAN & DIU	31	23	32				
26	DADRA & NAGAR HAVELI	16	22	18				
27	MAHARASHTRA	08	14	14				
28	ANDHRA PRADESH	04	11	07				
29	KARNATAKA	13	09	12				
30	GOA	22	07	22				
31	LAKSHADWEEP	34	33	34				
32	KERALA	26	17	25				
33	TAMIL NADU	10	06	13				
34	PUDUCHERRY	23	15	29				
35	ANDAMAN & NICOBAR ISLANDS	30	12	27				
	Source - Census 2011							

Source : Census 2011

#### DIFFERENTIAL BETWEEN THE RURAL & URBAN FWPR IN 2011

India's Rural Fwpr is almost the double the female work participation observed in Urban areas. The Rural FWPR is higher than Urban FWPR is majority of the States & UTs except in Chandigarh and Delhi where the Urban FWPR is marginally higher than Rural FWPR. The difference in the rural and urban female work participation is highest in the State of Rajasthan, followed by Chhattisgarh, Himachal Pradesh & Nagaland. Maharashtra also has a high difference in the rural and urban female work participation rate.

#### Table 2: Difference in Female Work Participation Rate (FWPR) in Rural & Urban Region

State	Name	RURAL FWPR	URBAN FWPR	Diff Rural-Urban FWPR
00	India	30.03	15.44	14.59
01	CHANDIGARH	14.24	16.05	-1.81
02	NCT OF DELHI	9.72	10.60	-0.88
03	ANDAMAN & NICOBAR ISLANDS	17.87	17.71	0.16
04	PUNJAB	14.34	13.18	1.16
05	GOA	22.64	21.48	1.16
06	DAMAN & DIU	15.86	14.47	1.39
07	LAKSHADWEEP	12.55	10.51	2.05
08	WEST BENGAL	19.35	15.35	4.00
09	KERALA	20.24	16.03	4.21
10	PUDUCHERRY	21.05	16.06	5.00
11	JAMMU & KASHMIR	20.79	14.46	6.34
12	UTTAR PRADESH	18.30	11.28	7.01
13	HARYANA	20.83	12.11	8.72

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14	ASSAM	23.69	14.86	8.83
15	MANIPUR	42.73	33.17	9.56
16	BIHAR	20.16	10.44	9.72
17	TRIPURA	26.28	16.00	10.28
18	MIZORAM	41.86	31.05	10.81
19	MEGHALAYA	34.97	23.59	11.38
20	ODISHA	29.69	14.12	15.58
21	KARNATAKA	38.79	20.81	17.97
22	ARUNACHAL PRADESH	39.50	21.31	18.18
23	DADRA & NAGAR HAVELI	33.39	14.66	18.74
24	TAMIL NADU	41.22	21.78	19.44
25	SIKKIM	44.63	24.80	19.83
26	GUJARAT	31.95	11.35	20.60
27	UTTARAKHAND	32.94	11.29	21.65
28	MADHYA PRADESH	39.25	15.14	24.12
29	JHARKHAND	34.96	10.07	24.90
30	ANDHRA PRADESH	44.65	19.14	25.51
31	MAHARASHTRA	42.52	16.78	25.74
32	NAGALAND	52.26	25.87	26.39
33	HIMACHAL PRADESH	47.40	19.88	27.52
34	CHHATTISGARH	46.29	17.42	28.86
35	RAJASTHAN	42.68	12.03	30.65

Source : Census 2011

#### CONCLUSIONS

The study shows that the work participation rate in India as per Census 2011 is 30.03 % only. In urban areas male work participation is high (53.76 %), but female work participation is very low (15.44 %). Female work participation is mostly higher in rural areas as compared to urban areas. Nagaland and Himachal Pradesh have high female work participation in rural region. Though Nagaland has high Female work participation in Rural as well as in Urban Areas, the difference in the said work participation is also very high. Delhi, Lakshadweep, Punjab, Chandigarh has poor female work participation in urban areas, while Bihar has low Female work participation in urban areas.

#### SUGGESTIONS

Based on the study following suggestions are made

- i. Measures should be taken by the Govt. to increase the female work participation in urban areas.
- ii. Govt. of Northern States like Delhi, Chandigarh and Punjab needs to take efforts to increase their female work participation in rural areas.
- iii. One needs to also study in details as to why Lakshadweep has such low female work participation levels in both urban and rural areas and Administration should take measures to improve the same.

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**Research Paper** 

## ASSESSMENT OF COPPER TOLERANCE IN SELECTED CROPS

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#### Abstract

Heavy metal pollution is one of the major environmental problems we face today, mainly due to rise of anthropogenic activities. Activities such as mining, smelting, oil extraction, several manufacturing processes, electroplating, fertilizers, pigment and dves manufacture and vehicular emissions are a source of heavy metals in contamination of soil and water. India is primarily an agrarian country, crops grown on heavy metal polluted soil adversely affects the growth of these crops and subsequently the consumers. In this paper the effect of copper on seed germination, root and shoot growth, fresh weight of common Indian crops has been studied. Our results show that seed germination and root and shoot growth is significantly reduced at high concentrations of the heavy metal. Copper being a micronutrient, increased the germination rate at lower concentrations producing a stimulating effect on the plants. According to our results, the morphological responses of selected plants to copper, we can conclude that highest growth was recorded for Vigna radiata L. to the other selected species. The germination and growth of Trigonella foenum graecum L. and Oryza sativa L. seedlings were found to be most sensitive. *The resistance of the plants can be represented as Vigna radiata L. > Vigna* aconitifolia L. > Pennisetum glaucum L. > Sorghum vulgare L. > Trigonella foenum – graecum L. > Oryza sativa L.

Key words: copper, seed germination, toxicity, seedling growth, crop.

#### **INTRODUCTION**

Deteriorating environment is one of the major issues that we face today. There are several reasons for the occurrence of pollution, the major one being urbanization. Intensive urban growth and industrialization started increasing the level of pollution converting our landscapes into vessels of waste. Developmental activities have depleted our natural resources and generated huge amount of wastes leading to the pollution of air, water and soil. Heavy metals is a general collective term, which applies to the group

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of metals and metalloids with atomic density greater than 4 g/cm<sup>3</sup>, or 5 times or more, greater than water [1]. Heavy metals naturally present in trace amounts are arsenic, cadmium, chromium, cobalt, lead, mercury, nickel and selenium are toxic even at very low concentrations, whereas few heavy metals such as copper, zinc and iron are of biological importance to growth, however at high concentrations, can cause damage to the organism by accumulating and displacing vital nutrients in the tissues. Copper is an essential micronutrient for all living organisms, including plants [2]. Copper is largely used in the chemical industry, metal piping, mining and pesticide production known to cause anaemia, gastrointestinal irritation, liver and kidney damage. The effect of Cu toxicity is seen on germination root growth and vigour of plants, causing chlorosis, necrosis and discolouration of leaf [3].

## MATERIAL AND METHODS

Seeds, Planting material and stock solution: Seeds of *Trigonella foenum-graceum* L. studied for the effects of Copper on seed germination were purchased from Pyramid Seeds at Namdeo Umaji Agritech (India) Pvt. Ltd. Seeds of *Vigna radiata* L., *Vigna aconitifolia* L., *Pennisetum glaucum* L., *Sorghum vulgare* L., and *Oryza sativa* L. were bought from a local seed dealer.

For the germination studies: Ten surface sterilized seeds uniform in colour, weight and size were placed on a Petri dish (9 cm diameter) on double-layered filter paper. The seeds were sterilized to kill the surface organisms by placing them in Bavistin solution prepared using 200mg of Bavistin dissolved in 100ml distilled water. The seeds were left in this solution for 5 minutes followed by a through rinse repeated twice, using sterile distilled water preceding the germination studies. The filter paper was moistened with varying concentrations of heavy metal solutions, 5mL on the first day followed by 2 ml on alternate days for 7 days. Triplicates of each treatment in a completely randomized designed were studied along with a separate control set using distilled water.

A 1000 ppm stock solution was prepared for Copper using 3.929g of Copper sulphate pentahydrate (CuSO<sub>4</sub>.5H<sub>2</sub>O) of analytical grade purchased from Loba Chemie. The stock solution was then diluted to prepare 1, 3, 5, 10, 50, 100, 200, 300, 500 ppm for the treatment of seeds. All the standards were prepared by non – serial dilutions.

Germination indices i.e. Total germination (GT) and Seedling vigour index (SVI) [4]

were selected and recorded for this study. Seed germination was observed after 24 hours, for a constant percentage of germination; other growth attributes viz. length of the root and shoot (cm) and fresh weight (g) of the seedlings was recorded on a digital balance after a period of 7 days.

Total Germination: the final Germination percentage is a measure of the time for a population of seeds to germinate in order to estimate its viability and is expressed as a percentage. The total germination (GT) was calculated using the following formula:

GT = no. of seeds germinated/total seeds x 100

Seedling Vigour Index: Seed vigour helps understand the potential for emergence and development of seedlings in field conditions. Compared to GT, SVI being more sensitive is an important component of germination studies as it provides a better understanding of seed damage and deterioration and response to stressors.

Seedling vigour index was calculated by following formula:

SVI = Germination % × Seedling length (cm)

Seedling length = RL + SL where RL is root length (cm), SL is shoot length.

To determine the significance between samples, a "Student's t – test" was carried out at p<0.05 level of significance. Box and Whiskers plot along with Histograms were used for data analysis. Statistical analysis was carried out using SPSS software version 11.0.

## [III] RESULTS

## 3.1. Effect of Copper on total germination

Being a heavy metal copper also showed a similar trend that higher concentrations of Cu solutions affected the germination of selected plants (Table 1.11, Fig 1.59). Since it is a micronutrient the effect copper produced on germination was observed to be not as pronounced as the non - essential heavy metals. Amongst the six species the germination percentage of:

*Vigna radiata* L. did not show extreme effects of copper treatment germinating up to 500ppm with 75% germination. However a steady decline was observed from control to the highest concentration applied.

*Vigna aconitifolia* L. was least affected as it showed an 80% germination at 500ppm, gradual decrease in the percentage germination was observed from 1ppm onwards, with 95% at 1ppm.

*Trigonella foenum – graecum* L. had a steady rate of germination up to 300ppm. 90% germination was recorded at 1ppm reducing to 85% at 300ppm, a sudden drop was observed from 300ppm to 500ppm with 55% seeds germinating at the highest applied concentration.

In *Pennisetum glaucum* L. 60% germination was observed at 500ppm and the highest was 100% germination at 3ppm.

In *Sorghum vulgare* L. 90% of the seeds germinated at 100ppm and only 50% germinated at 500ppm.

*Oryza sativa* L. was noted to be the weakest plant of all six selected plants when subjected to higher concentrations of copper. Only 25% of the seeds germinated at 300ppm and 500ppm, whereas lower concentrations had a favourable effect on rice showing 90% germination at 100ppm.

			-			
Ppm	Vigna radiata	Vigna aconitifolia	Trigonella foenum –	Pennisetum	Sorghum vulgare	Oryza sativa
*	L.	L.	graecum L.	glaucum L.	Ľ.	L.
Control	100	100	100	100	100	100
1	85	95	90	85	95	100
3	75	85	80	100	85	100
5	80	90	90	80	80	95
10	90	90	90	85	80	95
50	90	85	90	85	75	95
100	85	90	95	75	90	90
200	85	90	90	70	85	35
300	75	90	85	60	70	25
500	75	80	55	60	50	25

 Table 1.11: Effect of Copper on Total germination (%)

Values are average of 30 samples.

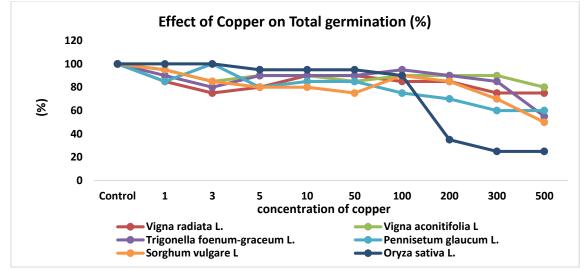




Table 1.12: Effect of Copper on Length of Kaucle (Chi)							
Ppm	Vigna radiata L.	Vigna aconitifolia L.	Trigonella foenum – graecum L.	Pennisetum glaucum L.	Sorghum vulgare L.	Oryza sativa L.	
Contro l	11.54±1.8 8	11.08±2.6 2	3.9±0.90	7.63±3.10	8.21±1.96	5.75±0.97	
1	4.77±0.78*	4.98±1.90*	3.09±1.59*	7.21±1.11#	4.27±0.92 *	1.17±0.48 *	
3	5.51±1.00*	5.16±0.79*	2.05±0.89 #	6.86±1.11* *	2.95±0.0*	1.50±0.35 *	
5	6.85±2.01*	5.00±2.04*	2.88±1.37*	6.44±1.14* *	2.57±0.49 *	1.25±0.21 *	
10	7.62±1.47*	4.51±1.55*	2.48±0.75 #	6.47±1.55* *	1.59±0.37 *	1.17±0.29 *	
50	4.12±1.03*	3.24±0.81*	1.59±0.80*	5.67±1.00#	1.65±0.68 *	1.18±0.40 *	
100	4.24±1.16*	1.84±0.90*	0.86±0.26*	5.48±1.03*	0.86±0.49 *	0.85±0.41 *	
200	1.66±0.55*	1.22±0.54*	0.62±0.37*	2.92±1.86*	0.52±0.23 *	0.27±0.13 *	
300	1.48±0.53*	0.75±0.42*	0.40±0.16*	2.77±0.73*	0.20±0.14 *	0.12±0.05 *	
500	0.87±0.37*	0.57±0.34*	0.35±0.19*	2.92±0.66*	0.18±0.13 *	0.23±0.09 *	

3.2. Effect of Copper on Length of Radicle
Table 1.12: Effect of Copper on Length of Radicle (cm)

\*significant at p < .01 \*\* not significant at p < .05 #significant at p < .05 values are average of 30 samples

*Vigna radiata* L.: Length of radicle in control was 11.54cm, followed by 7.62cm at 10 ppm. As shown in <u>Fig</u> 1.60, representing box and whisker plots for mung bean seeds, the length of radicle, increased gradually up to 10ppm after which a significant was observed with slight radicle emergence of 0.87cm at 500 ppm.

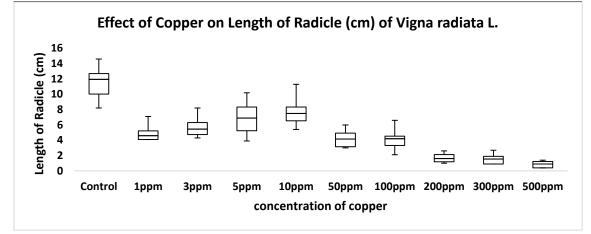


Fig 1.60: Effect of Copper on Length of Radicle (cm) of Vigna radiata L.

*Vigna aconitifolia* L.: The control value was 11.08 cm. The highest length of radicle upon treatment was 5.16cm at 3ppm. The results obtained for 1ppm and 5ppm are fairly comparable with the lowest reading recorded of 0.57cm at 500ppm. (Fig 1.61)

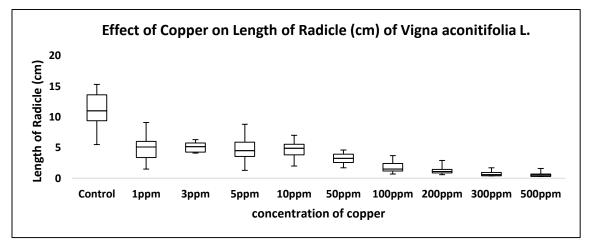


Fig 1.61: Effect of Copper on Length of Radicle (cm) of Vigna aconitifolia L.

**Trigonella foenum – graecum L.:** Showed a minor but steady decrease in the length of radicle with an increase in concentration. 3.09 cm was measured length of radicle at 1ppm showing a 20% difference from control (3.90 cm). The minimum radicle length for Trigonella seedlings was 0.35cm. (Fig 1.62)

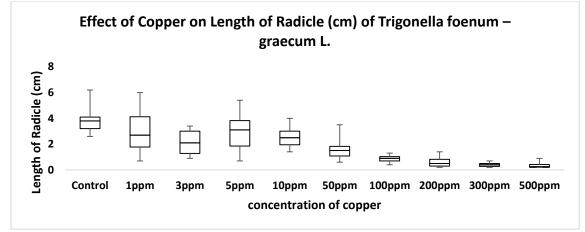


Fig 1.62: Effect of Copper on Length of Radicle (cm) of *Trigonella foenum – graecum* L.

**Pennisetum glaucum L.:** Showed a marginal 5% difference from control at 7.63cm to 7.21 cm of radicle length at 1ppm. A significant radicle length was recorded up to 100ppm, a drastic decline was noted at 200ppm. At 300ppm least radicle growth was observed with a length of 2.77cm. (Fig 1.63)

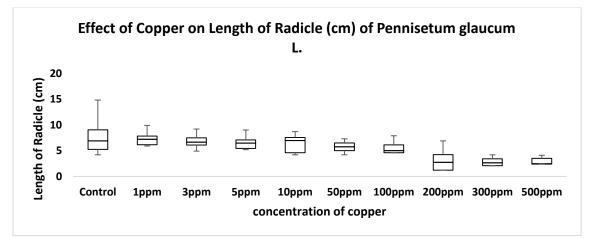


Fig 1.63: Effect of Copper on Length of Radicle (cm) of Pennisetum glaucum L.

**Sorghum vulgare L.:** Highest length of radicle in *Sorghum vulgare* L. was for control 8.21 cm, dropping to 4.27 cm at 1ppm while the lowest value was 0.18 cm at 500ppm. Adverse effects of copper were observed from 100ppm onwards with severe inhibition of radicle emergence. (Fig 1.64)

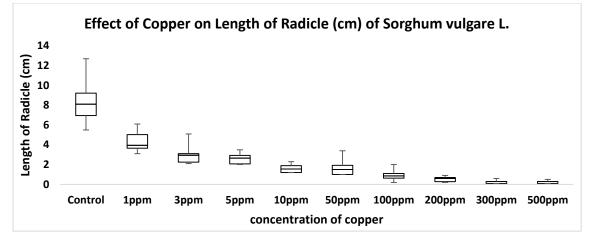


Fig 1.64: Effect of Copper on Length of Radicle (cm) of Sorghum vulgare L.

*Oryza sativa* L.: Severe inhibition of radicle length was observed in rice seedlings. *Oryza sativa* had the highest length of 1.50cm upon treatment with copper at 3ppm and 0.23cm was the lowest length at 500ppm. The length of radicle from 1 to 50 ppm is fairly comparable, the decrease in length is significant from 100ppm onwards. (Fig 1.65)

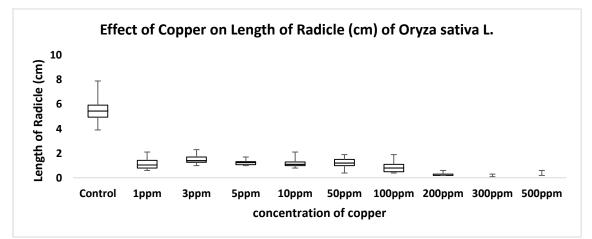


Fig 1.65: Effect of Copper on Length of Radicle (cm) of Oryza sativa L.

Ppm	Vigna radiata L.	Vigna aconitifolia L.	Trigonella foenum – graecum L.	Pennisetum glaucum L.	Sorghum vulgare L.	Oryza sativa L.
Contro l	12.04±1.36	9.82 ±1.22	6.69±0.72	5.95±1.10	6.74±2.51	4.77±0.4 0
1	9.47±2.50*	11.06±2.43 #	5.80±1.15 *	5.98±1.30* *	6.52±1.95* *	3.74±0.6 3
3	11.76±3.82* *	11.25±3.25* *	5.46±1.45 *	6.24±1.17* *	5.83±0.77* *	3.93±0.4 3
5	13.13±3.54* *	10.80±2.06* *	5.22±2.21 *	6.61±1.21 #	5.31±1.22 #	4.02±0.5 9

**3.3. Effect of Copper on Length of Plumule Table 1.13: Effect of Copper on Length of Plumule (cm)** 

10	11.63±1.63*	11.45±2.48	5.44±0.89	5.23±1.09	6.55±1.24*	3.89±0.4
10	*	#	*	#	*	2
۲O	11.22±1.78* *	10.82±2.42* *	4.85±0.9*	5.90±2.16* *	4.78±1.42*	3.94±0.4
50						0
100	12.64±2.81*			5.85±1.70*	2 10 10 01	3.68±0.5
100	*	9.44±1.75**	5.24±1.0*	*	2.19±0.91	3
200	9.50±2.08*	9.19±2.52**	$1.63 \pm 0.43$	3.29±2.27*	1.99±0.75	1.75±0.4
200	9.50±2.08	9.19±2.52	*	3.29±2.27	1.99±0.75	7
300	10.68±3.05*	8.21±2.16#	$1.18 \pm 0.30$	2.05±0.69*	0.68±0.49	0.58±0.4
500	10.08±3.05	0.21±2.10#	*	2.05±0.09	0.0810.49	4
500	10.13±2.33*		0.96±0.21	2.05±1.13*	0.91±0.41	0.59±0.4
500	10.15±2.33	5.58±1.86*	*	2.05±1.13 <sup>+</sup>	0.91±0.41	9

\*significant at p < .01 \*\* not significant at p < .05 #significant at p < .05 values are average of 30 samples

*Vigna radiata* L.: Maximum length of plumule in *Vigna radiata* L. was 13.13 cm at 5 ppm and the lowest length noted was 9.50 cm at 200 ppm. Mung bean seedlings showed higher tolerance to copper compared to the other plants selected. (Fig 1.66).

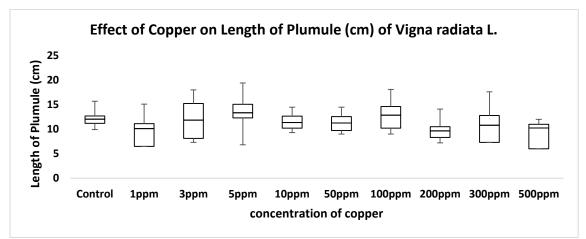


Fig 1.66: Effect of Copper on Length of Plumule (cm) of Vigna radiata L.

*Vigna aconitifolia* L.: Highest length of plumule in *Vigna aconitifolia* L. was 11.45 cm at 10 ppm and the lowest length noted was 5.58 cm at 500ppm. Moth bean seedlings showed consistent length of plumule up to 300 ppm. (Fig 1.67)

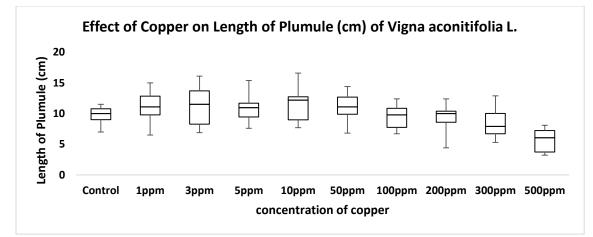


Fig 1.67: Effect of Copper on Length of Plumule (cm) of Vigna aconitifolia L.

**Trigonella foenum – graecum L.:** The length of plumule for control value was 6.69 cm, maximum length of plumule upon treatment with copper for Trigonella seedlings was 5.80 cm and minimum value was 0.96cm at 500ppm. The seedlings showed severe inhibition of growth at 200ppm and thereafter. (Fig 1.68)

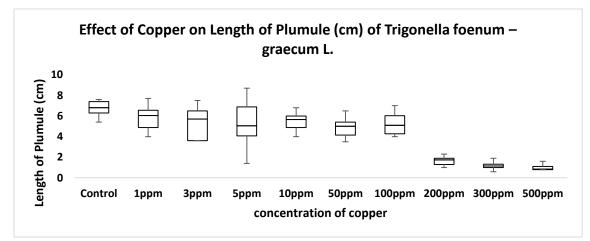


Fig 1.68: Effect of Copper on Length of Plumule (cm) of *Trigonella foenum – graecum* L.

**Pennisetum glaucum L.:** Control value showed 5.95 cm plumule. An increase in length of plumule of 6.61cm at 5ppm and 2.50 cm was the lowest noted length at 500ppm. The length of plumule was comparable and consistent up to 100ppm after which a significant drop was observed. (Fig 1.69).

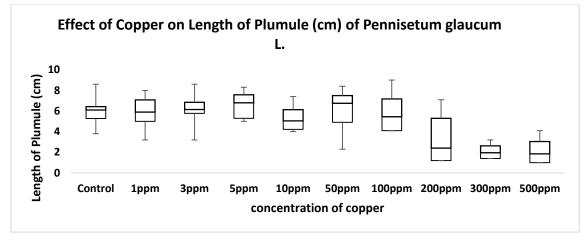


Fig 1.69: Effect of Copper on Length of Plumule (cm) of Pennisetum glaucum L.

*Sorghum vulgare* L.: Sorghum seedlings showed a highest length of 6.55 cm at 10ppm and the lowest value of plumule was 0.68 cm at 300ppm. The control value being 6.74cm. (Fig 1.70).

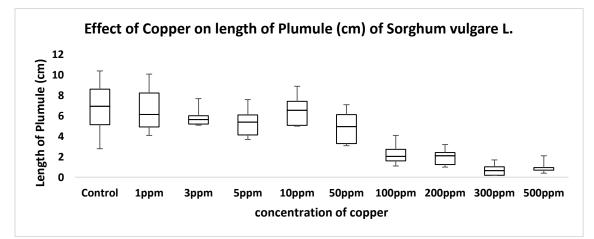


Fig 1.70: Effect of Copper on Length of Plumule (cm) of Sorghum vulgare L.

*Oryza sativa* L.: Seedlings were severely inhibited at higher concentrations, having a plumule length of 0.58 cm at 300ppm. The length of plumule was 4.02 cm at 5 ppm. The control value was 4.77cm. (Fig 1.71)

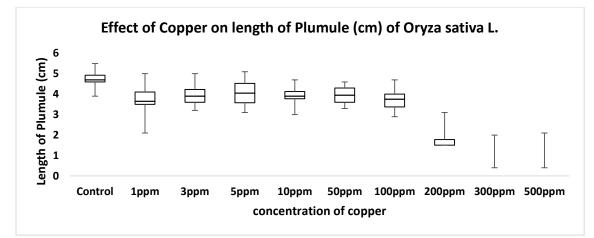


Fig 1.71: Effect of Copper on Length of Plumule (cm) of Oryza sativa L.

Table	Table 1.14: Effect of Copper on Fresh weight (g)								
Ppm	Vigna radiata L.	Vigna aconitifolia L.	Trigonella foenum – graecum L.	Pennisetum glaucum L.	Sorghum vulgare L.	Oryza sativa L.			
Contr	0.2937±0.0	0.1747±0.0	0.1673±0.	0.0663±0.0	0.1214±0.0	0.0451±0.0			
ol	5	3	03	1	1	04			
1	0.1811±0.0	0.1721±0.0	0.1547±0.	0.0611±0.0	0.1003±0.0	0.0410±0.0			
	5*	3**	01*	1**	2*	05**			
3	0.2470±0.0	0.1989±0.0	0.1385±0.	0.0640±0.0	0.1006±0.0	0.0383±0.0			
	6*	3#	04#	1**	1*	08**			
5	0.2647±0.0	0.1743±0.0	0.1258±0.	0.0448±0.0	0.1001±0.0	0.0343±0.0			
	4**	4**	02#	1*	0*	05**			
10	0.2862±0.0	0.1601±0.0	0.1317±0.	0.0494±0.0	0.0966±0.0	0.0296±0.0			
	5**	2**	02*	1*	1*	05**			
50	0.2200±0.0	0.1416±0.0	0.1227±0.	0.0461±0.0	0.0816±0.0	0.0365±0.0			
	7*	4*	02#	1*	1*	05**			
100	0.2175±0.0	0.1531±0.0	0.1330±0.	0.0312±0.0	0.0606±0.0	0.0337±0.0			
	6*	2#	01*	06*	1*	03**			

# 3.4. Effect of Copper on Fresh weight Table 1.14: Effect of Copper on Fresh weight (g)

200	0.2104±0.0	0.1304±0.0	0.1016±0.	0.0248±0.0	0.0541±0.0	0.0225±0.0
	5*	4*	01*	05*	07*	03#
300	0.2375±0.0	0.1137±0.0	0.0799±0.	0.0224±0.0	0.0496±0.0	0.0131±0.0
	3*	2*	01*	05*	0*8	04*
500	0.2126±0.0	0.0927±0.0	0.0714±0.	0.0188±0.0	0.0439±0.0	0.0200±0.0
	3*	2*	01*	04*	04*	01*

\*significant at p < .01 \*\* not significant at p < .05 #significant at p < .05 values are average of 30 samples

*Vigna radiata* L.: Upon treatment with copper solution it showed a highest weight 0.2862g at 10 ppm and the lowest weight was 0.1811g at 1ppm. The control value being 0.2937g. (Fig 1.72)

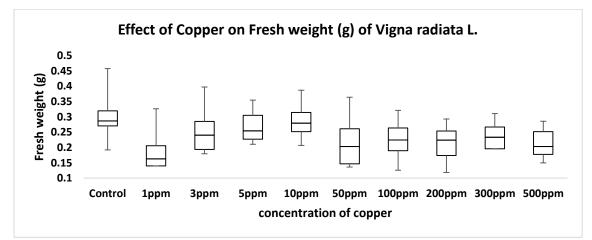


Fig 1.72: Effect of Copper on Fresh weight (g) of Vigna radiata L.

*Vigna aconitifolia* L.: A gradual decline in the fresh weight was noted from 0.1989g at 1ppm being the highest calculated average to 0.0927g being the lowest at 500 ppm. (Fig 1.73)

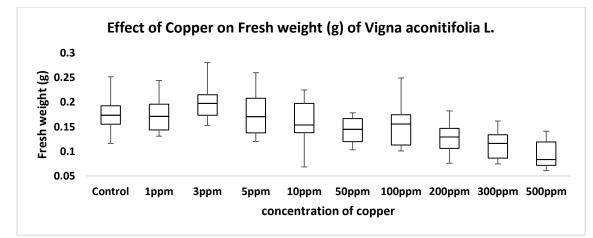


Fig 1.73: Effect of Copper on Fresh weight (g) of Vigna aconitifolia L.

**Trigonella foenum – graecum:** The control value was 0.1673g slightly higher than average fresh weight of Trigonella seedlings of 0.1547g at 1ppm of copper and a minimum fresh weight was recorded 0.071g at 500ppm. Severe reduction in fresh weight was observed at higher concentrations of 300 ppm and 500ppm. (Fig 1.74)

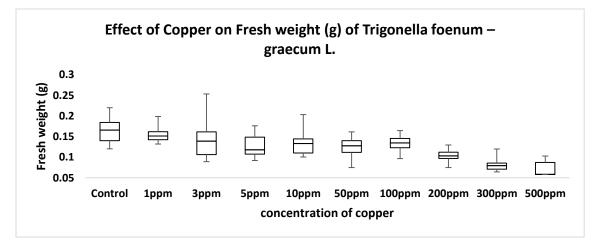


Fig 1.74: Effect of Copper on Fresh weight (g) of Trigonella foenum - graecum L.

**Pennisetum glaucum L.**: Fresh weight of *Pennisetum glaucum* L. was 0.0640g at 3ppm and a minimum value recorded was 0.0188g at 500ppm. A favourable increase in fresh weight was observed at 3ppm in comparison to 1 ppm. The value of control was 0.0663g. (Fig1.75)

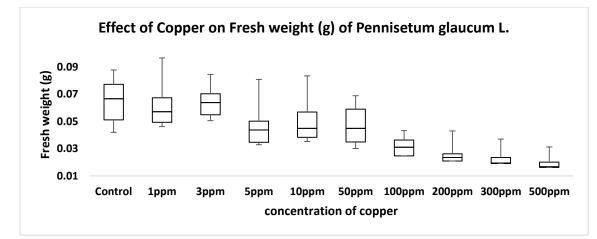


Fig 1.75: Effect of Copper on Fresh weight (g) of *Pennisetum glaucum* L.

*Sorghum vulgare* L.: Maximum fresh weight recorded in *Sorghum vulgare* L. was 0.1214g for control and 0.1006g at 3ppm and minimum weight noted was 0.0439g at 500ppm. (Fig 1.76)

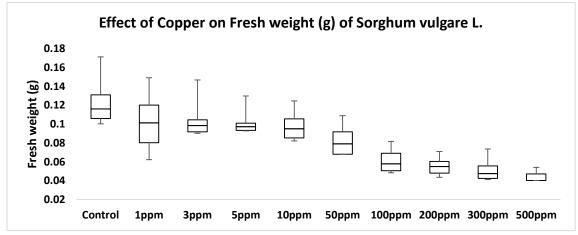


Fig 1.76: Effect of Copper on Fresh weight (g) of Sorghum vulgare L.

**Oryza sativa L.:** Seedlings of *Oryza sativa* L. showed a gradual decrease in fresh weight from control through 500ppm. Control value was 0.0451g and 0.0410g was at 1ppm. The minimum fresh weight was 0.0200g at 500ppm. (Fig 1.77)

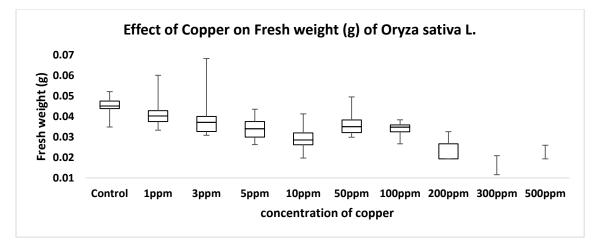


Fig 1.77: Effect of Copper on Fresh weight (g) of Oryza sativa L.

## 3.5. Effect of Copper on Seed Vigour Index (SVI)

Based on the data collected for the total germination percentage and early seedling growth which shows a decline in the overall length of radicle, plumule and fresh weight, the SVI calculations also show a decreasing value with an increase in the concentrations. (Table 1.15, Fig 1.78).

*Vigna radiata* L.: the control value was 2358, followed by 1799.10 at 5 ppm and a minimum of 759.75 at 500ppm.

A decline in the SVI was noted in *V. aconitifolia* L. from 1524.75 to 492.40 in concentrations 1 through 500 ppm. Control value was 2090.

*Trigonella foenum – graecum* L. was observed to be one the weakest plants, 800.55 was the highest calculated SVI value and 72.50 was the least at 500ppm. Control value was 1059. Despite the favourable increase in growth at lower concentrations, overall there was a decrease in SVI with an increasing concentration of copper.

In *Pennisetum glaucum* L. a drop in vigour from 1362.50 for control set to 298.5 at 500 ppm was calculated.

*Sorghum vulgare* L. showed a 94% difference from 1025.52 to 52.25 when the concentrations were increased from 1ppm to 500ppm. The highest SVI was calculated for control at 1495.50.

*Oryza sativa* L. also was amongst the weaker plants against copper stress, a drop was noted in the vigour of seeds 491.50 to 17.62 upon being treated with 1ppm of copper gradually advancing to 300 ppm concentration. Control value was 1034.50.

Tuble 1.15. Infect of copper on seed vigour muck (5vr)								
Ppm	Vigna radiata L.	Vigna aconitifolia L.	Trigonella foenum – graecum L.	Pennisetum glaucum L.	Sorghum vulgare L.	Oryza sativa L.		
Control	2358	2090	1059	1362.50	1495.50	1034.50		
1	1068.75	1524.75	800.55	1122	1025.52	491.50		
3	1382.40	1394.85	601.20	1310	747.15	543.50		
5	1799.10	1422.45	729	1044.80	630.40	501.60		
10	1733.40	1436.85	713.25	994.92	651.60	481.65		
50	1304.32	1195.52	579.60	983.45	482.62	487.35		
100	1434.80	1015.65	579.97	850.12	274.95	408.15		
200	949.45	937.80	202.50	434.70	213.77	71.05		
300	912.75	807.30	134.72	289.50	62.30	17.62		
500	759.75	492.40	72.05	298.50	52.25	20.50		
values are suprass of 20 semulas								

values are average of 30 samples.

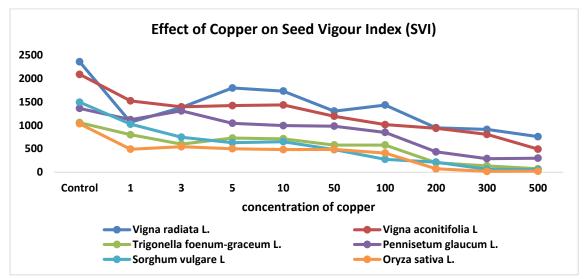


Fig 1.78: Trend graph showing the effect of Copper on Seed Vigour Index (SVI)

## DISCUSSION

Copper being a micronutrient, increased the germination rate at lower concentrations producing a stimulating effect on the plants. Copper has a negative effect on plants at high concentrations such as shortening of length of radicle and plumule, decrease in fresh weight and low germination rate. The recorded values for copper treatment at lower concentrations up to 5 ppm showed a favourable effect of the emergence and length of the radicle. Based on the values recorded, 50ppm can be considered as the threshold thereafter a significant decline can be seen in the growth of radicle. Detrimental effects of copper were most pronounced at 500ppm with slight emergence of radicle for all the selected plants. A reduction of germination indices was reported in many studies due to cell membrane injury by water deficit stress for rice [5] and in wheat [6]. Although a slight increase was observed in germination percentage and lateral roots in 5mg/L of copper concentration. Another study reported reduction in wheat plumule length, radicle length, number of lateral roots, fresh weight and dry weight with increased copper concentration. [7]

Copper was found to be beneficial to plant growth at 3ppm and 5ppm for all the selected species showing an increase in growth whereas copper was toxic at 100ppm and onwards, showing inhibition of root and shoot elongation. Based on the observations, severe inhibition was noted at 200ppm to 500ppm. Since the emerging radicle of seedlings subjected to higher concentrations of copper were inhibited, this affected the growth of plumule as well. 3ppm and 5ppm concentrations produced a favourable increase in the length of plumule for the plants selected. High phytotoxicity of copper on shoot length of wheat was reported at 500 ppm concentration [8]. Similarly, it was reported that increasing concentrations of copper significantly reduced the seedling growth in *Ipomoea batatas* [9].

The fresh weight of the seedling corresponds with the increase and decrease in radicle and plumule length at specific concentrations of copper. The fresh weight of seedlings of all plant species selected showed a minor increase at 3 ppm and 5 ppm whereas at higher concentrations a gradual decrease in weight was observed. Similar results were noted in *L. culinaris* plants at 100 ppm causing decreased the seedling growth [10]. The overall reduced can be attributed to the oxidative stress induced by heavy metals at a cellular level [11].

According to our results, the morphological responses of selected plants to copper, we can conclude that highest growth was recorded for *V. radiata* to the other selected species. The germination and growth of fenugreek and rice seedlings was found to be more sensitive.

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#### Green Synthesis and Characterization of Gold Nanoparticles using Mucuna monosperma

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#### ABSTRACT

The utility of plant-based phytochemicals in general synthesis and engineering of nano-phytomedicine is the association between plant science and nanotechnology that gives intrinsically green approach to nanotechnology referred as green nanotechnology. The present work aims at green synthesis of gold nanoparticles from different concentrations of *Mucuna monosperma* seed extract and its characterization by methods like scanning electron microscopy (SEM), UV-Visible spectrophotometer and Fourier transform infra red (FTIR) spectroscopy. The gold nanoparticles using 4% seed extract showed good stability over other concentrations. Analytical tools like FTIR, UV-Visible spectrophotometer and SEM helped understand the surface properties of the gold nanoparticles. The synthesized gold nanoparticles show spherical shape and also possibilities of L-DOPA from plant coating on it. This opens door to a lot of applications such as a major application in novel drug delivery system (NDDS).

#### 1. Introduction

Nanoscience and nanotechnology are the study and use of extremely small things and can be utilized over the various science fields, for example, chemistry, biology, physics, material science, and engineering [1]. Though modern technology demands the development of nanotechnologies in multidisciplinary science, including the production of nanoparticles (NPs), it dates back from the Before-Christ era [2]. Nanoparticles can be synthesised using multiple methods like physical, chemical or biological, also known as green synthesis. Green synthesis includes use of microorganisms like fungi, yeast (eukaryotes) or bacteria, actinomycetes (prokaryotes); use of plant extracts or enzymes or use of templates like DNA, membranes, viruses and diatoms. Several of the current processes of nanoparticle generation uses poisonous chemical either as reducing agent for metals or as stabilizing agents to stop agglomeration of the nanoparticles. In spite of the fact that chemical and physical strategies may effectively create unadulterated, well characterized nanoparticles, these are very costly and possibly unsafe to the environment. As an alternative to poisonous and costly physical strategies for synthesis of, using microorganisms, plants and algae will aid a lot. Also, the poisonous quality of the by-product would be very less as compared to other synthetic methods [3]. The utility of plant-based phytochemicals in general synthesis and engineering of Nanophytomedicine is the association between plant science and nanotechnology that gives intrinsically green approach to nanotechnology referred as green nanotechnology [4]. Phytochemicals show synergistic effect in the reduction of gold salt into its nanophytomedicine [5].

Au<sup>+3</sup> ions (in gold solution) reduced to Au<sup>+1</sup> and further Au<sup>0</sup> by reducing agents in the plant extract. Finally many Au<sup>0</sup> atoms assembled via nucleation process to form gold nanoparticles. Depending on the phytochemicals present in plant extract it support to form nanoparticles, which is charachterized by change in colour. Applications of nanotechnology have allowed overcoming the challenges and technical boundaries related to the insolubility, bioavailability, steadiness and delivery of bio-actives from foods/nutraceuticals. The most predominant strategy for the formation of monodisperse circular gold nanoparticles was pioneered by Turkevich et. al. in 1951 and afterward refined by Frens et. al. in 1973 [6-9]. This strategy uses the chemical reduction of gold salts such as hydrogen tetrachloroaurate (HAuCl<sub>4</sub>) utilizing a reducing agent. Besides, the gold surface offers an interesting opportunity to conjugate ligands such as oligonucleotides, proteins, and antibodies containing useful groups such as thiols, mercaptans, phosphines, and amines, which illustrates a strong affinity for gold surface [10].

*Mucuna monosperma* is a large climbing shrub from family Fabaceae. Literature survey revealed that the seeds of *Mucuna monosperma* possess various pharmacological properties like astringent, cardiotonic, restorative, expectorant and used in the treatment of asthma, cough and tongue infection [11]. It is a rich source of L-DOPA, which is a non essential amino acid and widely used in the treatment of Parkinson's disease.

#### 2. Experimental Methods

#### 2.1 Developing Herbal Gold Nanoparticle using M. Monosperma Seed Extract

#### 2.1.1 Preparation of M. monosperma Seed Extract [12]

Powdered seed was dissolved in methanol:water (50:50) (v/v). This solution was allowed to stand for 24 hrs. The resulting solution was centrifuged at 3000 rpm for 5 min and supernatant was collected and used further.

#### 2.1.2 Preparation of Different Concentration of Seed Extract

*Mucuna monosperma* seed extract was prepared at various % concentrations ranging from 10-100%, at intervals of 10%. Later 1-10% range at intervals of 1% was prepared.

#### 2.1.3 Preparation of HAuCl<sub>4</sub> Solution

Chloroauric acid (HAuCl<sub>4</sub>) salt crystals were obtained from Synthman Chem Industry, GIDC, Rajkot, Gujarat, India. 1 mM solution of HAuCl<sub>4</sub> was prepared as described by Subramanian and Sabesan [13].

#### 2.1.4 Preparation of Herbal-Gold Nanoparticles

10 mL of 1 mM HAuCl<sub>4</sub> was added to 10 mL of prepared different concentrations of seed extract (1%-100%) and subjected to heat in a water bath at 55 °C for 15 mins. The indication of gold nanoparticles formation identified by the colour change from pale yellow to purple [13].

#### 2.2 Characterization of Gold Nanoparticles

The UV-visible spectra of synthesized gold nanoparticles were measured through a range of 200-900 nm using Shimadzu UV-1800

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spectrophotometer to check to the surface modification of the gold nanoparticles.

The Fourier transform infrared (FTIR) spectroscopy was carried out to identify the biomolecules for the synthesis of gold nanoparticles and a possible overlap on them. The characterization was done by Bruker, Germany; Model 3000 Hyperion Microscope with Vertex 80 FTIR System at Sophisticated Analytical Instrument Facility, IIT Bombay, Powai.

Samples for Field Emission Gun - Scanning Electron Microscopic (FEG-SEM) analysis was prepared by drop coating Au nanoparticles solutions onto carbon-coated copper SEM grids. The films on the SEM grids were allowed to stand for 2 min following which the extra solution was removed using a blotting paper and the grid is allowed to dry, prior to the measurement. FEG-SEM measurements were performed by JEOL JSM-7600F instrument operated at an accelerating voltage at 0.1 to 30 kv at Sophisticated Analytical Instrument Facility, IIT Bombay, Powai. SEM provides detailed high-resolution images of the sample by bombarding a focussed electron beam across the surface and detecting secondary or backscattered electron signal. An energy dispersive X-ray spectroscopy (EDAX) is also used to provide elemental identification and quantitative compositional information.

#### 3. Results and Discussion

#### 3.1 Wet Lab Results of Gold Nanoparticles

The initial yellow color of HAuCl<sub>4</sub> solution, when added the seed extract and kept at 55 °C, changed in sequence to colorless, dark blue, and finally purple. At this final state the solution was then cooled untill it reach the room temperature.

Various concentration of *Mucuna monosperma* seed extract which were used for nanoparticle synthesis showed various colour solution and showed agglomerization in the range of 10-100% as shown in Fig. 1.



Fig. 1 Gradation of colour - formation of gold nanoparticles from 10%-100% at intervals of 10% seed extracts



Fig. 2 Gradation of colour - formation of gold nanoparticles from 1%-10% at intervals of 1% seed extracts

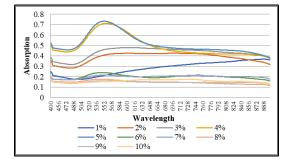


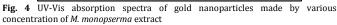
Fig. 3 Formation of gold nanoparticles from 4% and 5% seed extracts https://doi.org/10.30799/inst.309.20060301

As seen in Fig. 2, on further dilution, range of 1-10% seed extract used for synthesis of gold nanoparticles showed a good and stable colour change indicating the preparation of gold nanoparticles. Out of all the concentrations used, gold nanoparticles made from 4%, 5% and 6% *Mucuna monosperma* seed extracts showed deep purple colour indicating formation of gold nanoparticles as seen in Fig. 3. Gold nanoparticles made by 6% seed extract showed agglomerization in 1-2 hrs.

#### 3.2 UV-Visible Spectroscopy of Gold Nanoparticles

Gold nanoparticles show a particular optical property, otherwise known as, localized surface plasmon resonance (LSPR), that is, the collective oscillation of electrons in the conduction band of gold nanoparticles in reverberation with a particular wavelength of incident light. The gold nanoparticles made with various percent concentration of *Mucuna monosperma* seed extract when analysed by UV-Visible spectroscopy showed a single peak in the range of 540-570 nm indicating the formation of nanoparticles. 5% and 4% seed extract solutions show distinct Gaussian shaped peaks at 552 nm and 556 nm respectively indicating formation of more monodispered nanoparticles as compared to other concentrations which indicate flat type of peaks as shown in Figs. 4 and 5.





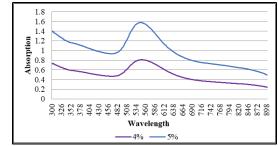


Fig. 5 UV-Vis absorption spectra of gold nanoparticles made by 4% and 5%  $\mathit{M.}$  monosperma extract



Fig. 6 Agglomerization of gold nanoparticles made by 5% seed extract

The gold nanoparticles made with 5% *M. monosperma* extract were not stable for more than 7 days and showed agglomeration as seen in Fig. 6. Also, the absorption spectra of gold nanoparticles made from 5% seed extract displayed dampening of absorption spectra, whereas nanoparticles made from 4% seed extract retains its peak as seen in Fig. 7, showing better stability. Also, when compared freshly prepared nanoparticles and 7-day old samples, nanoparticles showed similar peak as seen in Fig. 8, indicating the stability of monodispersed and spherical gold nanoparticles. Hence, gold nanoparticles synthesized by 4% extract were considered for further characterization.

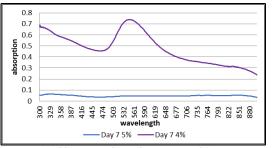


Fig. 7 Comparison of gold nanoparticles made using 4% and 5% *M. monosperma* seed extract after 7 days

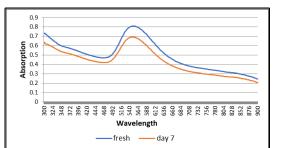


Fig. 8 Comparison of freshly prepared and 7 day old nanoparticles of 4%  $\it M.$  monosperma seed extract

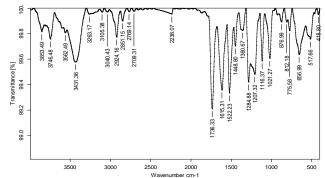


Fig. 9 FTIR spectrum of standard L-DOPA

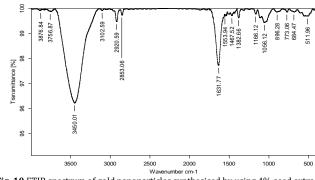


Fig. 10 FTIR spectrum of gold nanoparticles synthesised by using 4% seed extract

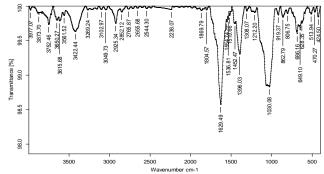


Fig. 11 FTIR spectrum of M. Monosperma seed extract

#### 3.3 FTIR Analysis of Gold Nanoparticles

Surface modification of gold nanoparticles with L-DOPA from seed extract was verified by comparing the FTIR spectra of gold nanoparticles, seed extract and standard L-DOPA. The following readings will help us https://doi.org/10.30799/jnst.309.20060301

understand the chemical composition of the gold nanoparticles. Table 2 and Figs. 9-11 helps us understand, various peaks in the L-DOPA standard and its corresponding peak in the seed extract and gold nanoparticles.

Peak between 2220-2260 cm<sup>-1</sup> indicates presence of cyanide indicating presence of toxic substances. As per the FTIR spectrum, this peak is present in the standard L-DOPA and also in the seed extract, but it is absent in the gold nanopartices. This gives the gold nanoparticles made an uper hand or advantage over the traditional seed extract or the synthetic L-DOPA and indicates the absence of toxic compounds from the gold nanoparticles synthesized [14].

Presence of aromatic ring and primary alcohol indicates that at L-DOPA from plants to have successfully adsorbed with the gold nanoparticles. The small change in the frequency could be because the hydroxyl groups of L-DOPA support cross-link reactions between L-DOPA from the seed extract and gold nanoparticles. This study shows that the aromatic ring system of L-DOPA functions as a surface anchor to the gold nanoparticles.

Table 2 FTIR results of syntheised gold nanoparticles, seed extract and std. L-DOPA

Peak	L-DOPA Std.	M. monosperma	Gold	Functional group
No.	(cm-1)	seed extract	nanopaticles	
		(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	
1.	3431.36	3422.44	3450.01	Primary amines
2.	3105.38	3102.97	3102.59	=CH and =CH <sub>2</sub>
3.	2924.16	2925.34	2920.59	Carboxylic acid
4.	2851.15	2852.12	2853.06	CH stretching
5.	1615.31	1629.49	1631.77	C=C bond
6.	1360.67	1396.03	1382.66	aromatic ring
7.	1021.27	1030.08	1056.12	Primary alcohol
8.	656.99	686.16	684.47	Weak O-H bonding
				out of the plane

#### 3.4 SEM and EDAX Analysis

SEM consolidates the benefits of a significantly easier example arrangement and higher depth-of-field imaging therefore giving a semi-3D data on the morphology and cell structure. SEM, nonetheless, offers a high spatial resolution and great depth of field. The gold nanoparticles made by 4% *M. monosperma* extract under scanning electron microscope showed the presence of clustered nanoparticles as shown in Fig. 12. When zoomed in a selected area, mostly spherical in shape, nanoparticles of size ranging from 10-50 nm were found as shown in Fig. 13.

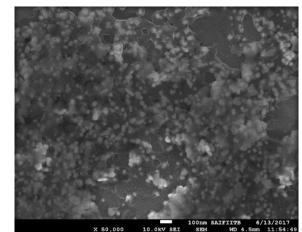


Fig. 12 SEM image of gold nanoparticles under 50000x

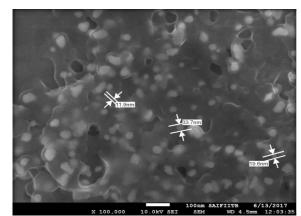


Fig. 13 SEM image of gold nanoparticles under 100000x

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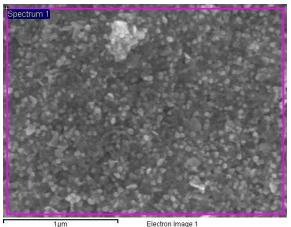


Fig. 14 SEM field of gold nanoparticles selected for EDAX analysis

Table 3 Composition of elements in the elemental analysis by EDS

Element	Weight%	Atomic%	
С	14.97	58.86	
N	4.57	15.42	
0	1.96	5.78	
Cl	1.02	1.35	
Au	77.48	18.58	

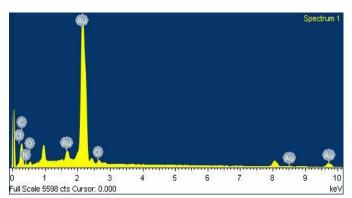


Fig. 15 EDS spectrum of gold nanoparticles synthesised by using 4%  $\it M.$  monosperma seed extract

EDAX provides supportive information as it gives elemental analysis of a sample. It depends on interaction of electrons and matter, where trademark X-beams are created, among different process. The EDAX analysis also showed the presence of elements like C, N, O other than Au (Figs. 14 and 15). Considering the use of HAuCl<sub>4</sub> and seed extract to prepare gold nanoparticles, the presence of elements other than Au as seen in Table 3 could possibly be due to the coating of L-DOPA from *M. monosperma* extract on nanoparticles.

### 4. Conclusion

The synthesis of gold nanoparticles using a seed extract was successfully achieved. Using *M. monosperma* seed extract, gold nanoparticles were successfully synthesised. The gold nanoparticles using 4% *M. monosperma* seed extract showed good stability over other concentrations. Analytical tools like FTIR, UV-Visible spectrophotometer and Scanning Electron microscope with EDAX helped to understand the surface chemistry of the gold nanoparticles. The gold nanoparticles synthesised showed spherical shape and also possibilities of L-DOPA coating on it. This could opens door to a lot of applications. One major application could be novel drug delivery system (NDDS).

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# EFFECT OF COAL FLY ASH ON EARLY GROWTH FACTORS OF VIGNA ACONTIFOLIA L. AND PENNISETUM GLAUCUM L. Effect of Coal Fly Ash on Early Growth Factors of Vigna Acontifolia L. and Penniset...

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Nitesh Joshi et al International Journal of Research VOL 8 (2) 2019 : PP 171 - 179

# Effect of Coal Fly Ash on Early Growth Factors of Vigna Acontifolia L. and Pennisetum Glaucum L.

Nitesh Joshi<sup>1</sup> Pallavi Menon<sup>1</sup>, and Ambika Joshi<sup>2</sup> <sup>1</sup>Associate Professor, Rizvi College of Arts Science and Commerce, Mumbai <sup>2</sup> Jai Hind College, Department of Botany, Mumbai.

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### Abstract

Fly ash from thermal power plants can be a resource of micronutrients but with poor disposal could manifest into a serious environmental threat. Fly ash escaping into the atmosphere is a major problem and in order to understand to this problem, a study was conducted to test the application of fly ash to agricultural soil in varying concentrations and its effects on early plant growth. In the present study to understand the effects of various concentrations of fly ash (10mg, 50mg, 75mg, and 100mg) on growth and yield responses of Vigna acontifolia L. and Pennisetum glaucum L. The seeds were aseptically sown on the solidified agar previously mixed with varying concentrations of fly ash in multi well plates. Each treatment was replicated in a randomised design and observed over a period of 7 days. The seedlings were studied for their response based on germination rate, seed, vigour index, length of radicle, length of plumule and fresh weight against seeds germinated using distilled water as control. The intensity of inhibitory effect on all other parameters was directly proportional to the concentration of fly ash employed and inhibition was most prominent from 75mg. Based on the overall health of the seedling, the observed effect of coal fly ash was pronounced in Vigna acontifolia L. than Pennisetum glaucum L.

Keywords: Crop, Fly Ash, Heavy Metals, Seed Germination Indices.

# INTRODUCTION

In India, promotion of industrialization, modernization and urban development releases a lot of toxic waste causing environmental pollution, a number of industries produce significant amount of solid wastes such as fly ash from thermal power, dust from cement plants, blast furnace slag, sludge from sewage systems to name a few. Coal fly ash is the residue of combustion of coal. Depending upon where the coal was mined, the elements present in coal are generally found in the ash. It has been reported that a lighter colour indicates the presence of high calcium oxide and darker colours suggest high organic content (Cockrell et. al., 1970). Fly ash is disposed either by dry or wet methods. In the dry method, the fly ash is dumped in landfills and fly ash basins. In wet method, the fly ash is washed out with water into artificial



lagoons and is called pond ash. Both methods ultimately lead to dumping the fly ash on open land, which degrades the soil and endangers human health and the environment. Therefore, disposal and utilization of ash requires careful assessment to stop conversion of productive land into landfills and accumulation of harmful metals in soil (Petruzzelli, G.; Lubrano, L. (Petruzzelli, G.; Lubrano, L. and Guidi, G., 1989). In order to mitigate pollution, fly ash from power plants has been recycled as cinders on roads, used in construction, landfills and as an agricultural fertiliser. Application of fly ash into soil has been reported to change the soil texture to improve the availability of water, air and nutrients by increasing its porosity, water holding capacity, electrical conductivity and hydraulic conductivity (Bilski, J.J et al 1995). Several field experiments have reported chemical constituents of fly ash may benefit plant growth and can improve properties of soil as well. (Elseewi, A.A. et al 1980; Sikka, R et al 1995; Singh, N.B et al 1986; Wong, M.H., Wong, J.W.C., 1989). The results of the study showed that blending of fly ash with agar as a medium for germination beneficial at lower concentrations, indicating of coal ash as an amendment for fertilizers along with an alternative for disposal of coal ash.

# MATERIAL AND METHODS

Planting material: Seeds of *Vigna acontifolia* L. and *Pennisetum glaucum* L. were studied for the effects of fly ash on seed germination were from a local seed dealer.

For the germination studies: Four surface sterilized seeds uniform in colour, weight and size were aseptically sown on the solidified agar previously mixed with varying concentrations of fly ash in multi well plates. The seeds were sterilized using Bavistin @ 200mg in 100ml distilled water for 5 minutes followed by a through rinse again, using distilled water.

The agar medium was prepared by adding 2gm of agar to 100ml distilled water. Triplicates of each treatment in completely randomized designed were studied along with a separate control series using only solidified agar.

Coal fly ash concentration: 10mg, 50mg, 75mg, and 100mg of fly ash was accurately weighed and mixed in 100 ml of agar solution. 10 ml of this solution was poured in each well on the multi plate and sealed for 7 days.

Parameters selected for the study: Germination indices i.e. Total germination (GT) and Seedling vigour index (SVI) (Abdul-Baki A.A. and J.D. Anderson 1973) were selected and recorded for this study. Seed germination and other growth attributes viz. length of the root and shoot (cm) and fresh weight (g) of the seedlings was recorded after a period of 7 days.

Total Germination: the final Germination percentage is a measure of the time for a population of seeds to germinate in order to estimate its viability and is expressed as a percentage. The total germination (GT) was calculated using the following formula:

GT = no. of seeds germinated/total seeds x 100

Seedling Vigour Index: Seed vigour helps understand the potential for emergence and development of seedlings in field conditions. Compared to GT, SVI being more sensitive is an important component of germination studies as it provides a better understanding of seed damage and deterioration and response to stressors.

Seedling vigour index was calculated by following formula:

 $SVI = Germination \% \times Seedling length (cm)$ 

Seedling length = RL + SL where RL is root length (cm), SL is shoot length.

# **RESULTS AND DISCUSSION**

# Elemental scan of Coal fly ash

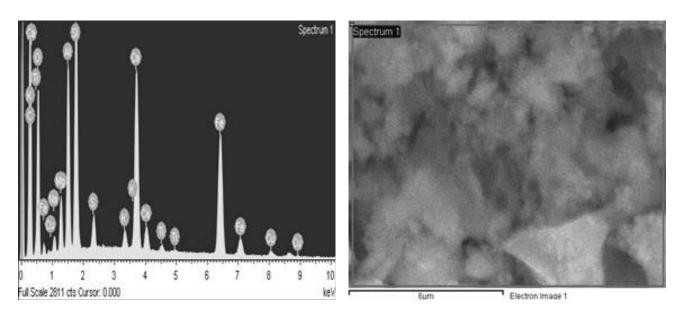
The coal fly ash used in this study was dry ash sourced from coal thermal power. The procured fly ash was scanned for its elemental composition on Electron diffusion spectroscopy (EDS). All the elements were analysed in 4 iterations, with no peaks omitted in the spectrum. Twelve elements, namely C, O, Na, Mg, Al, Si, S, K, Ca, Ti, Fe and Cu were quantified. These percentage concentrations were valuable in developing an approach for controlling pollution by various applications of fly ash in cement industry and as a source micro nutrient for plant growth.

Fig 2: Electron diffusion spectroscopy

Element	Weight%	Atomic%
C K	32.01	48.66
O K	27.8	31.73
Na K	0.79	0.63
Mg K	1.86	1.4
Al K	5.14	3.48
Si K	6.73	4.38
S K	1.05	0.6
KK	0.68	0.32
Ca K	7.81	3.56
Ti K	0.44	0.17
Fe K	14.67	4.8
Cu K	1.02	0.29
Total	100	100

### TABLE 1: Elemental scan of coal fly ash

Fig 3: Electron image of fly ash particles (EDS) scan of fly ash with peaks



### Effect of coal fly ash on seed germination

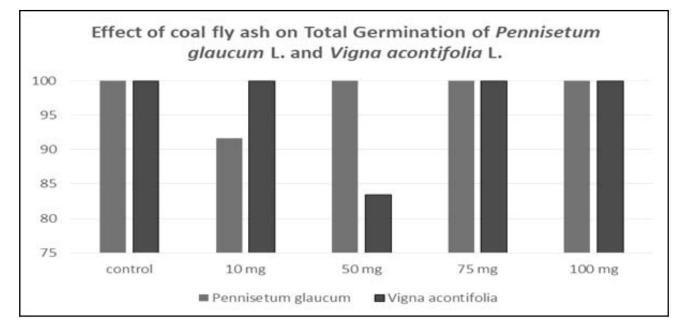
Upon application of coal fly ash to the seeds of *Vigna acontifolia* L. no significant effect of coal fly ash was observed on the germination. 100% was recorded for all the concentrations except 50 mg as seen in (table 2). The effects on germination of *Pennisetum glaucum* L. are fairly comparable for all concentrations, except for 10 mg showing a slightly lower germination percent of 91.66. No inhibitory effect being recorded on germination has been in accordance with several other studies on wheat (Sharma, S. K., et al 2001) and rice (Adriano, D. C. and John, T. Weber. 2001).



### TABLE 2: Effect of Coal fly ash on total germination percentage

Coal fly ash	Pennisetum glaucum L.	Vigna acontifolia L.		
Control	100	100		
10 mg	91.66	100		
50 mg	100	83.46		
75 mg	100	100		
100 mg	100	100		

Fig 4: Effect of Coal fly ash on total germination percentage



Effect of coal fly ash on the length of root (cm) Based on the observations, 10mg of fly ash had a beneficial effect on root length  $(5.24 \pm 1.29)$  cm in *Pennisetum glaucum* L. and  $(4.01 \pm 0.57)$  cm in *Vigna acontifolia* L. (table 3) detrimental effects were from 75mg onwards with a gradual reduction in the emergence of radicle. Comparing the root length of the species, *Pennisetum glaucum* L. performed better than *Vigna acontifolia* L. Reduction in root length may be due to compaction of FA particles which probably served as a physical barrier to root elongation. (Panda S, et al. 2015)

Effect of coal fly ash on the length of shoot (cm) Shoot length also followed a similar trend as root length in response to coal fly ash with the highest value recorded at  $(5.79 \pm 0.93)$  cm in *Vigna acontifolia L*. (table 3). Amendment with fly ash showed an increase in the length, it has been reported that there was an increase in the yield of tomato when grown in soil as an amendment of fly ash (Khan and Khan., 1996) as well as an increase in plant height was reported in lettuce grown in 5% fly ash amended with soil (Lau and Wong., 2001). The reduction in shoot length at higher concentrations could be attributed to the effect of heavy metal on the reduction in mer-

# EFFECT OF COAL FLY ASH ON EARLY GROWTH FACTORS OF VIGNA ACONTIFOLIA L. AND PENNISETUM GLAUCUM L.

istematic cells present in this region and some enzyme contained in cotyledon and endosperm and thereby, reduction the cell elongation and cell expansion (Houshmandfar A, Moraghebi F. 2011). It has also been that alkalinity of fly ash affects the availability of nutrients, mainly phosphorous, which has an adverse effect on plant growth (Jala S. & Goyal D, 2006)

Coal fly ash		Pennisetum glaucum L.	Vigna acontifolia L.
Control	RL	$6.90 \pm 1.38$	$3.45 \pm 1.20$
Control	SL	$3.75 \pm 1.18$	$3.95 \pm 1.91$
10 mg	RL	$5.24 \pm 1.29 **$	$4.01 \pm 0.57^{\#}$
10 mg	SL	$2.90 \pm 1^{**}$	$5.79 \pm 0.93*$
50 mg	RL	$4.61 \pm 0.92^{**}$	$2.55 \pm 0.42^{**}$
50 mg	SL	$2.78 \pm 0.95^{**}$	$5.00 \pm 0.47$ **
75 mg	RL	5.10 ± 1.38**	$1.68 \pm 0.57*$
75 mg	SL	$2.96 \pm 0.98^{**}$	$4.80 \pm 0.69^{\#}$
100 mg	RL	4.27 ± 1.37**	$1.76 \pm 0.45*$
100 mg	SL	$3.22 \pm 0.63^{\#}$	$4.85\pm0.90^{\text{\#}}$

TABLE 3: Effect of Coal fly ash on length of root (RL) and shoot (SL) in cm

\* significant at p < .01 \*\* significant at p < .05 # significant at p < .10

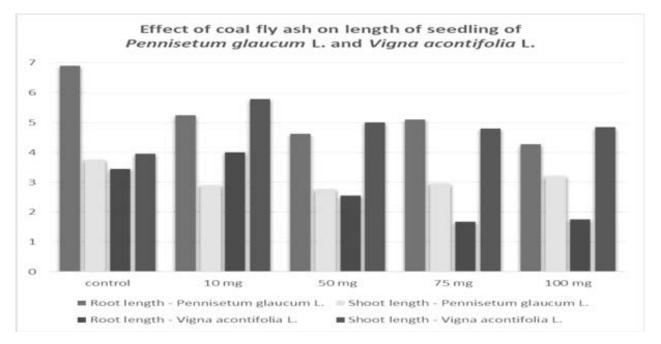


Fig 5: Effect of Coal fly ash on length of root (RL) and shoot (SL) in cm



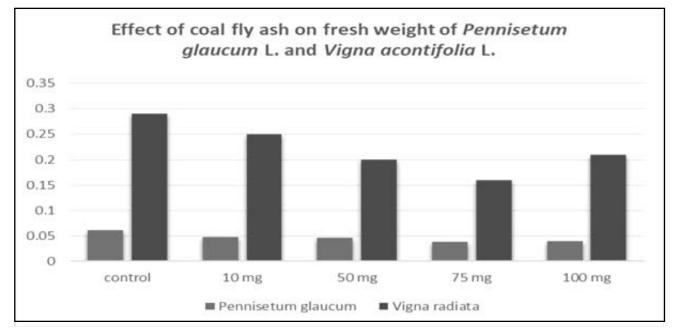
# Effect of Coal fly ash on fresh weight

Fresh weight of plants was affected by agar medium containing fly ash (table 4). As it has been observed that there is a decrease in the elongation of root and the height of the shoot, these factors will contribute to the lower weight of the seedling. The impact of the fresh of the plants is more significant in *Vigna acontifolia* L. compared to *Pennisetum glaucum* L. which showed an almost steady average weight of 0.04g.

Coal fly ash	Pennisetum glaucum L.	Vigna acontifolia L.		
Control	$0.06\pm0.015$	$0.29\pm0.07$		
10 mg	$0.04 \pm 0.021$ **	$0.25 \pm 0.03^{\#}$		
50 mg	$0.04 \pm 0.013*$	$0.20 \pm 0.04*$		
75 mg	$0.03 \pm 0.013*$	$0.16 \pm 0.03*$		
100 mg	$0.03 \pm 0.006*$	$0.21 \pm 0.04*$		

\* significant at p < .01 \*\* significant at p < .05 # significant at p < .10

Fig 6: Effect of Coal fly ash on fresh weight (g)



# Effect of coal fly ash on Seed Vigour Index (SVI)

The total germination percentage and a decrease in early seedling growth has contributed to the negative influence on seed vigour of both the species. (Table 5) A decline in the average SVI was observed from the highest recorded value of 1066.66 to 750 in *Pennisetum glaucum* L. whereas, in *Vigna acontifolia* L. there

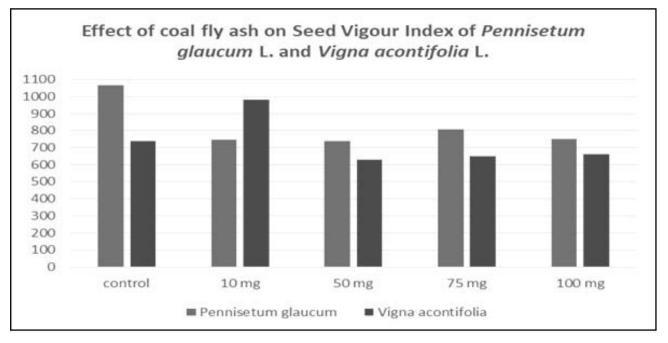
# EFFECT OF COAL FLY ASH ON EARLY GROWTH FACTORS OF VIGNA ACONTIFOLIA L. AND PENNISETUM GLAUCUM L.

has been an increased vigour at 10 mg (980.32) of fly ash added to the agar compared to control. Studies have shown that seed coats are effective barriers to metals and can prevent contamination of embryos until the seed coat is torn apart by the germinating embryonic root (Munzuroglu O., Geckil H. 2002). Increasing concentration of coal fly ash decreased seed vigour compared to the control samples for *Pennisetum glaucum* L. and in case *Vigna acontifolia* L. a gradual decrease was observed 980.32 to 662.5 when the concentrations were increased from 10mg to 100mg.

TABLE 5: Effect of Coal fly ash on seed vigour index

Coal fly ash	Pennisetum glaucum L.	Vigna acontifolia L.		
Control	1066.66	740		
10 mg	746.31	980.32		
50 mg	740	629.16		
75 mg	806.66	648.33		
100 mg	750	662.5		

Fig 7: Effect of Coal fly ash on seed vigour index



# CONCLUSION

The growth and the development of both the species was observed to be better upon adding fly ash in smaller concentrations. In particular, the growth best was at 50mg based on the length of the seedling. The observed high rate of germination in the present study, can be attributed to the water holding capacity of fly ash.



Usually, fly ash composed primarily of small, fine, hollow spherical particles considered to increase the water holding capacity. The major mineralogical constituents of fly ash were SiO<sub>2</sub>, CaCO<sub>3</sub> Al<sub>2</sub>O<sub>3</sub>, MgO, FeS<sub>2</sub>, albite, wollastonite. In addition to these fly ash also contained the macro and micronutrients (Fe, Mg, Cu, Na, P, K, S). These available nutrients present in fly ash can be considered beneficial up to certain levels however, at higher levels of fly ash reduction has been measured in growth parameters of crops. Therefore, the fly ash has a potential for utilization to improve soils with poor nutrient content at the same time it also gives us a safe option for disposal of large amounts of fly ash.

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# **COMPARATIVE SCREENING NORMS OF STOCKS**

T Mohammed Makhtar Khan" Dr. Ashfaq Ahmad Khan\*\*

# ABSTRACT

This paper titled "Comparative Screening Norms of stock" discusses at length different screening norms adopted by different institutions. For example in India, we have TASIS, internationally renowned Shariah Screening norms presented by AAOIFI and others had been discussed at length. From the Shariah point of view, if a person wants to invest in Shariah Compliant companies in the stock market, that company needs to be passed through some process and this process is known as Shariah Screening Process. The objective of this study is to put a light on different principles of shariah/ Islamic Finance and another objective is to do a comparative analysis of different shariah screening processes adopted by different institutions throughout the globe.

Keywords: Shari'ah, Screening process, Riba, Globe, Compliant

# 1. Introduction

'Shariah' which is all about Islamic laws. Islamic laws are followed by Muslims throughout the world. Islamic laws are basically based on the Quran (The book which is revealed by Allah towards its last messenger Prophet Muhammed(peace be upon him) and Hadith i.e. the teaching by its last messenger and its life. Shariah principles are followed by Muslims in all ways of their life. Shariah principles govern every aspect of a person's family life, business, etc. The ambit of Shariah laws covers from birth to death.

There are five pillars which are considered the most important aspects in Islam i.e.

Faith (Iman)

Prayer (Namaz)

Fasting (Roza)

Charity (Zakat)

Religious Pilgrimage (Hajj).

of Islam. The five important areas are Imaniyat (Faith) Ibadaat (Prayer) Muamulaat (Dealings) Mashirat (Culture)

Akhlaqiaat (Character Building).

The Mamulaat part deals with many aspects related to earnings, spending, business, etc. A person should earn from Shariah (Lawful) sources only and should avoid Haram(unlawful) earnings i.e prohibited in Islam. And should concentrate on those which are permitted. One of the areas which we want to focus is investment i.e. earning from investment. In these aspects Shariah Investment Principles are applicable. The Shariah laws related to Islamic Investment are being taken from the Quran, Hadith, Figh, and Ijtihad.

# Shariah Ethical Norms are for Investment

These five elements are considered to be five pillars

While investing in any company a person should

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5) TASIS, India Screening Norms	screened followed by all non shariah activities like Gambling, porpography, and	<ol> <li>Borrowings/Debts: Less than 25% of Total Assets</li> <li>Interest Income Plus returns (@8) from all non-compliant investment: Less than 3% of Total income</li> <li>Cash Plus Receivables: Less than 90% of Total Assets</li> </ol>
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# 4. Conclusion

Shariah the Islamic way of life has not kept muslims orphan in any walk of life. As discussed at length different Shariah Principles of finance and also different processes adopted by different institutions to make company shariah compliant in order to be eligible for investment purpose. After going through comparative analysis of different screening procedures adopted by different institutions, there is a need to have a common or similar screening process. This point needs to be addressed by shariah scholars as this is considered to be a big query from investors point of view.

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# Impacts of Print Media on India Society

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QR Code



# 1: Introduction:

Print media is one of the oldest and basic forms of communication. It includes newspapers, weeklies, magazines, monthlies, banners & graphics, posters and other forms of printed material the contribution of print media in providing information and transfer of knowledge is remarkable. Even after the advent of electronic media, the print media has not lost its charm or relevance.

Print media has the advantage of making a longer impact on the minds of the reader, with more in-depth reporting and analysis. Magazines and newspapers are the dominant traditional print media used in advertising. Brochures, flyers and other collateral pieces also are sometimes referred to as print collateral. While digital media expansion has affected use of print, it remains a viable way to advertise. Primary strengths of print relative to digital include tangibility, an enduring message and high credibility. Some people prefer to read media in print as opposed to digital formats.

Print media as both advantage and disadvantage at the same time print media also plays vital role and most important role in spreading knowledge and information amongst the peoples and a college students also and in the society but print media consist drawbacks such as and India there are a large number of persons who does not read print media and just go through images and beautifully captured photos and miss understand the meaning and interpretation of the news at the same time print media also provides good information about the societies and political backgrounds and keep youth and old age peoples connected with the recent realistic scenario

# 2: Review of literature:

A study of relevant literature shows one the various studies which pertain to the extent of value degeneration boosted by Printed Advertisements. There are statistics-based evidence to prove this situation and are very prominent in the current world. Some of the major studies carried out across different countries, during different periods, on the same have been reviewed. The following are the founding of a few books that have enlightened the minds of many.

Most of the reviewed literature showed that are generally criticized for targeting children (Kunkel, 1988; Haefner, 1991; Kunkel, 1992; Browne, 1998; Graves, 1999; Pechmann and Shih, 1999; Childs and Maher, 2003; Saffer and Dave, 2003; Sinha, 2005), excessive use of sex appeals (Pollay, 1986; Henthrone and LaTour, 1994; Ford et al., 1997), stereotypical presentations of women (Chatterji, 2005; Schaffter, 2006), negative psychological effects on the viewers (Richins, 1991; Fay and Price, 1994; Nuta, 2009) and promoting materialism (Richins, 1995; Roy, 2006; Chan and Cia, 2009; Nuta, 2009). While influence of investigating the advertisements directed at children, it was found that they do havean adverse influence on child behavior. Due to lack of positive vibes, the aids fail to give any positive effects. Effective balance in the children is lost and it has been seen that they have emotions pouring out in their most unexpected ways. Kunkel (1988) conducted a study in which the values of the advertisers who target children were questioned. It was suggested that advertisements which target children are unethical because children are not in a position to evaluate commercial persuasion. Arguments have been initiated by critics stating that advertisements directed at children are harmful because they serve to glorify the use of alcohol and tobacco, (Pechmann and Shih 1999; Saffer and Dave, 2003; Sinha, 2005) create awareness among children of their sexuality at a tender age (Kunkel, 1992) and inculcate stereotypes of gender among them (Browne, 1998; Graves, 1999; Childs and Maher, 2003).

# **3.OBJECTIVE OF STUDY:**

- To know the impacts of print media on Indian population.
- To eradicate the adverse impacts of print media from society.
- To understand the problems faces by Indian population.
- To spread the positive side of print media.
- To make understand the adverse effects of print media.

Impact Factor (SJIF) – 5.266

5:

# **4: HYPOTHESIS:**

1:H1 print media does not have adverse impacts on society

H0 print media have adverse impacts on society

2: H1 Print media plays an important role in societal development

H0 Print media does not play important role in societal development

# Interpretation

Research

The study of print advertisement is based on both primary and secondary data obtained. Primary data is totally derived from feedback bydifferent stakeholders from the society and secondary data is obtained from books and materials as and when available.

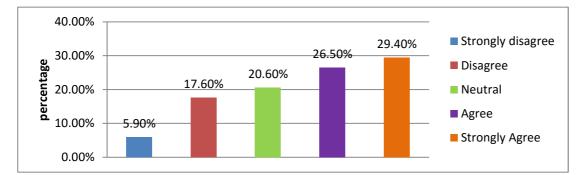
Methodology

Data

and

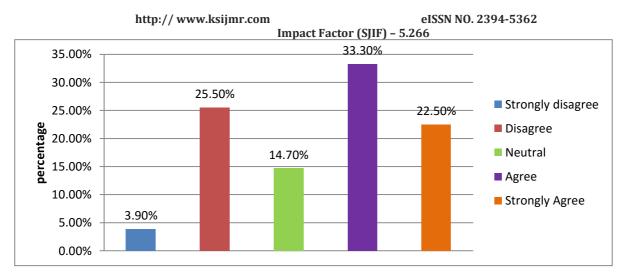
Q No. 1: Print media have negative impacts on society.

	Strongly disagree		igree	Neutral		Agree		Strongly Agree	
Count	%	Count	%	Count	%	Count	%	Count	%
6	5.9%	18	17.6%	21	20.6%	27	26.5%	30	29.4%



**Interpretation:**Since p-value for the chi-square test is less than that of 0.05 indicates that the proportion of respondents who agree hence we conclude that print media has negative impacts on society. Most peoples responded that print media does have negative impacts on Indian society. Q No. 2: Print media is not suitable for under educated peoples.

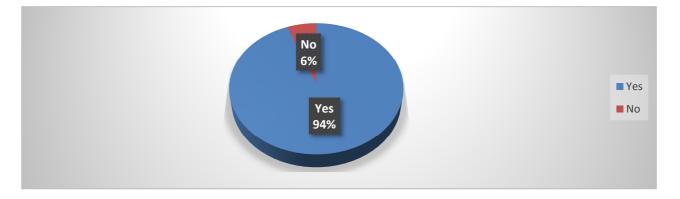
Strongly disagree		Disagree		Neutral		Agree		Strongly Agree		
Cour	t g	%	Count	%	Count	%	Count	%	Count	%
4	3.9	9%	26	25.5%	15	14.7%	34	33.3%	23	22.5%



**Interpretation:** Most peoples responded that print media is not suitable for under educated peoples. Since p-value for the chi-square test is less than that of 0.05 indicates that the proportion of respondents who agree that is more than that those who don't agree, hence we conclude that it is not suitable for under educated peoples.

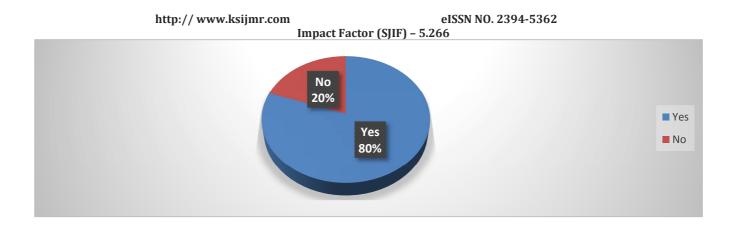
Q No.3: Do you accept that print media should not be given to minor children's?

	Count	Column N %
Yes	96	94.1%
No	6	5.9%



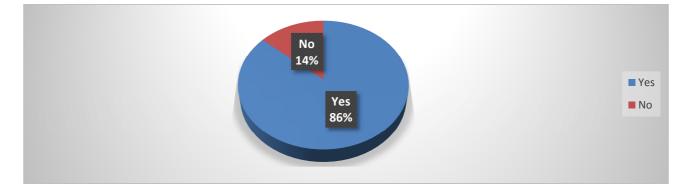
Q No. 4: print media is spreading rumors or irrelevant information

	Count	Column N %
Yes	82	80.4%
No	20	19.6%



# Q No. 5: does print media effects on person psychology?

	Count	Column N %
Yes	88	86.3%
No	14	13.7%



From the above discussion with students, small shop keepers, house wives, working peoples and individuals we can see that there is no understanding of print mediaamong Indian masses and even they are adversely affected due to wrong information and nudity in print media they don't want to share some magazine and newspaper with their children's. print media have both positive and negative impacts on Indian population irrespective of gender, age, income ,marital status etc.

# 6: Conclusion:

Print media have both positive and negative impacts on Indian population irrespective of gender, age, income, marital status etc. print media also provides good information about the societies and political backgrounds and keep youth and old age peoples connected with the recent realistic scenario. Print media is as necessary for information and it is our responsibility to use it as good source of information and we should not spread wrong information and should not misuse the power of print media

# **References:**

1:(Pechmann and Shih 19199; Saffer and Dave, 2003; Sinha, 2005)

- 2: <u>www.google.com</u>
- 3: Google scholars

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# The Study of financial literacy in Muslim minority in Mumbai

**Research** Guide

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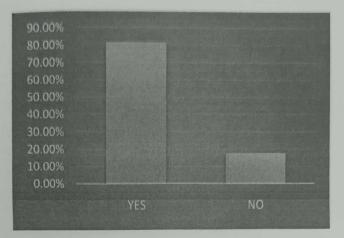
# Abstract:

phenomenon shariah financial literacy is Financial literacy is a means of success modern financial literacy is an evil and lack of advisorshould always be ethical about social concern. Muslim investments are not draining in the community. financial literacy is not just about knowing the financial products but also about Indian financial system therefore the researcher focus on financial avenues available Muslim investor. Muslims are financially sound but due to lack of financial literacy they invest their funds into unorganized sector like Ponzi scheme etc. and lost their funds. ethical products those are not harmful for that to be understood by each and every individual especially also an evil therefore financial literacy is a mandatory society because. Investor, financial Muslim for

(key word: financial literacy, Ponzischeme, Muslim, social investment)

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Interpretations: Since the p-value for the chi-square is less than that of 0.05 indicates that the responses are not equally distributed. It indicates that the proportion of respondents those who believe in akhirah and income question are significantly more than that of those who didn't.

# 6: Conclusion:

From the above discussion we can conclude that Muslims are financially sound but due to lack of financial literacy or illiteracy in community they don't invest their money in financial system and they invest in Ponzi scheme which exploits them on the basis of Islamic principal. it is suggested that some basic literacy programs should be organized in community so that financial literacy can be spread. Muslim are aware about akhirah just they don't understand the financial literacy concepts therefore they are reacting the concept religiously only.

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4: The Importance of Financial Education (OECD 2006)

5: www.ethicalnstitue.com

# Impacts of Print Advertisement on Indian Society

Research Guide

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Abstract: Print advertisement is one of the oldest and basic forms of communication. It includes newspapers, weeklies, magazines, monthlies, banners & graphics, posters and other forms of printed material. The contribution of print advertisement in providing information and transfer of knowledge is remarkable. Even after the advent of electronic media, the print advertisement has not lost its charm or relevance. Print advertisement has the advantage of making a longer impact on the minds of the reader, with more in-depth reporting and analysis. Magazines and newspapers are the dominant traditional print advertisement used in advertising. Brochures, flyers and other collateral pieces also are sometimes referred to as print collateral.

(Key words: advertisement, media, magazines, newspapers, posters)

- The advertisements in any media should enhance the public morality and living standards of the general Public. It is recommended to the prints owners that only the advertisement which will give women prestige, code of conduct, moral values and thereby increase the standard of living and maintaining good living style of the consumers should be permitted to be aired.
- Advertising should endeavor to gain the goodwill of the public on the basis of merits of the goods or services advertised. Hence the direct comparison with competing goods or films should be avoided and disparaging reference in no circumstances should be permitted
- No advertisement shall be aired which leads the consumers to believe that if they do not own or use the product advertised, they will be inferior in some way to others or that they are liable to be condemned or ridiculed for not owing or using it. Thus it is suggested that the advertisements shall not be allowed to take the advantage of the superstitions or ignorance of the general public.

# 7: Conclusion:

This study reveals the importance of ethics, morality and standards to be applied for designing the goodadvertisements copy, deciding for selective advertisement message and delivering the whole of advertisement inthe right prints and in a decent way.Print advertisements have both positive and negative impacts on Indian population irrespective of gender, age, income, marital status etc. Print advertisement also provides good information about the societies and political backgrounds and keep youth and old age peoples connected with the recent realistic scenario. Print advertisement is as necessary for information and it is our responsibility to use it as good source of information and we should not spread wrong information and should not misuse the power of print advertisement

# References:

1:(Pechmann and Shih 19199; Saffer and Dave, 2003; Sinha, 2005)

2: www.google.com

3: Google scholars

# Preluding Based Investment Instruments in Capital Market

# MOHAMMED MUKHTAR KHAN (RESEARCH SCHOLAR) (Rizvi College of arts, science and commerce) ( Affiliation to Mumbai University)

# Dr. ASHFAQ AHMAD KHAN (RESEARCH GUIDE) (VICE PRINCIPAL & ASSOCIATE PROFESSOR AT RIZVI COLLEGE OF ARTS, SCIENCE & COMMERCE, MUMBAI-INDIA) (Affiliation to Mumbai University)

# ABSTRACT

The shariah based capital market acts as an significant role in the development &Shari'ah based Islamic to financial institutions. Theshariah based capital market perform the functions as same as Conventional Capital market for funds aspirant to fund suppliers.

As per one of the reports by research and markets (the world's largest market research store) Report 2019,the industry total worth, basically from 3 main sectors ie Banking, capital markets, takaful (Islamic Insurance) was estimated to be a USD 2.05 trillion in 2017, reaching to an 8.3% growth is assets in USD terms) and reversing the preceding 2 years of assets growth stagnation

(2017:USD 1.89 trillion vs 2016:USD 1.88 trillion)

The purpose of this paper is to introduce the Shari'ah based investment intruments and to evaluate the potentiality of Shari'ah based investment intruments.

# **KEYWORDS**:

Shari'ah based capital market, Islamic unit trusts, Islamic commodity funds

# **INTRODUCTION:**

The shariah based capital market acts as an significant role in the development & Shari'ah based Islamic to financial institutions. Similar to traditional based Stock /Capital Market, Shariah based capital market

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# Sez Act 2005: A masterstroke

(W.r.t Pvt Seepz Sez).

CA Salim J Khan

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# ABSTRACT

The Sez Act ,2005 and its Rules 2006 is a master piece central legislation. The new Act is a reflection of contemporary approach on India's export policy and sow the seeds for rapid industrial development. It reinforces the objectives of classical Sez viz multiplication of economic activity, promotion of export, employment and investment, backed by strong infrastructure. To achieve the above goals, the Act provides a conducive legal framework by providing duty- free environment, single window clearance and attractive fiscal concessions to the developers and units of Sez. The present paper is an attempt to measure the expansionary effect of the Act on the development of Pvt Seepz Sez. The parameters chosen are export and sector-wise export. The researcher has applied suitable statistical tools such as percentage growth, mean, standard deviation and CAGR, to measure the performance. Pvt Seepz Sez export has been compared to the overall Sez export. Major sectorial contribution had been studied separately. The finding reveals that after the implementation of the Act the export performance is of Pvt Seepz Sez is commendable, no doubt sectorial imbalances exist. The Sez Act has added the required vigor, vitality and enthusiasm in the Sez arena.

KEY WORDS: SEZ, Sez Act, 2005, Pvt Seepz Sez, Sectorial export.

# INTRODUCTION SEZ AND SEZ ACT, 2005:

The urge for development of economies have given rise to various instruments and business organization. One such model is " special economic zones ". Sez became catch phrase across the globe in the last century. India is no exception. Sez as name suggest are "special", meaning dedicated enclaves, with distinct goals, exclusive environment and superior concessions. They enjoy liberalized business environment, coupled with unparalleled infrastructure. The Sez Act, 2005 defines " Sez as a specially delineated duty-free enclave and shall be deemed foreign territory for the purpose of trade operation, duties and tariffs".

The objectives of the classical Sez has been re-enforced by the Sez Act 2005. The revered objectives of setting up Sez are:

Mahanoo entreserentem

The Masterpiece legislation has played a master stroke the Sez Act, 2005 and rules 2006 have lived up to its expectation. The duty-free environment single window clearance ease of doing business coupled with fiscal incentives and concession has successfully revitalized and added vigor and vitality to the special economic zones few words of caution, this research focuses on one dimension of positives i.e. exports, the advantages in terms of employment and investment needs to be quantified and researched. Besides the benefit analysis the cost analysis is pending. The message remains that let complacency not creep in, there is still a long innings to be played.

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# Central SEEPZ: A Jewel in SEZ Crown

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## ABSTRACT

Special economic zones are called " Engine of growth". They act as a catalyst to rapid economic growth. The Central Sez is playing a vital role in India's foreign trade development. Since 2005, Private Sez have assumed importance. The present paper is an attempt to highlight the fact that Central Sez has not lost its shine and potential. They are still contributing in terms of export, employment and investment. The present paper undertakes a detailed analysis of the export of Central Seepz-sez. It is the second Central Sez to be set up after Kandla in the year 1973. It is located in the prime western suburb of Mumbai. The paper attempts to study and compare the Seepz Sez export with the overall Sez export. Sector-wise export has also been analyzed to the core. The findings reveal that Seepz is no more an electronic zone, rather it a gem and Jewellery zone. This gave rise to the title of the paper " Central Seepz: A jewel in Sez Crown".

**KEYWORDS:** Special economic zones, Sez policy, Minimum alternate Tax(MAT), Dividend distribution Tax (DDT).

# **INTRODUCTION**

Every nation endeavour for it economic growth and development. It cannot be achieved overnight. It calls for relentless and consistent tenacity by the government. It is this

National Conference on "New Frontiers of Innovation in Management, Social Science, and Technology and their Impact on Societal Development" There should be a balanced growth of other sectors as well. Dependency on a single sector may prove to be risky.

- Mumbai in general and Seepz Sez has not fully utilised its locational advantage to be an IT /ITES hub. They should follow Bangalore Hyderabad and Pune model to 4.
- Through Innovation and upgradation the electronic hardware sector should be revived.
- 5 The trading and service sector needs a special booster. 6.

Undoubtedly, the private Sez are in vogue, but one cannot forget the contribution of Central Sez. They contributed for nearly five decades and continue to do so till date. The performance is not limited to only export, they have provided jobs to millions of citizens and successfully attracted investment both from a domestic and foreign source. Their role in the current scenario cannot be debated. The should be realigned and reassigned special targets under the flagship programme of "Make in India".

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National Conference on "New Frontiers of Innovation in Management, Social Science, and Technology and their Impact on Societal Development"

**ORIGINAL ARTICLE** 



# Palladium Nanoparticle-Bentonite Hybrid Using Leaves of *Syzygium aqueum* Plant from India: Design and Assessment in the Catalysis of –C–C– Coupling Reaction

Satish B. Manjare<sup>1</sup> · Rajendra A. Chaudhari<sup>1</sup>

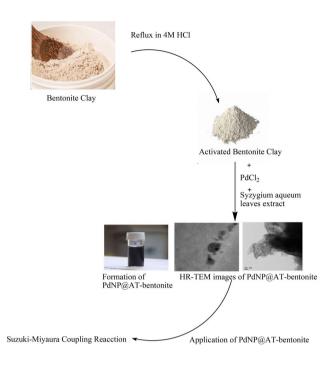
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### Abstract

An environment-friendly synthesis process has been developed with the aid of *Syzygium aqueum* (water apple) leaves extract. Pulverized leaves of *Syzygium aqueum* (water apple) are mixed with a universal solvent such as water for the preparation of Pd nanoparticle supported on activated Bentonite. The extract from the plant leaves acts both as a reducing agent and also as a capping agent for converting the PdCl<sub>2</sub> to PdNPs. The synthesized PdNPs are supported on modified clay and they are characterized by using FTIR, BET, HR-TEM, ICP-MS, TGA, XRD, and FE-SEM/EDX. It is found that the supported PdNPs give high rate of conversions of Suzuki–Miyaura coupling products and give greater than 90% products in universal solvent i.e. water at fairly low temperature. It shows the potential for the environment-friendly synthesis of prime organic molecules like excellent biaryl derivatives with TONs and TOFs with economical and efficient catalyst loading. We recorded high activity, chemoselectivity and excellent TONs (15,061–20,537) and TOFs (100,407–136,919) by using a small catalyst loading in short reaction time only 15 min. The catalyst shows a long lifetime (ten times). Experiments are performed, recycling it, which demonstrate the sustainability and efficiency of the catalytic process. The prepared catalyst gives a higher percentage

Extended author information available on the last page of the article

of coupling product in the lower time. The supported PdNPs help to form good selectivity and efficacy. The catalyst is found highly stable and can be recycled ten times with no appreciable loss in the efficiency. **Graphical abstract** 



Keywords Environment-friendly synthesis · Palladium nanoparticles · XRD · -C-C- coupling

# 1 Introduction

In the past decade, aromatic -C-C- bond coupling reaction has fascinated attention of researchers since these compounds are used mainly in the preparation of many pharmaceuticals and other organic compounds [1-3]. In this regards, the synthesis of loaded nanomaterials on support, which are heterogeneous catalysts, have received great importance as they have unique catalytic properties and catalytic stability in organic environment-friendly synthesis [4–10]. Among the various metal nanoparticles obtained from transition metals i.e. palladium, ruthenium etc. nanoparticles are popular for their excellent catalytic activity and selectivity in organic synthesis [11, 12]. Pd salts or complexes prepared by adding ligands are commonly employed as sources of Pd for cross coupling reaction. The reaction generally takes place in the presence of a homogeneous palladium catalyst, which makes the recovery of the metal nanoparticle catalyst difficult. However, agglomeration of metal nanoparticles without support is inadmissible. Due to agglomeration, high surface energy increases and that leads to the lowering of catalytic activity. In order to restrain agglomeration, considerable efforts have been made to develop suitable stabilizers or groups.

The use of a heterogeneous PdNPs catalyst has been widely exploited to achieve sustainable and environmentfriendly technologies for chemical reaction so as to overcome these difficulties. Recently, the Pd supported on silica, carbon and zeolite are commonly utilized in heterogeneous catalysis [13-18]. In another literature study, heterogeneous PdNPs catalyst has been widely used to achieve sustainable and environment-friendly technologies for chemical reaction so as to overcome these difficulties. There are very few reports available about the preparation of PdNPs supported on biopolymer like novel agar/pectin composite (APC) [19], O-carboxymethyl chitosan Schiff bases [20], chitosan [21], cellulose [22-24], sporopollenin [25], new biopolymer (chitosan)-based pincer-type [26], starch [27], cytosine complex immobilized on functionalized hexagonal mesoporous silica (HMS-CPTMS-Cy) [28] and mesoporous silica SBA-15 [29].

The Pd nanoparticles clay catalyst used in cross coupling reaction facilitates easily the separation of the catalyst from reaction mass. In comparison with other supports, Bentonite clay in particular, which is the most promising class of inorganic layered material, is exploited as catalyst and photocatalyst for several reactions such as alkylation, oxidation reaction of alcohol, CO, alkene, styrene and finally H<sub>2</sub> production. Bentonite belongs to the smectite groups of clay which are most abundant, easily available, environment-friendly and economical. It is an inorganic layered material which may be considered as a catalytic support. Efforts are now being made to develop new environment-friendly protocols for the synthesis of clay supported palladium nanoparticle. There are very few reports available about the preparation of PdNPs, which are formed using biological material like plant extract of Ocimum sanctum [4], Pistacia atlantica kurdica (P. a. kurdica) [30], Cinnamomum camphora [31], Solanum trilobatum [32]. The environment-friendly route that uses non-toxic solvents like water (green solvent guide) [33], reducing agents like biological extracts and stirring pathway or microwave assisted synthesis etc. is becoming ravishing [34-39]. The bio-chemicals in the leaves extract such as phenolic acids, flavonoids, propenyl polyols, terpenoids etc. act as magnificent reducing agents that are easily accessible, non-toxic, cheaper and eco-friendly natural source of that reduces metal salts and forms metal nanoparticles [30–40]. In the recent study, for instance, papaya peel extract was used to synthesize PdNPs, which is used as a catalyst for the Suzuki-Miyaura coupling reaction under aqueous conditions [41].

*Syzygium aqueum*, commonly known as water apple, is a plant native to Malaysia, New Guinea, Queensland and Indian subcontinent. The leaves of this plant are rich in phenolic acids, alkaloids, flavonoids, polyols, terpenoids etc.

In the present work, we report that an environmentfriendly synthesis of PdNPs, aqueous *Syzygium aqueum* leaves extract has been used as a reducing agent supported on modified Bentonite and the synthesized PdNPs are used in Suzuki–Miyaura coupling reaction. To the best of our knowledge, there are very few reports on the immobilization of Pd nanoparticles on dealuminated Bentonite clay for its application in the Suzuki–Miyaura coupling reaction.

# 2 Material and Methods

All the chemicals were purchased from Hi-Media and used as it is. Solvents were dried by standard methods to use for reactions. TLC was carried out with Merck silica gel 60-F<sub>254</sub> plates and column chromatography was performed over silica gel (60–120 mesh) obtained from commercial suppliers. <sup>1</sup>H NMR spectra were recorded on a Bruker Advance<sup>III</sup>, Switzerland spectrometer (400 MHz) spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane as an internal standard. The purified Bentonite clay is then treated with 4 M HCl in order to increase and fining the surface area by generating pores.

### 2.1 Preparation of Support

5.0 g of purified powder of Bentonite sample, 4 M HCl were taken a in a clean round bottom flask. Then the resulting mixture was refluxed for 3 h at temperature 90 °C. After cooling reaction mixture, the liquid was decanted and the activated dealuminated Bentonite was dialyzed with double distilled water till the conductance of the effluent water becomes nearly equal to that of double distilled water. The resulting reaction mass was dried in a hot air oven at 50 °C and designed as AT-Bentonite.

### 2.2 Preparation of Syzygium aqueum Leaves Extract

The *Syzygium aqueum* leaves were collected from sub-campus, Mirjole, Ratnagiri, MS, India, and they were sun-dried for 8 days and powdered by using grinder. 10.0 g of pulverized leaves were put into a beaker with 100 mL double distilled water and warmed it at 60 °C for 20 min. The resulting mixture was filtered and it collected in a glass bottle and stored at 5 °C in a refrigerator. The filtrate was named as SALE.

# 2.3 Preparation of Palladium Nanoparticles Supported on AT-Bentonite

In clean 100 mL two necked round bottom flask, 1.4 g powdered AT-Bentonite was suspended in 40 mL aqueous solution of 0.02 M PdCl<sub>2</sub>. Then the mixture was vigorously stirred with the help of overhead stirrer (Remi) at 400 rpm for 8 h at 90 °C in oil bath and followed by evaporation. Then the mixture was filtered and dried in hot air oven at 60 °C. The 310 mg of the dried mass was then transferred into 5 mL double distilled water and to this 30 mL SALE was added as a reducing agent under vigorous stirring with the help of overhead stirrer (Remi) at 400 rpm. Then resulting material was heated up to 100 °C and it stirred with the help of overhead stirrer (Remi) at 400 rpm for 10 h till the color changes from brown to black, which shows the reduction of Pd<sup>2+</sup> to Pd<sup>0</sup>. Then this black solid mass was filtered by using Whatman filter paper number 41 and washed repeatedly with double distilled water and finally dried in vacuum desiccators. This resultant material thus prepared was named PdNP@AT-Bentonite.

## 2.4 PdNP@AT-Bentonite Catalyzed Suzuki–Miyaura Coupling Reaction

Aryl halide (1 mmol), aryl boronic acid (1 mmol),  $K_2CO_3$  (2 mmol), PdNP@AT-Bentonite (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.25 mmol) and 10 mL water were taken in a clean double neck round bottom flask. Reaction mass was refluxed for 15 min at temperature 90 °C. The progress of reaction was monitored by TLC. After the completion of the reaction, reaction mixture was allowed to attain room temperature and then it was subjected to equilibrate with ethyl acetate (30 mL) for 5 min, and the mixture filtered through celite bed. The organic layer was washed repeatedly with water (30 mL  $\times$  2). The organic layer was separated and dried on sodium sulphate, and it was evaporated on rotary evaporator to get crude compound. The crude compound was then purified by column chromatography using silica (60–120 mesh) as stationary phase and 0–5% ethyl acetate: hexane as mobile phase. Purified compound was characterized by <sup>1</sup>H NMR.

# 2.5 Mercury Poisoning Experiments

Mercury poisoning test [22] were performed with the model reaction in the optimum conditions (Table 2, entry 1). This model reaction (Iodobenzene with phenylboronic acid) was performed for 24 h without adding mercury. Yield for catalyst PdNP@AT-Bentonite are 68%. Then, the 300 molar equivalents of mercury, relative to the PdNPs catalyst, were put in to the reaction mass and stirred with the help of overhead stirrer (Remi) for another 24 h. After the allowed time the procedure in Sect. 2.4 was repeated for Table 2 remaining entries. The desired products (3-methoxybiphenyl and 2-methoxybiphenyl) were obtained with lower yields after 48 h by using PdNP@AT-Bentonite. Yields for (3-methoxybiphenyl and 2-methoxybiphenyl) are 64, 62%, respectively.

### 2.6 Recovery of Catalyst

After the first reaction cycles, the solid catalyst was recovered by a centrifugation and was washed with ethyl acetate and was dried in a hot air oven at 50 °C. The recovered catalyst could be reused for the next reaction cycle. Recyclability and reusability of the catalyst was examined by introducing the used catalyst subsequently ten times at the optimum conditions for the synthesis of biaryl. The catalyst found effective enough in each cycle, which shows no significant loss in the catalytic activity.

# 2.7 Measurement and Characterization

The amount Pd was determined by the inductively coupled plasma mass spectrometer (ICP-MS, model Element XR) analysis. The PdNP@AT-Bentonite was dissolved in the concentrated HNO<sub>3</sub> and then the solution was subjected to the determination of the Pd content. Powder X-ray diffraction (XRD) patterns were collected on a Brucker D2 Phaser diffractometer equipped with a Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å). Diffraction patterns were recorded in the 5°–90° regions at a rate of 0.5° 20. FE-scanning electron micrographs were obtained with JSM-7600F microscope equipped with EDX spectrometer. Energy dispersive X-ray spectroscopy (EDX) was used in connection with FE-SEM for the elemental analysis. The surface area was measured by using nitrogen adsorption (SMART Instrument, India) at 77 K. Prior to taking measurement, the sample was activated at 300 °C for 3 h under vacuum. The FTIR (Fourier Transform Infrared) spectra were recorded on Brucker ALPHA 100508 double beam spectrometer using KBr water technique. TGA analysis was carried out by using Mettler Toledo Switzerland. HR-TEM analysis was performed with FEI, Tecnai G2, F30 microscope.

# **3** Result and Discussion

# 3.1 Pd Content

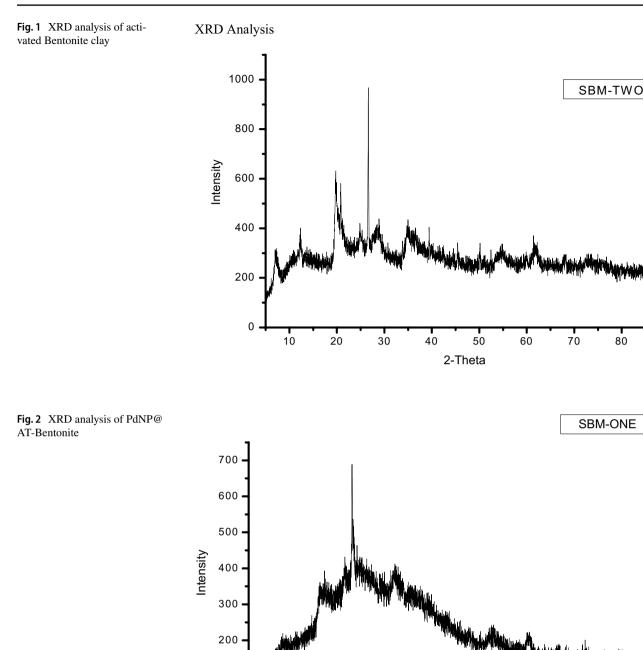
The Pd content from the PdNP@AT-Bentonite sample was analyzed by the ICP-MS. The Pd content was found to be 0.409 mg/500 mg from PdNP@AT-Bentonite. It was expected that the large surface, high ion exchange capacity and adsorptive capacity made this support excellent for load-ing metallic ions [38, 39].

# 3.2 XRD Analysis and BET Study

The Fig. 1 showed XRD analysis of Bentonite clay. XRD analysis was carried out to examine the structure of palladium loaded on clay as shown in Fig. 2. Powder X-ray diffraction measurements reveal that the structures of all the clay supports remain intact after dealumination and subsequent loading and treatment. The basal spacing  $d_{100}$  of the pure Bentonite sample shifted from 9.08 to 6.0 after Pd loading, which confirms that an increase in d spacing due to intercalation of Pd nanoparticles. The peaks at 40.1, 46 and 68° corresponds to the (111), (200) and (220) crystal planes confirm the presence of metallic Pd (0) having face centered cubic (fcc) structure. The specific surface area determined by N<sub>2</sub> adsorption decreases from 75 to 52 m<sup>2</sup> g<sup>-1</sup> after Pd loading.

### 3.3 FE-SEM and EDX Analysis

FE-SEM images of samples are represented in Fig. 3a. The FE-SEM is used to study the morphology i.e. external structural features of the samples prepared in this work. FE-SEM images show dominant flakes like particle morphology. The flakes type of morphology is due to the characteristic property of layered material and that is what has been reflected in the FE-SEM pictures. Apart from this, the small granules or agglomeration of grains is also visible in the FE-SEM pictures which may be due to the breaking of those flakes into the smaller particles. FE-SEM



pictures are in good agreement with layered structure of Bentonite clay. Energy dispersive spectroscopy was used to map the elements present in the sample. The results are given in the Table 1. Energy dispersive X-Ray analysis (EDAX) showed the presence of Si, Al, Mg, Ti, Fe, O and Pd (Fig. 3b). The EDS data confirms the presence of PdNPs on the surface of Bentonite clay sample.

100

0

10

20

30

### 3.4 FTIR Analysis

40

**5**0

2-Theta

The functional groups present in the catalyst were analyzed by using Bruker 400. The FTIR spectrum Fig. 4 of PdNP@ AT-Bentonite showed strong vibrations at 3211.64–3199.01, 1627.04, 1586.15, 1518.39 and 1026.70–1011.55 cm<sup>-1</sup>. This noticed peaks indicate the presence of –OH stretch, –CH

60

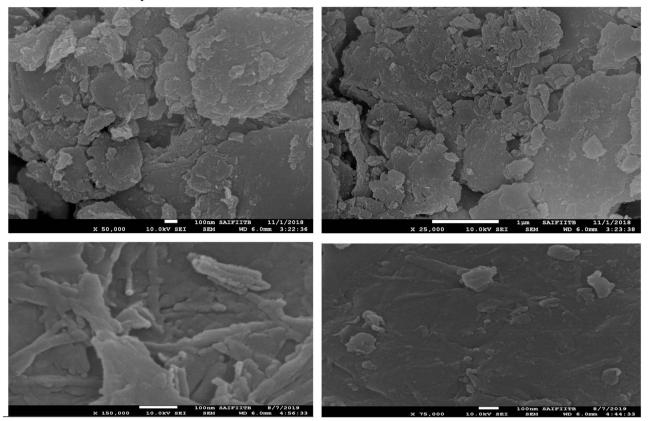
70

80

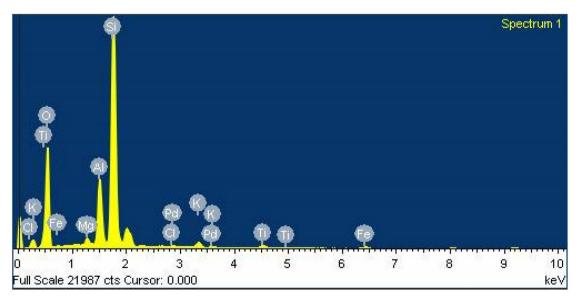
90

90

# FE-SEM/EDX Analysis



# a FE-SEM analysis of prepared PdNP@AT-bentonite



**b** EDS analysis of prepared PdNP@AT-bentonite



Table 1 EDS analysis of prepared PdNP@AT-Bentonite

Element	Weight %	Atomic %
ОК	44.31	59.39
Mg K	0.93	0.82
Al K	8.85	7.04
Si K	39.20	29.93
Cl K	0.27	0.17
КК	1.80	0.99
Ti K	1.41	0.63
Fe K	2.12	0.81
Pd L	1.10	0.22
Totals	100.00	

stretch, -C=C- stretch and -C-O-C stretch respectively. These above bands proved stretching and vibrational bands of compounds like terpenoids, alkaloids and polyols present in the leaves extract and so they may be held accountable for stabilization and efficient capping of obtained PdNP@ AT-Bentonite.

### 3.5 HR-TEM Analysis

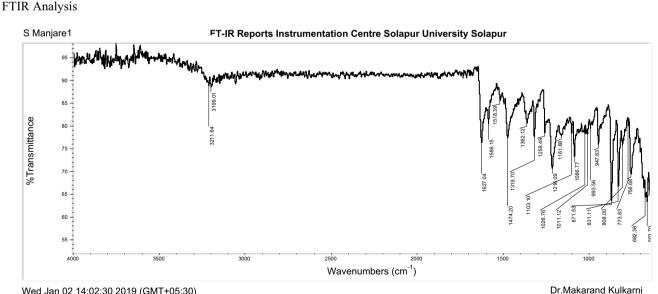
The HR-TEM image of the catalyst is shown in Fig. 5. The selected-area electron diffraction (SAED) pattern of PdNP@ AT-Bentonite is presented in the Fig. 5 which possesses five well resolved rings corresponding to fcc structure. The particle size of Pd is in the range of 5 to ~20 nm, which are distributed on the surface of clay catalyst.

#### 3.6 TGA Analysis

The TGA plots of PdNP@AT-Bentonite sample is shown in Fig. 6. The first weight loss of 10% of PdNP@AT-Bentonite sample in the temperature range 298-400 K can be correlated to the removal of physically adsorbed water and the desorption of the organic groups on the surface of the catalyst. The second weight loss of 35.1% in the temperature range 573-1273 K is associated to the dehydroxylation of -OH species and the elimination of residual carbonaceous species. Similarly, no phase transition was observed in the TGA data.

### 3.7 Catalytic Activity of PdNP@AT-Bentonite

The Table 2 shows the activity of the PdNP@AT-Bentonite catalyst at 90 °C in the -C-C- coupling reaction for the synthesis of biaryl compounds. The catalyst shows 80% conversion with 100% selectivity of biaryl compound. It is observed that there was no conversion without addition of the catalyst. Although, PdNP@AT-Bentonite catalyst shows activity at room temperature but we noticed that catalysts show negligible leaching as confirmed by ICP-MS. In our catalytic system, aryl bromide having strong electron group -COCH<sub>3</sub>, the reaction proceeded very efficiently and gave the corresponding coupled product in a short duration of time. When reaction in the Sect. 2.4 was carried out in the presence of activated Bentonite we don't get biaryl compound.



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Fig. 4 FT-IR spectrum of prepared PdNP@AT-Bentonite

## **HR-TEM Analysis**

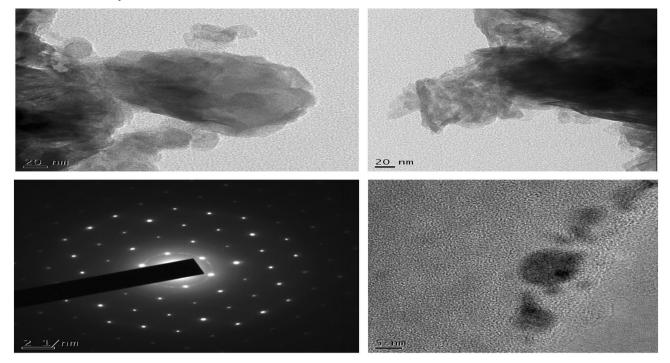


Fig. 5 HR-TEM analysis of prepared PdNP@AT-Bentonite

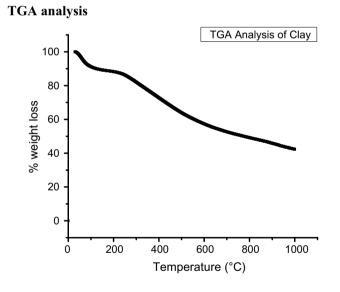
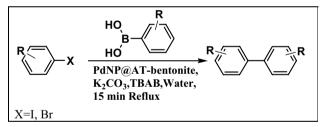


Fig. 6 TGA analysis of PdNP@AT-Bentonite

### 3.8 Reaction Scheme



Biphenyl (Table 2, entry 1): Iodobenzene (0.22 ml), phenylboronic acid (0.242 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. Biphenyl was obtained as a white solid M.P=70 °C (Rf=0.75, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.20–7.24 (m, 6H),  $\delta$  7.60 (dd, 4H).

4-Acetylbiphenyl (Table 2, entry 2): 4-Bromoacetophenone (0.398 g), phenylboronic acid (0.242 g),  $K_2CO_3$ (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0. 06 g) and water (10 mL) were used. 4-Acetylbiphenyl was obtained as an off white solid M.P=118 °C (Rf=0.65, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR

Sr. No	Aryl halide	Boronic acid	Biaryl Compound	Time	% Yield	TON	TOF (hr <sup>-1</sup> )
1				15 min	94	15061	100407
2	O H <sub>3</sub> C Br			15 min	95	19168	127791
3	I		H <sub>3</sub> C	15 min	93	16430	109535
4	I	HO B HO H <sub>3</sub> C	CH <sub>3</sub>	15 min	92	16234	108231
5	I	HO B HO	CICI	15 min	96	18190	121271
6	I	HO B HO HO CH <sub>3</sub>	$\begin{array}{c} \swarrow \\ \hline \\$	15 min	95	20537	136919
7		HO B	F	15 min	94	16821	112143
8		HO B HO OCH <sub>3</sub>	ОСН3	15 min	95	17799	118663
9	I	H <sub>3</sub> CO HO B HO	H <sub>3</sub> CO	15 min	96	17995	119967
10		OH HO <sup>-B</sup>		15 min	92	19951	133007

#### Table 2 Biaryl compound synthesized by PdNP@AT-Bentonite

TON mole of product/Pd mole, TOF TON/time in hours

 $\ \ \ (^{1}H).\ ^{1}H\ NMR\ \delta\ 8.05\ (dd,\ 2H),\ \delta\ 7.70\ (dd,\ 2H),\ \delta\ 7.50\ (d,\ 2H),\ \delta\ 7.40\ (m,\ 2H),\ \delta\ 2.6\ (s,\ 3H),\ \delta\ 10.07\ (s,\ 1H).$ 

3-Methylbiphenyl (Table 2, entry 3): Iodobenzene (0.22 mL), 3-methyl phenylboronic acid (0.271),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium

bromide (TBAB) (0.06 g) and water (10 mL) were used. 3-methylphenyl was obtained as a white solid B.P = 273 °C (Rf = 0.75, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.30 (d, 5H),  $\delta$  8.10 (dd, 6H, J=8.1 Hz)  $\delta$  1.58 (s, 3H). 2-Methylbiphenyl (Table 2, entry 4): Iodobenzene (0.22 mL), 2-methyl phenylboronic acid (0.271 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0. 06 g) and water (10 mL) were used2-methylbiphenyl was obtained as a brown gel B.P=258 °C (Rf=0.72, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.60 (d, 6H),  $\delta$  7.10 (d, 5H)  $\delta$  1.58 (s, 3H).

4-Chlorobiphenyl (Table 2, entry 5): Iodobenzene (0.22 mL), 4-chlorophenylboronic acid (0.312 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 4-chlorobiphenyl was obtained as a white solid M.P=78 °C (Rf=0.70, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.53 (m, 4H),  $\delta$  7.40 (m, 5H).

4-Tertbutylbiphenyl (Table 2, entry 6): Iodobenzene (0.22 mL), 4-tertbutylphenylboronic acid (0.356 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 4-tertbutylbiphenyl was obtained as a white solid M.P=50 °C (Rf=0.50, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.80 (m, 5H),  $\delta$  7.40 (m, 4H),  $\delta$  1.40 (s, 9H).

4-Flurobiphenyl (Table 2, entry 7): Iodobenzene (0.22 mL), 4-flurophenylboronic acid (0.270 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0. 06 g) and water (10 mL) were used4-flurobiphenyl was obtained as a white solid M.P=77 °C (Rf=0.68, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.60 (m, 4H),  $\delta$  7.25 (d, 4H),  $\delta$  7.20 (m, 1H).

3-Methoxybiphenyl (Table 2, entry 8): Iodobenzene (0.22 mL), 3-methoxyphenylboronic acid (0.288 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0. 06 g) and water (10 mL) were used. 3-methoxybiphenyl was obtained as a white solid M.P=76 °C (Rf=0.65, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.60 (m, 5H),  $\delta$  7.15 (d, 2H),  $\delta$  6.90 (m, 2H),  $\delta$  3.85 (s, 3H).

2-Methoxybiphenyl (Table 2, entry 9): Iodobenzene (0.22 mL), 2-methoxyphenylboronic acid (0.288 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 2-methoxybiphenyl was obtained as a brown solid B.P=274 °C (Rf=0.62, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.55 (m, 4H),  $\delta$  7.48 (d, 4H),  $\delta$  7.10 (m, 1H),  $\delta$  3.10 (s, 3H).

2-Phenylnapthalene (Table 2, entry 10): Iodobenzene (0.22 mL), napthalen-2-yl-2-boronic acid (0.343 g), K<sub>2</sub>CO<sub>3</sub> (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 2-phenylnapthalene was obtained as a white solid M.P=107 °C (Rf=0.75, hexane: ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the

product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  8.10 (d, 2H),  $\delta$  8.00 (d, 2H),  $\delta$  7.90 (dd, 2H),  $\delta$  7.80 (dd, 2H),  $\delta$  7.85 (dd, 1H),  $\delta$  7.50 (d, 1H),  $\delta$  7.40 (dd, 1H),  $\delta$  7.35 (dd, 1H),  $\delta$  7.30 (d, 1H).

## 3.9 Catalytic Recyclability

The recyclability experiment was carried out for reaction with iodobenzene with phenylboronic acid in order to investigate the stability of the catalyst. After every reaction, the catalyst was separated from the reaction mixture by simple filtration and then washed with ethyl acetate, and dried in the desiccators. The dried catalyst was repeatedly used up to ten times. It was observed that the catalyst shows a slight decrease in its activity after ten consecutive cycles which is shown in recyclability Fig. 7. The structure of the recycled PdNP@AT-Bentonite was examined by using XRD to compare with the freshly prepared catalyst. The XRD of recycled PdNP@AT-Bentonite is shown in Fig. 8. We concluded that recycled and fresh PdNP@AT-Bentonite of XRD spectra is nearly indistinguishable. The XRD results discovered that chemical structure of PdNP@AT-Bentonite was conserved after ten successive runs. This high activity and high sustainability of PdNP@ AT-Bentonite manifest that it is suitable for various industrial applications. Moreover, the transfer any catalysts from laboratories to commercial applications, the catalyst should have distinctive properties such as high efficiency, high yields of expected products. Finally we conclude that the catalysts with maximum conversion > 90% which are used in pharmaceutical and chemical industry [25, 42]. In addition, the prepared catalyst shows high sustainability and high efficiency and is economical. This prepared catalyst reduces the cost of industrial operations due to their excellent TON, TOF and greater reusability with no appreciable loss (Table 3).

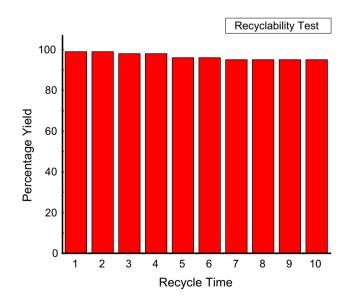


Fig. 7 Recycle test of Catalyst

Fig. 8 XRD analysis of recycled PdNP@AT-Bentonite

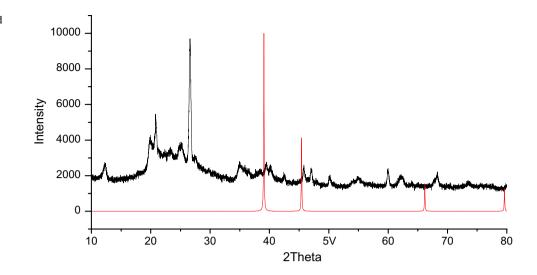


 Table 3
 Catalytic recyclability

Sr. no.	Recyclability times	Percent- age yield
1	1st time	98
2	2nd time	98
3	3rd time	97
4	4th time	97
5	5th time	96
6	6th time	96
7	7th time	95
8	8th time	95
9	9th time	95
10	10th time	95

# 4 Conclusion

The PdNP@AT-Bentonite catalyst has been prepared by an environment-friendly biosynthesis method where generated PdNPs have a small agglomeration due to modified Bentonite. The palladium nanoparticles were successfully loaded on dealuminated Bentonite clay under mild conditions which is confirmed by ICP-MS. It was characterized using FTIR, ICP-MS, TGA, XRD, FESEM-EDS, HR-TEM and BET (surface area analysis). The capacity showed efficient activity for Suzuki-Miyaura coupling reaction in universal solvent i.e. water under mild base with 100% chemoselectivity and maximum conversion > 90%. This prepared catalyst is of heterogeneous in nature and can be recovered by simple filtration method and is reused without any notable loss in its catalytic activity (maintained > 90%) even after ten times. These beneficiary things of this catalyst divulge that palladium PdNPs on activated Bentonite clay have greater superiority than the other catalysts reported in the literature.

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## **Compliance with Ethical Standards**

**Conflict of interest** The authors declare that they have is no conflict of interest.

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# Environment-friendly synthesis of palladium nanoparticles loaded on Zeolite Type-Y (Na-form) using *Anacardium Occidentale* shell extract (Cashew nut shell extract), characterization and application in -C-C- coupling reaction



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ARTICLE INFO	A B S T R A C T
Editor: Teik Thye Lim	Environment-friendly synthesis of heterogeneous nanoparticles is more effective in action of their properties. In
Keywords:	the present study, PdNP@Zeolite Type-Y (Na-form) has been successfully synthesized by applying a simple
Heterogeneous palladium nanocatalyst	reduction method using an aqueous extract of Anacardium Occidentale shell as a reducing and stabilizing agent.
XRD	The aqueous extract from the Anacardium Occidentale shell acts both as a reducing agent and a capping agent for

HR-TEM

–C–C– coupling

TGA

FTIR

#### 1. Introduction

Nanomaterials have higher surface to volume ratio than their bulk counterparts, which, in turn, lead to enhanced catalytic activity and impact their quality too. At nano scale, quantum mechanics play a crucial role in determining the characteristic features and qualities that make up the requisite material. The field of catalysis has a wider scope not only in altering the rate of certain reaction, but also in making the process ecofriendly and economically viable [1]. In any catalytic reaction, efficiency and the recyclability of catalyst are important aspects [2]. The recent studies show that the researchers have shown an immense interest in modifying the catalyst so as to improve yield and efficiency [3]. Amongst their varied properties, nanoparticles have some peculiar characteristics of higher reactivity due to high surface area and high activity [4]. Homogenous catalysts are heterogenized by immobilization on various solid supports [5]. The synthesis and the use of metal nanoparticles (MNPs) such as Pd [6-8], Pt [6], Ru [9], Ag [10], and Au [11] as catalyst are used in coupling, oxidation, reduction and acetylation reactions due to their large specific surface area, high activity and high specificity. Also, the largest efficiency of them has been reported. However, due to the unpredictability of small sized MNPs, such nanoparticles usually need

suitable solid supports. Aggregation of nanoparticles during catalytic reactions limits their catalytic activity. So to prevent the agglomeration caused by high surface energy and Vander Waals force between the nanoparticles, supporting agents like PVP [12], clay [13,14], graphene hybrid [15], MCM-41 [16] and resin [17] are used. In recent publication, the palladium nanoparticles supported on chalcogel [18] and polyaniline [19] are commonly utilized in heterogeneous catalysis. These reported catalysts shows high catalytic activity and high selectivity in coupling reaction. Generally, MNPs are produced by either physicochemical method or biological method. However, many of these methods require copious volume of harmful and expensive chemicals as a stabilizer to prevent agglomeration of nanoparticles, which in turn, produce a huge amount of dangerous and toxic by-products. The by-products are unacceptable in the drug and cosmetics industry, that's why there is a need to focus on benign synthesis of MNPs. The designed heterogeneous nanosized biocatalyst was used for CO<sub>2</sub> hydration property [20]. The biosynthesis of PdNPs, using extract of leaves of Origanum vulgare L [21], Ocimum sanctum [22] and extract of fruit of Diospyros peregrine [23] has been reported.

converting the Pd<sup>2+</sup> to Pd°. The PdNP@Zeolite Type-Y (Na-form) is characterized using FTIR, FE-SEM/EDS,

PXRD, ICP-AES, BET, TGA and HR-TEM. The crystal structure of PdNP@Zeolite Type-Y (Na-form) is determined

by powder X-ray diffraction analysis. The experimental studies have revealed that when palladium nanoparticles

are loaded on zeolite Type-Y (Na-form) they exhibit excellent catalytic activity for Suzuki-Miyaura cross coupling reaction. We showed high efficiency, high selectivity and excellent TONs (1540–2100), TOFs (6160–8400) by using small amount of PdNP@Zeolite Type-Y (Na-form) catalyst at lower time. Moreover, the catalyst can be recycled without significant loss of its catalytic activity. The present strategy is the reliable for preparing het-

erogeneous nanocatalyst and has a broad application in organic transformations.

In the present study, Zeolite Type-Y (Na-form) is used as a raw material. Zeolite Type-Y (Na-form) belongs to the family of aluminosilicate molecular sieves. The structure of Zeolite Type-Y (Na-form) has a faujasite structure

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(FAU), and is of basic molecular formula  $|(Ca, Mg, Na_2)_{29} (H_2O)_{240}|[Al_{58} Si_{134} O_{384}]$ – FAU [. Availability of Faujasite is a less and synthetic counterparts Linde X and Linde Y are largely used as adsorbents and Fluid Cracking Catalyst (FCC) of heavy petroleum distillates [24]. Zeolite Type-Y (Na-form) has a higher Si/Al atomic ratio of  $2.4\pm0.8$  [25]. Therefore, the higher content of silica imparts higher thermal stability to zeolite Type-Y. This zeolite is also considered for its ion exchange and adsorptive properties [26]. Indeed, zeolite support compared to other solid supports has an advantage as it can stabilize metal nanoparticles due to the inherent functional groups (electrostatic stabilization) and porosity (steric stabilization) [26].

The cashew tree is a tropical, evergreen tree that produces cashew fruit. The cashew tree is native to Central America, Vietnam and India, especially in Konkan region of Maharashtra, Goa and some part of Karnataka [27]. Cashew nuts are commonly used in Indian cuisine to make curries and sauces of curries i.e. Korma or some sweet like kaju barfi. The cashew nut shells contain oil compounds that contain organic compounds like phenolic compounds, anacardic acid and cardanol [28]. That's why cashews with their shells intact are not sold to consumers. The peeled off shells are usually thrown its way as biowaste, which found its way to the environment. Hence, cashew nuts processing industries remove shells from cashew nuts before selling them. This is generally as biowaste which found its way in the environment. This anthropogenic biowaste can be hazardous to the environment.

In the present paper, the biowaste of cashew shells is used to synthesize PdNPs supported on Zeolite Type-Y (Na-form). In compliment to this, Zeolite Type-Y (Na-form)/Pd nanocomposite causes Suzuki-Miyaura coupling reaction in a few minutes. We have successfully prepared heterogeneous catalyst by adopting a simple protocol to fabricate Zeolite Type-Y (Na-form)/Pd nanocomposite using *Anacardium Occidentale shell* extract as a reducing and stabilizing agent. The catalytic activity and recyclability of the nanoparticles in Suzuki-Miyaura reaction have been studied. Overall, Zeolite catalysts give promising results in comparing to others catalysts and are less expensive too.

#### 2. Experimental details

All the chemicals were purchased from Hi-Media and used as it is without further purification. Solvents were dried by adopting standard methods and used for reactions. TLC was carried out with Merck silica gel 60-F<sub>254</sub> plates and column chromatography was performed over silica gel (60–120 mesh) obtained from commercial suppliers. <sup>1</sup>H NMR spectra were recorded on a Bruker Advance<sup>III</sup>, Switzerland spectrometer (400 MHz) spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane as an internal standard.

#### 2.1. Calcination of Zeolite Type - Y (Na-form)

In dry silica crucible, 3.0 gm of Zeolite Type – Y (Na-form) is calcinated in muffle furnace at about 600 °C for 10 h, then it is cooled and finely powdered. The finely powdered form is recalcinated in the muffle furnace at 600 °C for 3.0 h to prepare good solid support.

#### 2.2. Preparation of Anacardium Occidentale shells (cashew cover) extract

The Anacardium Occidentale shells were collected from cashew nut processing industries, MIDC Mirjole, Ratnagiri, MS, India, and they were sun-dried for 5 days and powdered by using a grinder. The 10·0 gm of dried Anacardium Occidentale shell powder is boiled in 100 mL of double distilled water for 20 min in 250 mL beaker. The resulting mixture was cooled, filtered and stored at 5 °C in well stoppered bottle. The filtrate is designated as Anacardium Occidentale shell extract.

# 2.3. Preparation of palladium nanoparticles supported on calcinated Zeolite Type-Y (Na-form)

In double necked 100 mL round bottom flask, 10 mL of *Anacardium* Occidentale shell extract is transferred to 27 mL of 0.02 M PdCl<sub>2</sub> containing

1.3 gm of Zeolite Type – Y (Na-form). The mixture was stirred with the help of overhead stirrer (Remi) at 500 rpm for 8 h at 100 °C in oil bath. The color of the reaction mass was changed from brown to black. This black reaction mass indicates the conversion of  $PdCl_2$  to PdNPs. The reaction mass is cooled, filtered, washed with double distilled water and dried in petridish at 100 °C in hot air oven for 2 h. The material thus prepared was designated as PdNP@Zeolite Type-Y (Na-form).

Percentage Yield of PdNP@Zeolite Type-Y (Na-form) = 99.00 %

# 2.4. PdNP@Zeolite Type-Y (Na-form) catalyzed Suzuki-Miyaura coupling reaction

In clean 100 mL round bottom, aryl halide (0.00198 mol), aryl boronic acid (0.00198 mol),  $K_2CO_3$  (0.002 mol), PdNP@Zeolite Type-Y (Na-from) (0.0002 mol), tetrabutyl ammonium bromide (TBAB) (0.00187 mol) was subjected to 10 ml distiller water. This reaction mass was refluxed at temperature 90 °C for 15 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was allowed to cool at room temperature and then it was subjected to equilibrate with ethyl acetate (30 mL) for 5 min, and then it was filtered through celite bed. The organic layer was repeatedly washed with water (30 ml X 2). The organic layer was separated and dried on sodium sulphate, was evaporated on a rotary evaporator to get a crude compound. The crude compound was purified by column chromatography, using silica (60–120 mesh) as stationary phase and 0–5 % ethyl acetate: hexane as mobile phase. The purified compound was then characterized by <sup>1</sup>H NMR spectra.

#### 2.5. Recovery of catalyst

The catalyst recyclability was investigated with iodobenzene with phenylboronic acid at 90 °C in water. The catalyst was separated from the reaction mixture after every reaction by using whatman filter paper No. 41 is washed with 2–3 times with small volume of ethyl acetate to remove impurities. It is dried under hot air oven at temperature  $50 \pm 5$  °C for 30 min and reused in catalytic reaction.

#### 2.6. Measurements and characterization

The powder X-ray diffraction (XRD) patterns were collected on a Ultima IV, Rigaku Corporation, Japan diffractometer equipped with a Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). Diffraction patterns were recorded in the 5–90° regions at a rate of 0.5° 20/minutes. FE-scanning electron micrographs were obtained with JSM-7600 F microscope equipped with EDS spectrometer. Energy dispersive X-ray spectroscopy (EDS) was used in connection with FE-SEM for the elemental analysis. The amount of Pd nanoparticles were determined by the inductively coupled Plasma Atomic Emission spectrometer (ICP-AES, model SPECTRO Analytical Instruments GmbH, Germany) analysis. The PdNP@Zeolite Type-Y (Na-form) was dissolved in the mixture of conc. HNO3 and conc. HCl, and then the solution was subjected to the determination of the Pd content. The FTIR (Fourier Transform Infrared) spectra were recorded on Brucker ALPHA 100508 double beam spectrometer using KBr water technique. TGA analysis was carried out by using Mettler Toledo Switzerland. HR-TEM analysis was performed with FEI, Tecnai G2, F30 microscope and the specimen which is to be analyzed were prepared by mixing sample in isopropanol and after that placing this on carbon coated copper grid. The surface area was measured by using nitrogen adsorption (SMART Instrument, India) at -196 °C. Prior to the measurement, the sample was activated at 300 °C for 3.0 h under vacuum.

#### 3. Result and discussion

#### 3.1. FTIR analysis

Functional groups present in the catalyst were analyzed by using Bruker 100508. The FTIR spectrum Fig. 1. of PdNP@Zeolite Type-Y (Naform) showed strong vibrations at 3866.56, 3740.56, 3628.02, 2896.78,

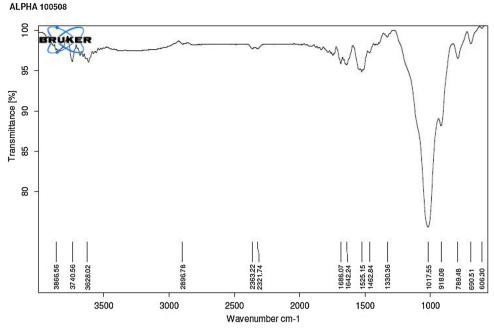


Fig. 1. FTIR spectrum of prepared PdNP@Zeolite Type-Y (Na-form).

2363.22–2321.74, 1686.07, 1525.15 and 1330.36 Cm<sup>-1</sup>. This observed peak are due to the presence of -OH- stretch, -NH stretch, -CH stretch,  $-C\equiv N$  stretch,  $-C\equiv C-$  stretch, -C-H bending vibrations respectively [29]. In the FTIR spectrum of PdNP@ Zeolite Type-Y (Na-form), the other characteristic peak observed at 1017.55 and 918.8 Cm<sup>-1</sup> can be related to the Si–O stretching frequency [30]. The next characteristics peaks denoted at 789.48, 690.51 and 606.30 Cm<sup>-1</sup> are assigned to the Al-O stretching frequency [31,32]. The structure of PdNP@Zeolite Type-Y (Na-form) was confirmed by the peaks observed at -NH stretch, -OH stretch,  $-C\equiv N$  stretch,  $-C\equiv C-$  stretch and -C-H bend is for alkaloid, terpenoids, carotenoids and flavonoids present in the *Anacardium Occidentale shells* extract acted as a reducing and stabilizing agent [33], and the Si–O and Al–O stretching vibration the Zeolite Type-Y (Na-form) support [34].

#### 3.2. FE-SEM & EDX

FE-SEM images of the samples are represented in the Fig. 2a. The FE-SEM is used to study the surface topography and morphology of samples. It is observed that small agglomerations of PdNPs are selforiented in forming bigger particles with some porous features. FE-SEM images show dominant flakes like particles morphology and also small granules. The flakes type of morphology is found due to the characteristic property of layered material and the same has been reflected in the FE-SEM pictures. Apart from this, the small granules or agglomeration of grains are also visible in the FE-SEM pictures which may be due to the breaking of those flakes into the smaller particles. FE-SEM pictures are in good agreement with layered structure of Zeolite Type-Y (Na-form). Energy dispersive spectroscopy was used to map the elements present in the sample. The results are given in the Table 1 below. Energy dispersive X-Ray analysis (EDAX) showed the presence of Na, Mg, Al, Si, Cl, K, Ca, Fe, Cu and Pd (Fig. 2b). The EDS data confirms the higher exchange of palladium and the presence of PdNPs on the surface of Zeolite Type-Y (Na-form) sample.

#### 3.3. XRD analysis

PXRD analysis was carried out to examine the structure of PdNPs loaded on Zeolite Type-Y (Na-form) and the Zeolite Type-Y (Na-form) are

shown in Fig. 3 a) and b) respectively. The distinct peaks of PdNPs were observed at  $2\theta = 40.41^{\circ}$ ,  $47.64^{\circ}$ ,  $69.51^{\circ}$  and  $80.94^{\circ}$  (JCPDS: 87-0643) correspond to (111), (200), (220) and (222) reflections respectively. The predominant peak observed at (111) plane is more intense peak corresponds to the fcc lattice. The peaks observed at  $2\theta = 7.21$ , 10, 18, 21.70, 24.04 and 27.14 is for supported material zeolite Type-Y (Na-form) [25]. The Fig. 3 a) shows the powder XRD patterns of PdNPs which exhibit the formation of the face-centered cubic (fcc) lattice system of the palladium nanostructure. The ring originated is demonstrated to the crystallographic planes (111), (200), (220) and (222) of face centered cubic PdNPs [35]. The crystallite size of the PdNP@Zeolite Type-Y (Na-form) was determined by the Scherrer's formula:

#### $D = K\lambda/\beta \cos\theta$

Where K is the shape factor and its value is 0.9,  $\lambda$  is the X-ray wavelength (Cu  $K_{\alpha}$  = 1.5406 A°),  $\beta$  is the full width half the maximum (FWHM),  $\theta$  is the peak positions. The crystallite size determined by using Scherrer's formula is 0.61805 nm. This crystallite size is consistent with the average particle diameter obtained from HR-TEM images.

#### 3.4. TGA analysis

The TGA plot of PdNP@Zeolite Type-Y (Na-form) sample is shown in the Fig. 4. The thermogravimetric analysis was carried out in order to understand thermal stability of the PdNP@Zeolite Type-Y (Na-form) and studied thermodegration pattern of the stabilizing agent present on the surface of the catalyst. The TGA plot of the catalyst revealed that the PdNP@Zeolite Type-Y (Na-form) is stable up to 900 °C with only one step weight loss of 16.25 %. The TGA plot of PdNP@Zeolite Type-Y (Naform) shows one step weight loss of 16.25 % in the region 30 °C–386 °C, probably due to the removal of physically adsorbed water and surface hydroxyl group on the surface of the catalyst [36]. This result revealed that PdNPs loaded on Zeolite Type-Y (Na-form) is more thermally stable than its support.

#### 3.5. HR-TEM analysis

Furthermore, high resolution transmission electron microscopy (HR-TEM) data of catalyst prepared is shown in the Fig. 5 [a), b), c)].

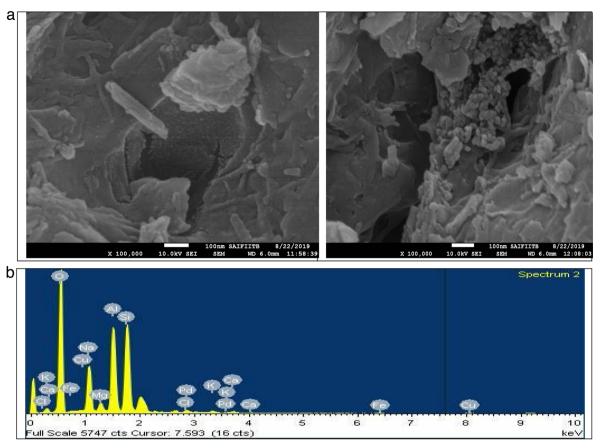


Fig. 2. a FE-SEM analysis of prepared PdNP@Zeolite Type-Y (Na-form). b EDS graph of prepared PdNP@Zeolite Type-Y (Na-form).

#### Table 1 Energy dispersive X-Ray analysis (EDAX) of prepared PdNP@Zeolite Type-Y

Element	Weight%	Atomic%
О К	52.03	65.24
Na K	9.55	8.34
Mg K	1.49	1.23
Al K	14.13	10.51
Si K	18.33	13.09
Cl K	0.52	0.30
КК	0.63	0.32
Ca K	0.62	0.31
Fe K	0.59	0.21
Cu L	0.49	0.15
Pd L	1.62	0.30
Total	100	

The HR-TEM images show dark spot of PdNPs that are loaded on the surface of Zeolite Type-Y (Na-form).In the Fig. 5 [a), b) and c)], the histogram of the particle size distribution shows the average particle size of the PdNPs is in the range of  $0.7367 \pm 0.11$ nm- $1.7198 \pm 1.00$  nm. These Fig. 5 [(a), b), c)] confirms the PdNPs are small sized and well distributed on the surface of Zeolite Type-Y (Na-form). These PdNPs have spherical in shape. The HR-TEM images of PdNPs along with lattice fringe of with an inter fringe distance of 0.22 nm corresponding to the (111) plane of PdNPs. The corresponding selected-area electron diffraction (SAED) pattern of PdNPs is presented in the Fig. 5(d) which possesses five well resolved rings corresponding to fcc [37]. The result of HR-TEM and SAED pattern is concordance with the XRD pattern of diffraction.

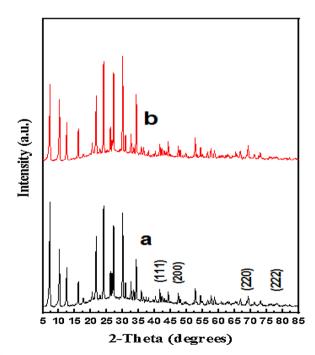


Fig. 3. X-ray diffraction pattern of a) PdNP@Zeolite Type-Y (Na-form), b) Zeolite Type-Y (Na-form).

#### 3.6. Pd content

Pd content was loaded on PdNP@Zeolite Type-Y (Na-form) and it was analyzed by the ICP-AES. The Pd content in 500 mg of PdNP@ Zeolite Type-Y (Na-form) is found to be 0.450 mg. What is noticed is

that increased ion exchange capacity, large surface area as well as adsorptive capacity caused this support excellent to load metal ions.

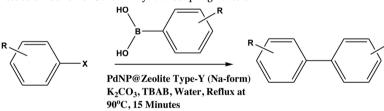
#### 3.7. BET study

The specific surface area determined by  $N_2$  adsorption using BET equation is decreases from 5.79 to  $1.60 \text{ m}^2 \text{ g}^{-1}$  after Pd loading. The decreased specific surface area proved that PdNPs loaded on Zeolite Type-Y (Na-form).

# 3.8. Suzuki-Miyaura coupling reaction over PdNP@Zeolite Type-Y (Naform)

The Table 2 shows the catalytic activity of the PdNP@Zeolite Type-Y (Na-form) at 90 °C in the Suzuki-Miyaura coupling reaction for the synthesis of biarvl compounds. The catalyst shows above 90 % conversion with larger selectivity of biaryl compound. When the reaction scheme in the Section 2.4 was performed for Table 2. Entry-1 in only Zeolite Type-Y (Na-form) as a catalyst, it does not give coupling product. The base used in this reaction is K<sub>2</sub>CO<sub>3</sub> which is weak base as compared with KOH. The reaction time taken to complete the Suzuki-Miyaura reaction was only 15 min. In the present work, solvent used for the Suzuki-Miyaura reaction is green solvent i.e. water. When this Suzuki-Miyaura reaction (Table 2, entry-1) was performed without TBAB in water solvent. This reaction doesn't give the biaryl coupling product. To get better results for the Suzuki-Miyaura reaction in water, we used TBAB as a phase transfer catalyst. Although, the PdNP@Zeolite Type-Y (Na-form) catalyst shows an activity at the room temperature but we observed that catalyst show negligible leaching as confirmed by ICP-AES. We observed that, the aryl bromide that has electronically strong electron withdrawing group -COCH<sub>3</sub> is para-position to -Br, the reaction proceeds very competent to give the corresponding coupled products in a the lower time. In our catalytic system, if the electron donating and electron withdrawing groups are present at ortho, meta or para- positions of phenyl boronic acids the reaction proceeds with higher efficacy and excellent selectivity.

Reaction scheme- Suzuki-Miyaura coupling reaction



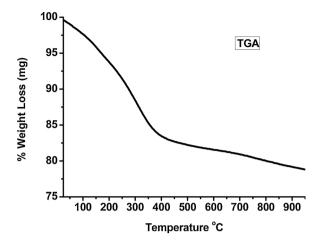


Fig. 4. TGA analysis of prepared PdNP@Zeolite Type-Y (Na-form).

#### 3.8.3. 3-Methylbiphenyl (Table 2, entry 3)

Iodobenzene (0.22 mL), 3-methyl phenylboronic acid (0.271),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 3-methylphenyl was obtained as a white solid (Rf = 0.72, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.30 (d, 7 H),  $\delta$  1.58 (s, 3 H).

#### 3.8.4. 2-Methylbiphenyl (Table 2, entry 4)

Iodobenzene (0.22 mL), 2-methyl phenylboronic acid (0.271 g), K<sub>2</sub>CO<sub>3</sub> (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 2-methylbiphenyl was obtained as a brown gel (Rf = 0.72, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.30 (d, 7H, J = 8.1 Hz),  $\delta$  1.58 (s, 3 H).

#### 3.8.5. 4-Chlorobiphenyl (Table 2, entry 5)

Iodobenzene (0.22 mL), 4-chlorophenylboronic acid (0.312 g),

#### 3.8.1. Biphenyl (Table 2, entry 1)

Iodobenzene (0.22 mL), phenylboronic acid (0.242 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. Biphenyl was obtained as a white solid (Rf = 0.72, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.20–7.24 (m, 6 H),  $\delta$  7.60 (d, 4 H).

#### 3.8.2. 4-Acetylbiphenyl (Table 2, entry 2)

4-Bromoacetophenone (0.398 g), phenylboronic acid (0.242 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 4-Acetylbiphenyl was obtained as an off white solid (Rf = 0.60, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  8.05 (d, 2 H),  $\delta$  7.70 (d, 2 H),  $\delta$  7.50 (d, 2 H),  $\delta$  7.40 (m, 2 H),  $\delta$  2.6 (s, 2 H),  $\delta$  10.07 (s, 1 H).

 $\rm K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 4-chlorobiphenyl was obtained as a white solid (Rf = 0.70, Hexane: Ethyl acetate).  $^{1}$ H NMR was obtained to confirm the product and solution NMR ( $^{1}$ H).  $^{1}$ H NMR  $\delta$  7.53 (m, 4 H),  $\delta$  7.40 (m, 5 H).

#### 3.8.6. 4-Tertbutylbiphenyl (Table 2, entry 6)

Iodobenzene (0.22 mL), 4-tertbutylphenylboronic acid (0.356 g), K<sub>2</sub>CO<sub>3</sub> (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 4-tertbutylbiphenyl was obtained as a white solid (Rf = 0.50, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.80 (m, 4 H),  $\delta$  1.40 (s, 9 H).

#### 3.8.7. 4-Flurobiphenyl (Table 2, entry 7)

Iodobenzene (0.22 mL), 4-flurophenylboronic acid (0.270 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB)

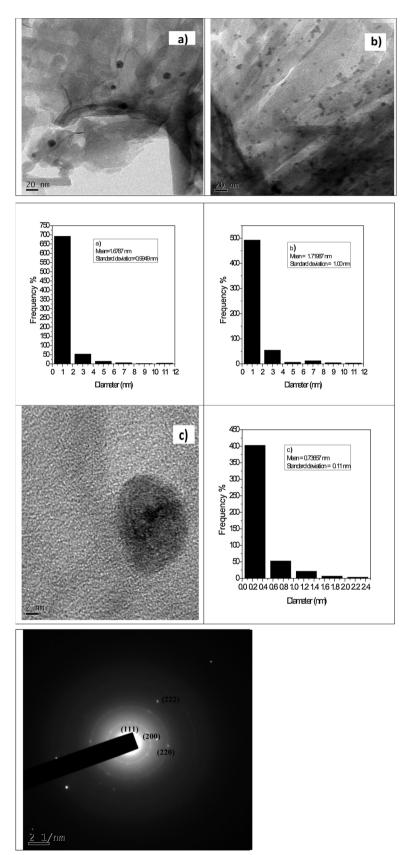


Fig. 5. HR-TEM analysis and particle size distribution of distribution `of PdNP@Zeolite Type-Y (Na-form) [a), b), c)] and d) SAED pattern of PdNP@Zeolite Type-Y (Na-form).

#### Table 2

Biaryl compounds synthesized	by	PdNP@Zeolite	Type-Y	(Na-form).
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Sr. No	Aryl halide	Boronic acid	Biaryl Compound	% Yield	M.P /B.P (°C)	Reported M.P/B.P (°C)	TON	TOF $(h^{-1})$
1	Г	но		94	M.P = 71	M.P = 65 - 68 [38]	1540	6160
2	Br			95	M.P = 116	M.P = 117 [39]	1960	7840
3				93	B.P = 271	B.P = 273 [14]	1680	6720
4	ν Γ	HO B HO		92	B.P = 256	B.P = Oil [38]	1650	6600
5			c c	96	M.P = 76	M.P = 69-72 [38]	1880	7520
6	Г	HO B HO CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	95	M.P = 51	M.P = 53 [17]	2100	8400
7	Г	HO HO HO	F	94	M.P = 75	M.P = 77 [14]	1720	6880
8		но в но	ОСН3	95	M.P = 75	M.P = 76 [14]	1820	7280
9	√I	HO B	H <sub>3</sub> CO	96	B.P = 275	B.P = Oil [38]	1840	7360
10	Γ <u></u>	HO OH HO <sup>B</sup>		92	M.P = 105	M.P = 104-106 [38]	2040	8160

TON = Mole of product/Pd mole; TOF = TON/time in hours.

(0.06 g) and water (10 mL) were used. 4-flurobiphenyl was obtained as a white solid (Rf = 0.68, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.60 (d, 2 H),  $\delta$  7.35 (d, 2 H),  $\delta$  7.25 (m, 1 H).

#### 3.8.8. 3-Methoxybiphenyl (Table 2, entry 8)

Iodobenzene (0.22 mL), 3-methoxyhenylboronic acid (0.288 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 3-methoxybiphenyl was obtained as a white solid (Rf = 0.65, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.60 (m, 4 H),  $\delta$  7.40 (d, 2 H),  $\delta$  7.24 (m, 2 H),  $\delta$  3.85 (s, 3 H).

#### 3.8.9. 2-Methoxybiphenyl (Table 2, entry 9)

Iodobenzene (0.22 mL), 2-methoxyhenylboronic acid (0.288 g), K<sub>2</sub>CO<sub>3</sub> (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide

(TBAB) (0.06 g) and water (10 mL) were used. 2-methoxybiphenyl was obtained as a brown solid (Rf = 0.62, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.55 (m, 4 H),  $\delta$  7.48 (d, 4 H),  $\delta$  7.10 (m, 2 H),  $\delta$  3.10 (s, 3 H).

#### 3.8.10. 2-Phenylnapthalene (Table 2, entry 10)

Iodobenzene (0.22 mL), napthalen-2-yl-2-boronic acid (0.343 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 2-phenylnapthalene was obtained as a white solid (Rf = 0.75, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  7.95 (dd, 1 H),  $\delta$  7.85 (m, 2 H),  $\delta$  7.78 (m, 2 H),  $\delta$  7.40 (m, 4 H).

These above results were comparable with other literature reported catalyst.

Table 3 catalytic performance compares our catalyst PdNP@Zeolite Type-Y (Na-form) with different catalysts in the Suzuki-Miyaura

#### Table 3

Catalytic performance of different	catalysts in the	e coupling reaction of	iodobenzene with phenylboronic acid.

Entry	Catalyst (Wt in gm)	Conditions	Time (min)	TOF $(h^{-1})$	References
1	Pd-imi@MCM-41/Fe <sub>3</sub> O <sub>4</sub> (0.014 gm)	PEG-400, Na <sub>2</sub> CO <sub>3</sub> , 120 °C	60	118.1	[40]
2	Pd-adenine@boehmite (0.005 gm)	Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 80 °C	30	146.2	[41]
3	Pd(0)-TBA@biochar (0.005 gm)	PEG-400, Na2CO3, 120 °C	125	64	[38]
4	Pd-imi CC@MCM-41/Fe <sub>3</sub> O <sub>4</sub> ,(0.008gm)	PEG-400, Na2CO3, 80 °C	40	98	[42]
5	PdNP@Zeolite Type-Y (Na-form), (0.025 gm)	K <sub>2</sub> CO <sub>3</sub> , TBAB, Water, 90OC	15	6160	[this work]

reaction. According to Table 3, the current catalyst reported high TON and TOF at greener condition as compared with other literature reported catalysts. These PdNPs modified by Anacardium occidentale shell extract could be useful in design of supported catalyst because of excellent TON, TOF and excellent reusability of the catalyst.

#### 3.9. Mercury poisoning experiments

The heterogeneous nature of catalyst was confirmed by performing Mercury poising test [43]. The model reaction taken for the Mercury poising test was Iodobenzene with phenylboronic acid in the optimum condition (Table 2, entry 1). This model reaction i.e. iodobenzene with phenylboronic acid was carried out for 24 h without adding mercury. The yield observed for the catalyst PdNP@Zeolite Type-Y (Na-form) is 72 %. Then, further 300 M equivalents of mercury metal, relative to the PdNP@Zeolite Type-Y (Na-form) catalyst, were added in to the reaction mixture and then the mixture was stirred with the help of overhead stirrer (Remi) for another 24 h. After that in the allowed time the procedure in Section 2.4 was repeated for Table 2 remaining entries. Out of the all entries in the Table 2, the desired products (3-methoxybiphenyl and 2-methoxybiphenyl) were obtained with lower yields after 48 h by using PdNP@Zeolite Type-Y (Na-form). The yields for (3methoxybiphenyl and 2-methoxybiphenyl) are 68, 64 %, respectively.

#### 3.10. Recyclability of PdNP@Zeolite Type-Y (Na-form)

The process of recycling of catalyst for the reaction (Table 2, entry 1) was repeated up to ten times to recheck its catalytic efficacy. It is observed that the catalyst exhibit high thermal and hydrothermal stability up to ten times. The pores of calcinated Zeolite Type-Y (Na-form) loaded catalyst play a very crucial role to stabilize and increase the electron density of PdNPs and hereby prevent the leaching of metal. It has exhibited excellent catalytic activity above 90 % with range of substrates and provides ten recycle runs without any loss of catalytic activity as shown in Fig. 6. The structure of the recycled PdNP@Zeolite Type-Y (Na-form) was investigated by using XRD to compare with the freshly prepared catalyst. The XRD analysis of recycled PdNP@Zeolite Type-Y (Na-form) is shown in Fig. 7. Then we observed that recycled and fresh PdNP@Zeolite Type-Y (Na-form) of XRD spectra is nearly same. The XRD results observed that

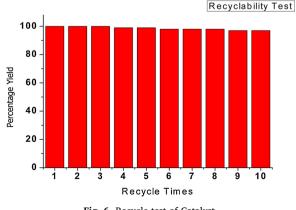


Fig. 6. Recycle test of Catalyst.

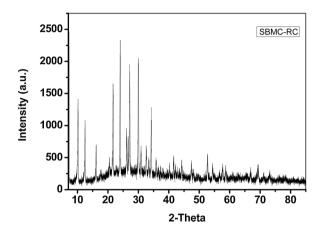


Fig. 7. X-ray diffraction pattern of recycled PdNP@Zeolite Type-Y (Na-form).

the structure of PdNP@Zeolite Type-Y (Na-form) was conserved after ten recycle runs. The mercury poising test leaching test proved the catalyst is in heterogeneous in nature.

#### 4. Conclusions

The result of zeolite loaded catalyst was good after calcination. The size of pores of zeolite increased after calcination. Also, the loading of palladium on zeolite showed a good efficacy with high chemoselectivity. The PdNP@Zeolite Type-Y (Na-form) was successfully prepared by adopting the environment-friendly procedure by using *Anacardium Occidentale shells* extract. The result of ICP-AES confirmed that palladium was successfully loaded on Zeolite Type-Y (Na-form) under mild conditions. To the best of our knowledge, PdNP@Zeolite Type-Y (Na-form) can catalyze the Suzuki-Miyaura reaction in the shortest time, good stability, highest activity and excellent TONs and TOFs compared to the catalysts reported in literatures. The catalyst was reused up to ten times without any significant loss of efficiency. We anticipate that Zeolite Type-Y (Na-form) offers new opportunities for designing highly active catalysts with tailored compositions.

#### Author statement file

Satish B. Manjare develop a new method for synthesizing PdNPs supported on zeolite Type-Y (Na-form). I made a draft of this work.

The co-author Dr. Rajendra A. Chaudhari helps me to develop a new method for the synthesizing PdNPs. He helps me to draw particles size diagram by using imageJ. He also helps me to make the draft of the manuscripts.

#### **Declaration of Competing Interest**

The corresponding author states that there is no conflict of interest.

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**Research Article** 

# Resin loaded palladium nanoparticle catalyst, characterization and application in -C-C- coupling reaction



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## Abstract

Macroporous ion-exchange resins were used to immobilize palladium (Pd) metal in order to produce nanoparticle catalysts. The complexation of palladium acetate and the following reduction with NaBH<sub>4</sub> resulting Pd nanoparticles are loaded on to DIANION<sup>™</sup> PK228 macroporous cation exchange resins. Palladium loading was characterized by inductively coupled plasma-atomic emission spectroscopy, field emission scanning electron microscope/energy-dispersive X-ray spectrometry, BET (Brunauer–Emmett–Teller) and HR-TEM. Palladium nanoparticles are loaded on to DIANION<sup>™</sup> PK228 macroporous cation exchange resin which shows and excellent catalytic activity for Suzuki–Miyaura cross coupling reaction. Furthermore, the catalyst can be recycled without significant loss of its catalytic activity up to ten times.

**Keywords** Environment-friendly synthesis · Palladium nanoparticles · ICP-AES · FESEM/EDS · HR-TEM · BET (Brunauer-Emmett-Teller) · Cation exchange resin · C–C coupling

## Abbreviations

ICP-AES	Inductively coupled plasma-atomic emission
	spectroscopy
FE-SEM/EDX	Field emission scanning
	electron microscope/energy-
	dispersive X-ray spectrometry
BET	Brunauer–Emmett–Teller
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane
PdNP@DIANION <sup>™</sup> PK228	Palladium loaded on the
	surface of resin
EDS	Electron diffraction
	spectroscopy

# 1 Introduction

Homogenous Pd nanoparticle catalysts are widely used in many coupling and cross coupling reactions, such as Heck, Stile, Suzuki–Miyaura, Sonogashira, and Buckwald-Hartwig reactions. These catalysts trigger high reaction rates and great selectivity [1]. The field of catalysis has evolved to focus not only on altering the rate of a certain reaction, but also making the process environment-friendly, more efficient and more economical. On the other hand, homogenous catalysts are difficult to recycle and difficult to separate them easily, which leads to the loss of the expensive metals and hence it is essential to remove the impurities from the products [2]. This problem poses a big challenge to the industry as to how to make application of homogenous Pd nanoparticles catalysts in coupling reactions.

In order to solve this problem, heterogeneous Pd nanoparticles catalysts are better alternatives for the coupling reactions. Various solid supports, such as activated carbon

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[3–5], zeolite [6–10] and silica [11–13] and poly vinyl pyrrolidine (PVP) [14] have been used as supports, which can sometimes allow reaction under unfavourable conditions [10].

After studying recent publications, it is found that various modified catalysts have been developed to improve the efficiency of the reaction and to make the process environment-friendly. Other than the report on the immobilization and the characterization of Pd<sup>0</sup> nanoclusters on gel-type functional polymers [15] and the use of amberlyst-supported systems [16], ion exchange resins [17] were somewhat less probed. However, the industrial process developed in recent years on Pd nanoparticles on ion exchange resin indicates that they are effective catalysts. Compared with the other solid supports, ion exchange indicates several inherent advantages. Firstly, most of these are commercially available at low cost. Secondly, they can stabilize metal nanoparticles due to the use of functional groups which give electrostatic stabilization and porosity gives steric stabilization. Also, they are easy to handle and they integrate into reactor equipment. Palladium has long been one of the most efficient metals in catalysis [18, 19], and its application in the Suzuki-Miyaura cross coupling is one of the most powerful and useful tools for the formation of carbon-carbon bonds for the synthesis of pharmaceuticals, drugs, agrochemicals, polymers, natural products and specialized engineering materials. The Suzuki–Miyaura coupling reaction has indeed come a long way. There are numerous publications related to its development and improvement in terms of various parameters such as catalytic systems and solvents. Overall, most of these catalysts gave promising results for Suzuki-Miyaura cross coupling reaction. But expensive reagents have been utilized by some and it is found that the reactions take longer times, whereas others have used reagents that are not easy to handle.

In the present work, we have used DIANION<sup>™</sup> PK228 which is a porous type strongly acidic cation exchange resin. It has 14% cross-linked and excellent properties. It has a functional group sulphonic acid and ionic form is Na<sup>+</sup>. The catalyst that we synthesized is an alternative catalyst for the Suzuki–Miyaura cross coupling reaction in which we used macroporous cation exchange resin as a solid support. In this technique, water solvent is used and inert conditions are not required. This synthesized catalyst is of heterogeneous nature and it can be recovered and reused several times without any substantial loss in its catalytic efficiency. The catalyst shows a good reusability. The yields obtained by this method are excellent.

# 2 Materials and methods

The purchased cation exchange resin (procured from DIANION<sup>™</sup> PK228, Mitsubhihi Chemical, Japan), contains styrene-DVB that has a strong cation exchange resin. All the chemicals were purchased from Hi-Media, Ratnagiri, Maharashtra, India and used without purification. Solvents were dried by standard methods to use for reactions. TLC was carried out with Merck silica gel 60-F<sub>254</sub> plates and the technique column chromatography was used. Silica gel (60–120 mesh) obtained from commercial suppliers inserted in the column for purification of coupling products. <sup>1</sup>H NMR spectra were taken on a Bruker Advance<sup>III</sup>, Switzerland spectrometer (400 MHz) spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane as an internal standard.

# 2.1 Preparation of PdNP@DIANION™ PK228 catalyst

The resin (2.7 g) and palladium acetate (Pd  $(OAc)_2$ ), (0.23 g) were placed inside a 100 mL round bottom flask. methnol solvent (30 mL, distilled) was added and the mixture was sonicated (Make Ultrasonic Cleaner) until the Pd (OAc)<sub>2</sub> dissolved. The mixture was then shaken by using a mechanical overhead stirrer (Remi) at 400 rpm speed for 24 h. When the catalyst formed, the color of the resin changed from tan to blackish. Then the resin was washed with methanol several times to ensure that no unreacted Pd (OAc)<sub>2</sub> remained in the resin. The resin was air-dried and 26 mL MeOH:dioxane (2:1) solvent was poured into the flask in addition to NaBH<sub>4</sub> (0.12 g). The mixture was shaken for 24 h using a mechanical overhead stirrer (Remi) at 400 rpm. The resin was filtered, washed with methnol several times and finally with acetone. Finally, the resin, now silver in color, was air-dried. This catalyst was further used for Suzuki-Miyaura coupling reaction.

Percentage Yield of PdNP@DIANION<sup>TM</sup>PK228 = 100%

# 2.2 PdNP@DIANION™ PK228 catalyzed Suzuki-Miyaura coupling reaction

Aryl halide (1 eq.), Arylboronic acid (1 eq.), K<sub>2</sub>CO<sub>3</sub> (2 eq.), PdNP@DIANION<sup>™</sup> PK228 (0.025 g) and tetrabutyl ammonium bromide (TBAB) (0.25 eq.) were poured into a clean round bottom flask and then 10 mL water was added to the mixture. The reaction mixture was heated to reflux for 10–15 min. The reaction was monitored by TLC. After the completion of reaction, the reaction mixture was cooled to room temperature. Then ethyl acetate (30 mL) was added and the mixture was filtered through celitebed. 30 mL water was added to the filtrate. The organic layer was separated and washed with water ( $30 \text{ mL} \times 2$ ). The organic layer was dried on sodium sulphate and was evaporated on rotary evaporator to get crude compound. Then the crude compound was purified by column chromatography using silica (60-120 mesh) as a stationary phase and 0-5% ethyl acetate: hexane as mobile phase. Purified compounds were characterized by <sup>1</sup>H NMR.

# 2.3 Characterization of supports

Surface area analysis was carried out by BET (Brunauer-Emmett-Teller), SMART Instrument, India. Magnification and agglomeration of the catalyst were analyzed by field emission gun-scanning electron microscope (FE-SEM, SPECTRO Analytical Instruments GmbH, Germany). Adsorption of palladium was analyzed by energy-dispersive X-ray spectroscopy (EDS, SPECTRO Analytical Instruments GmbH, Germany). Element analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPECTRO Analytical Instruments GmbH, Germany). The synthesized catalyst was dissolved in the mixture of conc. HNO<sub>3</sub> and conc. HCl, then the solution was suspended to the determination of the Pd content. Particle size analysis were recorded by emission gun-scanning electron microscope (HR-TEM, FEI Tecnai F30) and the specimens were prepared by diffusing samples in isopropyl alcohol and placing this on carbon coated copper grid.

# 3 Result and discussion

## 3.1 Macroporous resin support

To develop better solid supports, we considered macroporous ion exchange resins. Their characteristic rigid beads provide an advantage in easy separation after completion of reaction from reaction mixture and were investigated reusability in organic synthesis reaction. Macroporous cation resin were used, namely DIANION™ PK228 cation exchange styene DVB matrix. The starting material bead was moist, and tan in color. Beads were dried to remove water to get maximum loading. Complexation was evident by change in color of the beads. Color changed from colloidal brown to silver. The reactivity of catalyst was investigated using Suzuki-Miyaura coupling reaction and it was showed an excellent reactivity on preliminary observation. The specific surface area determined by N<sub>2</sub> absorption decreases from 14.19 to 9.80 m<sup>2</sup>/g. This catalyst was recycled up to ten times without significant loss of reactivity. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis showed that the 44.05 mg Pd loaded on resin/500 mg of PdNP@DIANION™ PK228. The catalyst was further characterized using FE-SEM/EDS and HR-TEM.

The FE-SEM data of prepared catalyst is shown in Fig. 1. The FE-SEM pictures, taken at lower magnification, show very nice spherical resin particles. No separate agglomerates of palladium are seen at even higher magnification on resin structures. Small spheres of palladium nanoparticles were homogenously dispersed on the DIANION<sup>™</sup> PK228 resin. Also catalyst reduction was carried out at room temperature and which prevent the particle aggregation on the resin surface.

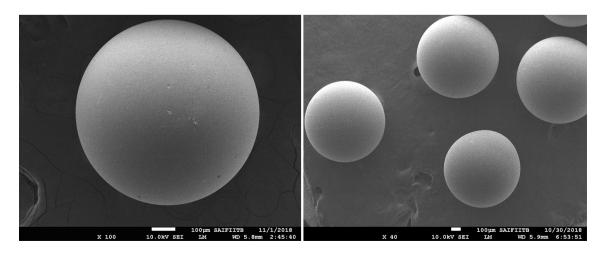


Fig. 1 FE-SEM analysis of prepared PdNP@DIANION™ PK228

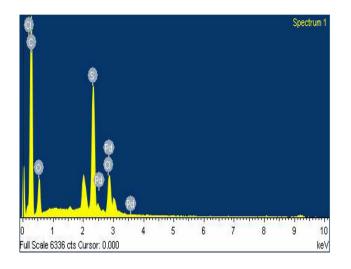


Fig. 2 EDS analysis of prepared PdNP@DIANION™ PK228

The EDS data of catalyst prepared is as shown in Fig. 2. Energy dispersive spectroscopy (EDS) was used to map the element present in the sample. The EDS data confirms that the present of palladium in the given sample. Pd exchange resin sample the EDS data confirms the presence of element C, Pd, D and Na. The concentration of carbon prominent in the resin and the resin is made up of polymeric organic compounds. The S and O content in the sample is due to sulphonic acid (SO<sub>3</sub>H) group responsible for cation exchange. The lower traces of sodium in the EDS data indicates the higher degree of palladium (counter cation exchange). The higher exchange of palladium is reflected in the EDS data (9.88%). The apparent higher content of palladium in this sample might be due to the fact that most of the palladium is present at the sulphonic group (SO<sub>3</sub>H) this surface saturation of palladium is reflected in the repulsion of the resin beads in the sample container when be observed these beads the appears like metallic (color) beads (Table 1).

Furthermore, high resolution transmission electron microscopy (HR-TEM) data of catalyst is as shown in Fig. 3. The HR-TEM image of the catalyst was also obtained, showing nanoparticles having a narrow size distribution of 20 nm.

Table 1EDS Data of PdNP@DIANION™ PK228

Element	Weight%	Atomic%
СК	65.86	80.94
ОК	14.15	13.06
S K	9.80	4.51
CI K	0.30	0.12
Pd L	9.88	1.37
Totals	100.00	



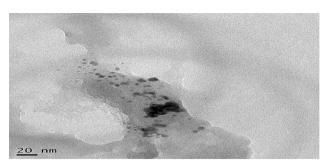
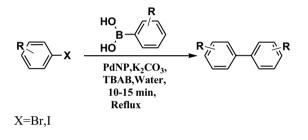


Fig. 3 TEM analysis of prepared PdNP@DIANION<sup>™</sup> PK228

## 3.2 Suzuki–Miyaura coupling reaction over PdNP@ DIANION PK228

Reaction scheme



#### 3.2.1 Biphenyl (Table 2, entry 1)

lodobenzene (0.22 ml), phenylboronic acid (0.242 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. Biphenyl was obtained as a white solid M.P = 69 °C (Rf = 0.72, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR δ 7.19–7.24 (m, 6H), δ 7.61 (dd, 4H).

#### 3.2.2 4-Acetylbiphenyl (Table 2, entry 2)

4-Bromoacetophenone (0.398 g), phenylboronic acid (0.242 g),  $K_2CO_3$  (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 4-Acetylbiphenyl was obtained as a white solid M.P = 117 °C (Rf = 0.68, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR  $\delta$  8.07 (dd, 2H),  $\delta$  7.68 (dd, 2H),  $\delta$  7.52 (d, 2H),  $\delta$  7.42 (m, 2H),  $\delta$  2.60 (s, 3H),  $\delta$  10.08 (s, 1H).

Entry no.	Aryl halide	Arylboronic acid	Product	Time (Min)	Yield (%)
1		НО В-С НО		10–15	98
2	O H <sub>3</sub> C		CH <sub>3</sub>	10–15	94
3	I	HO B-CI HO	✓ → CI	10–15	95
4	I	HO B HO CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	$\overbrace{\qquad }^{CH_3}_{CH_3}$	10–15	90

#### Table 2 Biaryl compound synthesized by PdNP@DIANION PK228

#### 3.2.3 4-Chlorobiphenyl (Table 2, entry 3)

lodobenzene (0.22 ml), 4-chlorophenylboronic acid (0.312 g), K<sub>2</sub>CO<sub>3</sub> (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 4-chlorobiphenyl was obtained as a white solid B.P = 77 °C (Rf = 0.70, Hexane: Ethyl acetate). <sup>1</sup>H NMR δ 7.54 (m, 4H), δ 7.42 (m, 5H).

#### 3.2.4 4-Tertbutylbiphenyl (Table 2, entry 4)

lodobenzene (0.22 ml), 4-tertbutylphenylboronic acid (0.356 g), K<sub>2</sub>CO<sub>3</sub> (0.276 g) and catalyst (0.025 g), tetrabutyl ammonium bromide (TBAB) (0.06 g) and water (10 mL) were used. 4-tertbutylbiphenyl was obtained as a white solid M.P = 53 °C (Rf = 0.50, Hexane: Ethyl acetate). <sup>1</sup>H NMR was obtained to confirm the product and solution NMR (<sup>1</sup>H). <sup>1</sup>H NMR δ 7.80 (m, 5H), δ 7.42 (m, 4H),  $\delta$  1.41 (s, 9H).

## 3.3 Recyclability of PdNP@DIANION PK228

The catalyst recyclability was investigated for reaction with iodobenzene with phenylboronic acid at 90 °C. The catalyst was separated from the reaction mixture after every reaction by simple filtration and then washed with ethyl acetate, followed by drying in desiccators and reused in fresh reaction and the process of recycling was repeated up to ten times. It was observed that used catalyst remained active without any significant loss in catalytic efficiency

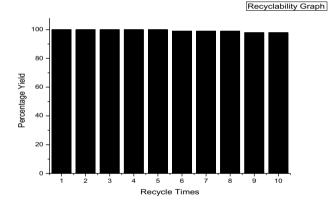


Fig. 4 Recycle test of catalyst

Fig. 4. The better reusability of the catalyst, which can be used ten times and the yield was more than 90%.

# **4** Conclusion

The result of ICP-AES confirmed that palladium was successfully loaded on cation exchange resin under mild conditions. It was characterized using BET, ICP-AES, FE-SEM-EDS, HR-TEM. The capacity showed efficient activity for Suzuki–Miyaura Coupling reaction in water under base with 100% selectivity and maximum conversion > 93%. The catalyst was recovered by simple filtration and the used catalyst was washed with ethyl acetate several times and was air-dried. Then the dried catalyst was reused up to ten times without any significant loss of efficiency. The simple

environment-friendly process, easy recovery and operational simplicity are the advantages of the synthesized catalyst. The reusability of the catalyst after ten times gave more than 90% yield.

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## **Compliance with ethical standards**

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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"What is important is the translation of research outcomes into products, services, policies—things that actually change the way that we live, hopefully for the better."

- Professor Ned Pankhurst

In our endevour to make this possible we at Rizvi Education Society have started with the International Journal of Research in 2011. Since then there has no looking back. Our partners in this have been all the contributing researchers who have provided the foundation in maintaining the quality that we owe to society. We can proudly say that this focus on quality has earned us a UGC listing and an Impact factor of 5.002 (SJIF) 2017.

We promise to continue to provide a platform for new directions and thoughts in Research so as to make a change for the better.

> Adv. Rubina A. H. Rizvi Director Rizvi Education Society

# FROM EDITOR'S DESK



I consider myself very fortunate to get an opportunity to serve as the Chief Editor of IJR. It gives me immense pleasure to present this volume of IJR to all our subscribers. This Volume 7(2) January - June 2018 of IJR includes double-blind peer reviewed research papers coming from different places in India and abroad and covers a wide variety of subjects.

All writers from relevant fields have taken tremendous efforts to screen and maintain the quality of research papers. They have taken utmost care to make their papers error free.

The Management and staff of Rizvi College of Arts, Science and Commerce are very much supportive in making this task gorgeous and prolific. I am sure that all papers will help the subscribers for their purpose of application in research activities in their related fields.

We will be highly obliged and thankful for the valuable remarks and suggestions from all the readers for improving the quality of our journal in future issues.

> Prof. Paul Raj. P Chief Editor

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Paul R P and Malan Zardi International Journal of Research VOL 7 (2) 2018 : PP 1 - 8

# An Exploratory Study on Evolution and Implementation of GST in India

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#### Abstract

This paper aims at capturing the change in the indirect tax structure in India due to the implementation of the Goods and Services Tax. It captures the formation of GST in India, and studies the structure of GST in India. The GST structure is contrasted with the previously existing tax structure, and brings out the problems in the previous structure that emphasized the need foe improving tax system in India. The paper then brings out how GST is being implemented, and the benefits that are accruing as a result.

Keywords: Indirect Tax, GST, CGST, SGST, IGST, e-way Bill

#### INTRODUCTION

Indian Goods and Services Tax (GST), a new consolidated indirect tax, slated to be implemented from 1<sup>st</sup> July 2017 as per current indications, is a common tax on supply of both, goods and services to be commonly levied and collected by Centre, 28 States and 7 Union Territories, on a common base, at common rates, having common procedures to be administered fully electronically through a common digital platform. It is a single tax on the supply of goods and services, right from the manufacturer to the consumer. Credits of input taxes paid at each stage will be available in the subsequent stage of value addition, which makes GST essentially a tax only on value addition at each stage. The final consumer will thus bear only the GST charged by the last dealer in the supply chain, with set-off benefits at all the previous stages.

#### **COMPONENTS OF GST**

There are 3 taxes applicable under GST: CGST, SGST & IGST.

- **CGST:** Collected by the Central Government on an intra-state sale (Eg: Within Maharashtra)
- **SGST:** Collected by the State Government on an intra-state sale (Eg: Within Maharashtra)
- IGST: Collected by the Central Government for



Transaction	New Regime	Old Regime	
Sale within the State	CGST + SGST	VAT + Central Excise/Service tax	Revenue will be shared equally between the Centre and the State
Sale to another State	IGST	Central Sales Tax + Excise/Service Tax	There will only be one type of tax (central) in case of inter-state sales. The Center will then share the IGST revenue based on the destination of goods.

inter-state sale (Eg: Maharashtra to Tamil Nadu or any other state) In most cases, the tax structure under the new regime will be as follows:

### TAX RATES UNDER GST

GST rates are divided into five categories which are 0%, 5%, 12%, 18%, 28%.

All the basic need requirement goods are pleased in 0% category like food grains, bread, salt, books etc. Goods like paneer, packed food, tea coffee etc. are placed under 5% category. Mobiles, sweets, medicine, are under 12%. All types of services are under 18% category. All other remaining luxury items are placed under the last head of 28%.Petrol, gas, crude oil, diesel etc. are still out from the criteria of GST.

#### **Objectives:**

- 1. To study the various aspect of Goods and Service Tax system in India.
- 2. To understand the structure of Goods and Service Tax system in India.
- 3. To understand the filing returns of GST via eway bill in India.
- 4. To analyze the impact of GST on Indian economy.

#### **RESEARCH METHODOLOGY**

The research paper is based on secondary data, it has been taken from the research journals, books and internet. The data is assembled from various internet sites and arranged in the order to gain the outlook of GST system in India. Major chronological events that have led to the introduction of GST

GST is being introduced in the country after a 13 year long journey since it was first discussed in the report of the Kelkar Task Force on indirect taxes. A brief chronology outlining the major milestones on the proposal for introduction of GST in India as per next page.

# **GST RETURN**

A return is a document containing details of income which a taxpayer is required to file with the tax administrative authorities. This is used by tax authorities to calculate tax liability. Under GST, a registered dealer has to file GST returns that include:

- Purchases
- Sales
- Output GST (On sales)
- Input tax credit (GST paid on purchases)
- To file GST returns, GST compliant sales and purchase invoices are required.

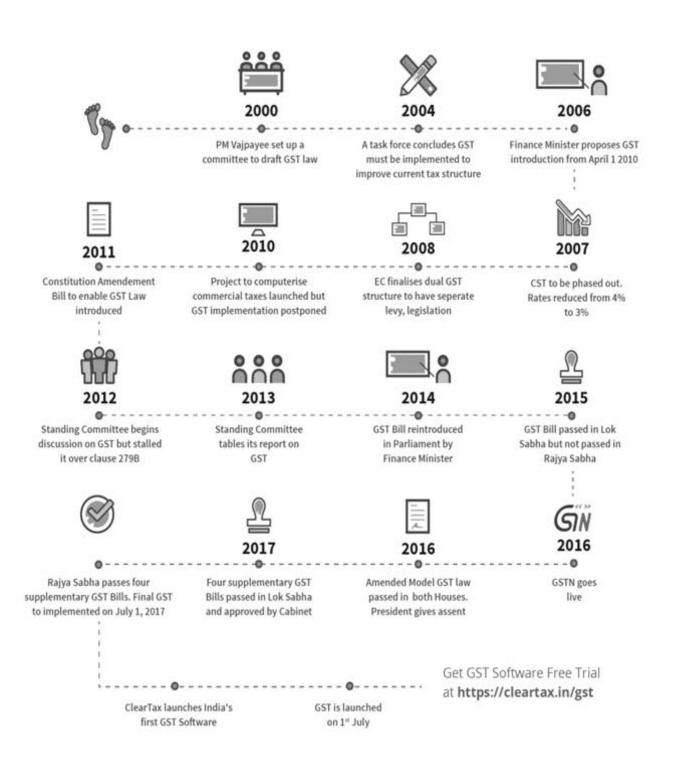
#### **Types of GST Returns**

Here is a list of all the returns to be filed under the GST Law along with the due dates.

#### Any regular business:

As per Act

#### AN EXPLORATORY STUDY ON EVOLUTION AND IMPLEMENTATION OF GST IN INDIA





#### **BENEFITS OF GST**

# For Business and

Industry

Easy compliance
 Uniformity of tax rates and structures

- Removal of cascading
- Improved competitiveness
- ·Gain to manufacturers and exporters

#### For Central and State Government

Simple and easy to administor
 Better controls on leakage

·Higher revenue efficiency

#### For the consumer

•Single and transparent tax proportionate to the value of goods and services •Relief in overall tax burden

#### As per Act

Return Form	Particulars	Interval	Due Date
GSTR-1	Details of outward supplies of taxable goods and/or services effected	Monthly*	10th of the next month
GSTR-2	Details of inward supplies of taxable goods and/or services effected claiming input tax credit.	Monthly*	15th of the next month
GSTR-3	Monthly return on the basis of finalization of details of outward supplies and inward supplies along with the payment of amount of tax.	Monthly*	20th of the next month
GSTR-9	Annual Return	Annually	31st December of next financial year
GSTR-3B	Provisional return for the months of July 2017 to March 2018	Monthly	20th of the next month

#### FILING OF GST RETURNS

In the GST regime, any regular business has to file three monthly returns and one annual return. This amounts to 37 returns in a year. The ease of the system is that one has to manually enter details of one monthly return – GSTR-1 and the other two returns – GSTR 2 & 3 will get auto-populated by deriving information from GSTR-1 filed by you and your vendors. There are separate returns required to be filed by special cases such as composition dealers.

#### E-WAY BILL

E-Way Bill is an electronic way bill for movement of goods which can be generated on the e-Way Bill Portal. Transport of goods of more than Rs.50,000 in value cannot be made by a registered person without an e-way bill. E-way bill can also be generated or cancelled through SMS. When an e-way bill is generated a unique e-way bill number (EBN) is allocated and is available to the supplier, recipient, and the transporter.

#### When should an e-Way Bill be issued?

E-way bill will be generated when there is a movement of goods of value more than Rs. 50,000 -

- In relation to a 'supply'
- For reasons other than a 'supply' ( say a return)
- Due to inward 'supply' from an unregistered person

For this purpose, a supply may be either of the following:

- A supply made for a consideration (payment) in the course of business
- A supply made for a consideration (payment) which may not be in the course of business

- A supply without consideration (without payment)In simpler terms, the term 'supply' usually means a:
  - 1. Sale sale of goods and payment made
  - 2. Transfer branch transfers for instance
  - 3. Barter/Exchange where the payment is by goods instead of in money

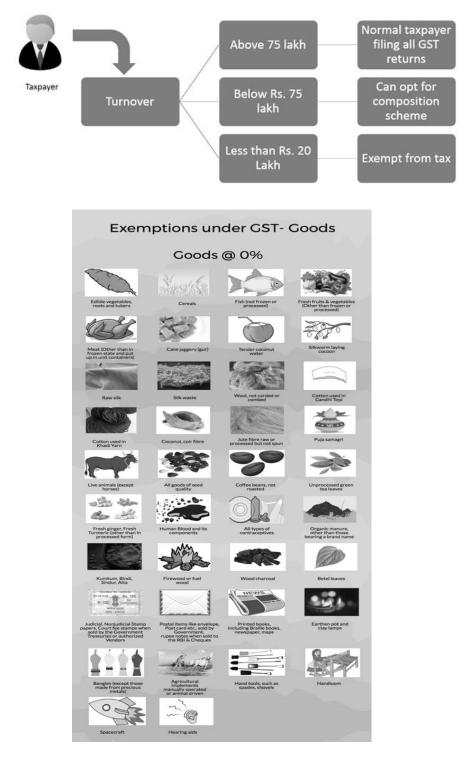
Therefore, e-Way Bills must be generated on the common portal for all these types of movements.

#### Who should generate an e-Way Bill?

- **Registered Person** E-way bill must be generated when there is a movement of goods of more than Rs 50,000 in value to or from a Registered Person. A Registered person or the transporter may choose to generate and carry e-way bill even if the value of goods is less than Rs 50,000.
- Unregistered Persons Unregistered persons are also required to generate e-Way Bill. However, where a supply is made by an unregistered person to a registered person, the receiver will have to ensure all the compliances are met as if they were the supplier.
- **Transporter** Transporters carrying goods by road, air, rail, etc. also need to generate e-Way Bill if the supplier has not generated an e-Way Bill.



#### Exemption limit and exemptions under GST



#### **IMPACT OF GST**

In the case of indirect taxes, the burden was on end customer or consumer. But due to the implementation of one tax in the whole country the overall cost of production of all goods will be reduced but on the other hand in case of services, it will increase after the implantation of GST but CST gets abolished which ultimately reduces the cost of goods. Currently, we pay 30-35% tax on a commodity. In the case of some goods, direct and indirect taxes imposed by government raise its cost upto 30%. After the implementation of GST, it will reduce. The GST also reduces the cascading effect of tax which helps in making the trade simple and reduces the tax Burden of Entrepreneurs.

#### CONCLUSION

Implementation of GST is one of the best decision taken by the Indian government. For the same reason, July 1 was celebrated as Financial Independence day in India when all the Members of Parliament attended the function in Parliament House. The transition to the GST regime which is accepted by 159 countries would not be easy. Confusions and complexities were expected and will happen. India, at some point, had to comply with such regime. Though the structure might not be a perfect one but once in place, such a tax structure will make India a better economy favorable for foreign investments. Until now India was a union of 29 small tax economies and 7 union territories with different levies unique to each state. It is a much accepted and appreciated regime because it does away with multiple tax rates by Centre and States. And if you are doing any kind of business then you should register for GST as it is not only going to help Indian government but will help you also to track your business weekly as in GST you have to make your business activity statement each week.

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Home / Archives / Vol. 21 No. 2 (2019) / Articles

# **DIGITAL INDIA: OPPORTUNITY FOR SERVICE SECTOR**

Paul Raj P

#### Abstract

This paper focus on **Digital India: Opportunity for Service Sector** Digital India is a Program to prepare India for a knowledge future. Hon'ble Shri Narendra Modi, Prime Minsiter of India has laid emphasis on National e- governance plan and has gave its approval for Digital India A programme to transform India into digital empowered society and knowledge economy. This will be for preparing the India for the knowledge based transformation and delivering good governance to citizens by co-ordinate engagement with both Central Government and State Government. The Digital India vision provides the intensified impetus for further momentum and progress for e-Governance and would promote inclusive growth that covers electronic services, products, devices, manufacturing and job opportunities.

🖾 PDF

Published 2019-09-11

# WOMEN EMPLOYEES IN BANKING SECTOR: A STUDY ON OCCUPATIONAL STRESS

Paul Raj P

# Abstract

There is no such issue like stress- free job. activity stress arises as a results of causes like lack of free time, job setting disadvantage, high workloads, low salary, unreasonable deadlines, job insecurity, lack of clarity of roles, and some way of feeling undervalued .Stress and its fateful consequences has unfold its tentacles altogether the sectors, heaps of considerably inside the banking sector thanks to the quick changes that's taking place throughout this sector. industry is not associate exceptional one. This paper seeks to figure out the impact of various constituents of activity stress on the women employees of banking sector. The employees inside the banking sector area unit experiencing an out of this world amount of pressure at the work place. thus the target of this study was to identify and compare the factors inflicting stress among girls employees publicly and private sector banks and counsel applicable remedies for a similar. Keywords: activity stress, tension, role conflict.



Home / Archives / Vol. 21 No. 6 (2019) / Articles

# A GLIMPSE OF BPO AND CALL CENTRES: THE CASE OF INDIA

Dr. Paul Raj P

#### Abstract

During the last 20 years, Business Process Outsourcing (BPOs) Companies have increased in number to a large extent due to IT revolution. The skilled and cheap labour force with good command over spoken English contributed a lot of flouring call centres in the country. A BPO is vested with the task of outsourcing its non-core activities such as administration, payment services and customer services whereas a call centre is a voice-based part of a BPO organisation.

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Published 2019-10-11

Issue Vol. 21 No. 6 (2019)



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# A STUDY OF IMPACT OF SKILL INDIA ON RURAL YOUTH

Paul Raj P

#### Abstract

The Goods and Services Tax (GST) is one of the biggest economic and taxation reforms undertaken in India. Parliament initiated a seven-hour marathon debate on four supplementary GST Bills. The Goods and Services Tax Bill or GST Bill, also referred to as The Constitution (One Hundred and Twenty-Second Amendment) Bill, 2014, initiates a Value added Tax to be implemented on a national level in India. The GST aims to streamline the taxation structure in the country and replace a gamut of indirect taxes with a singular GST to simplify the taxation procedure. GST is one indirect tax for the whole nation, which will make India one unified common market. It would also enhance the position of India in both, domestic as well as international market. The system will phase out all indirect taxes and only GST will be applied as an indirect tax. It will apply on both Goods and Services. Taxes like excise duty, VAT, service tax, luxury tax etc will go with GSTs implementation.

🖾 PDF



# OPPORTUNITIES AND LIMITATION OF CASH LESS ECONOM

#### Dr.Paul Raj P

#### Abstract

Solapur district is most significant town of geographical region as a result of Solapur district currency press, Farming, Education, Industries and . Solapur district fifteen tehsil but7 tehsil is huge population of social group .The main issues of cashless economy is education, out there facility instrumentation. The Hon. Prime Minister, government minister and run batted in Governor was determined the currency five hundred and one thousand RS currency has not tender and impact on nine November 2016 time of day. The run batted in and Government square measure creating many efforts the utilization of in economy by promoting the digital payment devices and main object of the cashless in zero corruption, increase if taxes in India and Digital India Nation. Digital group action brings transparency measurability and responsibility. The new move can compel a lot of distributor and repair supplier settle for digital cash money group action was restricted or minimum has object of cashless Indias Nation.



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Scope Database Indexed

# THE ROLE OF CULTURAL DIVERSITY AND HOW THEY IMPACT WORK TEAM PERFORMANCE

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#### ABSTRACT

Cultural diversity plays a major role in the productivity of a corporation in this thriving business world. The workplace is a platform where individuals from different backgrounds come together to work and share an organization's goals and objectives. This research focuses on the impact of cultural diversity on work team performance in Abu Dhabi University and whether the multicultural environment results in a positive, negative or dual impact.

Quantitative and qualitative approaches were used in order to determine the impact and the research findings showed that a dual impact of culturally diverse teams is present in Abu Dhabi University. The results that were analyzed are specific to Abu Dhabi University and will differ from business to business because of cultural diversity.

Keywords: Motion Control; Modular Design; Real-time Control; Trajectory Planning.

**Cite this Article:** Jacob Cherian, Gaikar Vilas B and Paul Raj P, The Role of Cultural Diversity and how they Impact Work Team Performance. *International Journal of Mechanical Engineering and Technology*. 11(9), 2020, pp. 11-22. https://iaeme.com/Home/issue/IJMET?Volume=11&Issue=9

# **1. INTRODUCTION**

# 1.1. Background of the Company

Abu Dhabi University was established in September 2003, after three years of planning by Sheikh Hamdan Bin Zayed Al Nahyan and other residents of UAE, and it welcomed around 1000 students in both of its campuses located in Abu Dhabi and Al Ain. Throughout the years, ADU has gained multiple accreditations and has increased its status as one of the best universities in the gulf countries. Abu Dhabi University is known for having a vibrant faculty and student community, as individuals from over 55 nationalities work and learn together [1].

# **1.2. Statement of Problem**

This research discusses the impact of cultural diversity on work team performance at Abu Dhabi University (ADU). It examines the multicultural environment at ADU and evaluates the effect of such an environment in the performance. Since the work environment of ADU encourages multicultural teams, issues such as favoritism may exist. The research will explore if this diverse culture has a positive, negative, or dual impact on the level of performance at ADU? A qualitative and quantitative approach is used to gain an in-depth understanding of the topic.

# 1.3. Aims and Objectives

The aim of the study is to evaluate the impact of multicultural work team performance and identify the multiple ways that cultural diversity impacts ADU's productivity levels. Moreover, the terms: Culture, cultural dimensions, and diversity will be defined and conceptualized

The objectives of this research are to assess the various impact of multicultural work team performance at ADU, to evaluate the importance of training employees to adjust to other cultures and to contribute in expanding the behavioral management research sector in the field of Industrial Psychology.

# **1.4. Focus of the Study**

The main focus of this study is to examine the culturally diverse work team environment and its impact on Abu Dhabi University's work team performance. An insight of the work environment and how different languages, cultures, values, and religions affect the team will be provided.

# **1.5. Significance of the Study**

The significance of the concept of cultural diversity on teamwork is crucial as it is an important aspect for future companies. Multicultural teams are noticeably increasing in organizations all over the world and therefore, such a research is required to widen the understanding of this topic and provide reasoning for the success of international businesses [2].

# 2. LITERATURE REVIEW

This literature review discusses previous studies that were done regarding the impact of culture and inter-cultural diversity on organizational behavior. This section will give readers an insight on the topic as culture is an important factor when it comes to how employees behave at their workplace. This topic of study is an essential aspect of any organization since it can greatly affect the performance of its employees.

Furthermore, cultural diversity in its broadest form can be defined as a learned behavior highly influenced by values, beliefs, and religion shared by a group of people and passed from one generation to another [3]. Moreover, according to Kokemuller, cultural diversity is the existence of employees from different ranges of backgrounds and different characteristics in an organization. In his article, Kokemuller states that employees differ in experience, age, culture, race, ethnic origin, and sexual orientation and all these aspects are contributed to diversity [4]. Thomas, in his research, distinguishes three key ways in which culture influences teams in an organization, these include: the norms of the cultures present in the work team, how culturally different individual team members are, and the proportion of cultural diversity in a team's composition [5]. Diversity is known to be a positive feature in an organization as it leads to an increase in the productivity levels; however, diversity also creates major challenges for company leaders as multiple individuals from different regions, religions, and traditions come to work together [4].

The article 'managing ethically cultural diversity: learning from Thomas Aquinas' by Joao Cesar das Neves and Domenec Mele discusses how cultural diversity is now an essential part of any organizational structure. It provides an innovative and creative organizational environment along with a hybrid of working techniques that in the long run lead to high competitiveness in the global market, cost effectiveness, increased job motivation, and product diversity [6]. Furthermore, teams that consist of employees with different backgrounds, view pints and cultural values can help to generate a wide range of ideas that may encourage cautious team members to express their own opinions. In addition to that, diversity encourages constructive conflicts that enhance creativity and increase the efficiency and the quality of decisions [7], [8].

On the other hand, some researchers argue that employees from the same culture tend to form teams in an efficient manner while employees from diversified cultures have a tendency to experience several cultural issues which lead to a delay in team formation processes [9]. Moreover, culturally diversified team members tend to have different opinions about desirable team behaviors due to varying cultural backgrounds and such perceptions may lead to conflicts in the workplaces [10]. Additionally, culturally diverse team members are subject to experience low satisfaction and performance levels due to poor communication and decision-making [11]. In his article, Chevrier (2003) argues that uncertainty, confusion, and complexity exist within multicultural team members and may lead to a less effective team [12]. Furthermore, a culturally diverse work team is subject to many issues related to language, norms, and communication, such issues can negatively affect team performance and should be resolved in order to ensure effective team performance [7].

The main concerns when managing a culturally diverse team can be dissimilar attitudes, disagreements, and lack of communication within team members. Managers at any organization must be able to deal with such issues and treat all employees in a fair manner. Joao Neves and Domenec Mele state that management should adopt a rational thinking method towards employees by pursuing good and rejecting evil. The practice of rational thinking will increase employee's loyalty towards the organization as well as encourage a healthy and positive environment [13]. Multiple researchers agree that a culturally diverse workforce represents a source of competitive advantage for organizations in the long run [14]. Many also agree that a culturally diverse workforce can lead to high organizational performance [15]. In these present times, Organizations focus on increasing their flexibility and responsiveness in the global market through implementing a culturally diverse environment [16].

The article 'Cross-Level culture congruence: Implications for managing diversity in multinational corporation' by Jennifer Palthe discusses the importance of interconnecting the

national, individual and organizational culture in a multinational organization. According to Palthe, the effects of diversity are most apparent in the multinational environment since they are the centers of a diverse workforce and in order to be competent in an international organization, an employee must be capable and flexible of working with others regardless of their cultural background. Palthe discusses how employees tend to contribute on an individualistic level which acts as a major step backward since most organizations are involved in eradicating differences. This may serve as a problem to the firm as teamwork is then compromised through the focus on an individualistic approach [17].

A research paper by Lynne Leveson, Therese Joiner and Steve bakalis discuss an employee's perception of cultural diversity within an organization. The research highlights the relationship between organizational support and management of cultural diversity. A major concern in a diverse workforce is the support of the management towards their employees. Management may respect and appreciate employees based on differences such as race, gender, color, ethnicity and cultural background [18]. A study suggests that a culturally diverse organization requires managers to have proper tools, training, evaluation, monitoring programs, and support from top management in order to provide appropriate training to other employees. Such training is required in the workforce so employees are aware of prejudices and have the ability to manage their own actions [19]. Additionally, managers that lead multicultural teams should be able to guide the development of the team and provide a clear division of roles and responsibilities by hiring individuals with positive attributes [7],[20]. Furthermore, researchers recommend that managers must understand the diverse culture in their organization, set specific goals, policies and expectations for their employees, adapt leadership styles to employees' types, and manage conflicts in order to obtain positive outcomes [21].

According to Leveson and Joiner, employees perform efficiently and have more motivation to work in an environment where diversity is appreciated and holds high value. This provides employees with a sense of belonging and involvement thus ensuring the existence of a united team at the workplace [22]. All in all, taking into account the abovementioned reviews, cultural diversity plays a major role in the success of a firm and the outcomes are highly dependent on how well multicultural team members work with each other along with the guidance of the management department to deal with issues that result from a multicultural team.

# **3. RESEARCH DESIGN & METHODOLOGY**

# 3.1. Research Design

This research focuses on the impact of cultural diversity on work team performance at Abu Dhabi University (ADU). This section will provide an insight on the methods used to gain information regarding the topic and what will be used in order to construct this research paper.

# **3.2.** Sources of Data

Primary and secondary sources will be used throughout this research, our primary source consists of a questionnaire that contains 11 questions regarding the impact of cultural diversity on work team performance, while our secondary sources focus on research papers and articles found through ADU's library database. Our questionnaire will provide quantitative data that will be used to analyze statistics and formulate graphs.

# 3.3. Sample Size

The sample size used for this research is 39 employees, this number was determined through a sample size calculator from a survey software system. As shown below, the calculator assisted in clarifying the total sample size needed, while the inputs were the confidence level, confidence interval and the population of the company. Amounts of 95%, 15, and 500, were used, respectively. This sample size will be used to survey the employees at Abu Dhabi University.

Determine Sample Size				
Confidence Level:	●95% ○99%			
Confidence Interval:	15			
Population:	500			
Calculate	Clear			
Sample size needed:	39			

Figure 1 Sample Size Calculator [23].

# **3.4. Method for Data Collection**

Quantitative and qualitative approaches will be used throughout this research. The quantitative method consists of 11 questions that focus on the employee's personal details, cultural diversity at ADU, and job satisfaction levels. The statistics and graphs resulting from the questionnaire will be formed through a survey analysis program known as survey monkey. Survey monkey will analyze the result of each question and provide a graph that discusses the result in depth. This questionnaire will be distributed to 39 employees from multiple nationalities and different genders at Abu Dhabi University. Secondary sources such as previous research articles, journals, and books are used in order to construct the literature review section of this study. The ADU library database was used in order to attain articles that focus on the impact of multicultural teams on work performance.

# 3.5. Limitation

The only limitation present in this research is the number of employees used for the survey analysis and the focus on only one institute. This research can be expanded and cover a wider number of individuals and companies in order to gain an even more in-depth analysis result. This limitation can be fulfilled by collecting primary data from multiple other organizations that focus on building multicultural teams.

# 4. ANALYSIS AND INTERPRETATION OF DATA

This research focuses on five demographic variables: gender, age, nationality, education qualification, and years of work experience at ADU. The mentioned variables are considered since they have the ability to affect the outcome of the survey. The results showed that from 39 employees, the gender response was 64.1% for females while 35.9% for males. The majority of the respondents belonged to the age group of 40 and above, this group consisted a response rate of 64.10%, followed by 33.33% in the age group of 25 - 40, and 3.56% in the age group of below 25 years. ADU consists of employees from all over the world and therefore the highest percentage of response is 43.59% in the "other" category, 38.46% in the Southeast Asian group, and 17.95% in the Arab group. The highest range for education qualification was 69.23% for respondents with a postgraduate degree. In addition, the

employees of ADU differ in the years of work experience with the highest response as 41.03% in the category of 7-12 years, 38.46% in 1-6 years, 15.38% in the group of 12 months and under, and 5.13% in the category of 12 years and above.

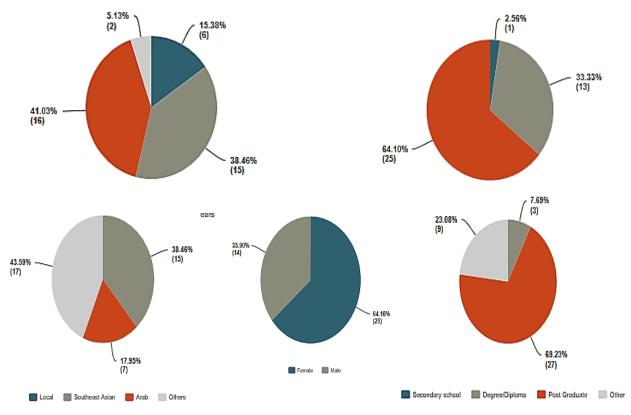


Figure 4 Nationality

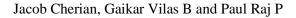
Figure 5 Gender

Figure 6 Educational Qualification

Answer Choices ~					Resp	onses	~
-	Strongly Agree (1)				0.005	6	0
-	Agree (2)				20.51	%	8
-	Neutral (3)				12.82	:%	5
-	Disagree (4)				38.49	%	15
*	- Strongly Disagree (5)				28.21%		11
Tot	al						39
Bas	sic Statistics						Θ
Min 2.00	l <b>mum</b>	Maximum 5.00	Median 4.00	Mean 3.74		Standard Deviation	

Table 1 ADU employs based on culture

As shown above, the majority of the respondents believe that Abu Dhabi University does not hire employees based on their culture or country since the response rate is 38.46% for the disagree option and 28.21% for strongly disagree. 12.82% replied as neutral and 20.51% responded as agree.



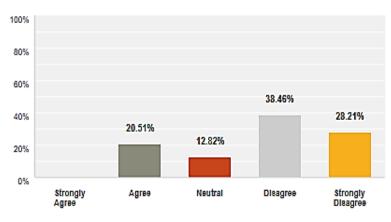


Figure 7 ADU employs based on culture

Table 2 Conflicts faced when working in a multicultural environment

	1 - Strongly Agree (1)	2 - Agree (2)	3 - Neutral (3)	4 - Disagree (4)	5 - Strongly Disagree (5)	Total Respondents
Miscommunication in Languages	10.53%	26.32%	18.42%	31.58%	13.16%	
	4	10	7	12	5	
Cultural Differences Awareness	15.79%	26.32%	28.95%	21.05%	7.89%	
	6	10	11	8	3	:
Attitudes/Behaviours Toward Time	17.95%	43.59%	28.21%	7.69%	2.56%	
	7	17	11	3	1	
Team Members Structure and	5.26%	60.53%	23.68%	5.26%	5.26%	
expectations	2	23	9	2	2	
Decision making issues	15.79%	42.11%	15.79%	21.05%	5.26%	
-	6	16	6	8	2	

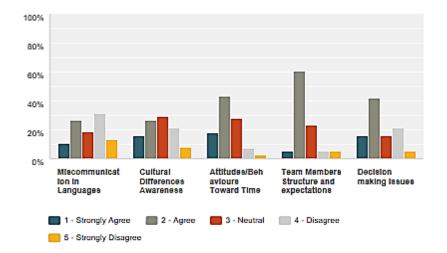


Figure 8 Conflicts faced when working in a multicultural team

The graph above discusses the conflicts that employees at ADU may face when working in a multicultural team. First, 31.58% and 13.16% disagree and strongly disagree that they face miscommunications in languages, 28.95% are neutral, and 26.32% and 10.53% agree and strongly agree that they face this issue. Second, the majority of 28.95% are neutral with the cultural difference awareness at ADU, 15.79% and 26.32% agree and strongly agree that this conflict is present, while 21.05% and 7.89% disagree and strongly disagree with it. Third, 43.59% and 17.95% agree and strongly agree that there are different behaviors towards time present at ADU, 28.21% are neutral, and 7.69% and 2.56% disagree and strongly disagree. Fourth, the highest percentage of 60.53% and 5.26% agree and strongly agree that there are

specific team member expectations based on culture, 23.68% are neutral, and 5.26% disagree and strongly disagree. Last, 42.11% and 15.79% agree and strongly agree that they face decision-making issues in a multicultural team, 15.79% are neutral, and 21.05% and 5.26% disagree and strongly disagree.

An:	swer Choices	Responses	Y	
7	Yes (1)	74.36%	29	
Ŧ	No (2)	15.38%	6	
<b>T</b>	Other (please specify) (3)	10.26%	4	
Tot	al	-	39	

Table 3 Do you feel appreciated at ADU?

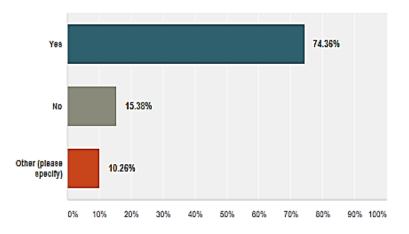


Figure 9 Do you feel appreciated at ADU?

According to the above graph and table, the majority of respondents, 74.36%, state that they do feel appreciated at ADU, however, 15.38% responded the opposite, while 10.26% said that the feel appreciated sometimes.

Answer Choices	Responses	Ŧ
- Yes (1)	44.74%	17
- No (2)	52.63%	20
- Other (please specify) (3)	2.63%	1
Total		38

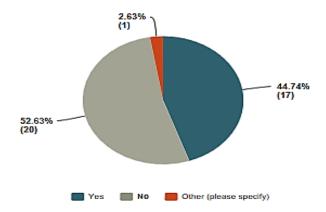


Figure 10 Conflicts caused due to cultural differences at ADU.

This chart displays the percentages of employees that have faced conflicts due to the cultural difference at Abu Dhabi University. The majority of 52.63% state that they have never experienced such issues, while 44.74% responded that they have experienced such problems.

An	wer Choices	Responses	*
*	Yes (1)	35.14%	13
Ŧ	No (2)	45.95%	17
Ŧ	Other (please specify) (3)	18.92%	7
То	al		37
Yes	35.	14%	
		_	
No		45.95%	
er (please specify)	18.92%		
	0% 10% 20% 30% 40%	6 50% 60% 70% 80%	90% 10

 Table 5 Would you stay if you receive an attractive offer?

Figure 11 Would you stay if you receive an attractive offer?

As seen above, this table discusses whether employees would stay at ADU if they received an attractive job offer from somewhere else. 45.95% responded that they would not stay, 35.14% would stay, and 18.92% specified different responses such as "it would depend on the type of offer".

# **5. OBSERVATION**

Abu Dhabi University is a culturally diverse workforce as shown in this research, the 39 respondents were Arab, Southeast Asian, and from other continents such as Europe. This

shows that ADU focuses on bringing a multicultural work team in order to increase their efficiency and become one of the top universities in the GCC. The respondent's ages ranged from 25 to 40 and above since the majority that was interviewed were professors holding PhDs. The gender variable was more favorable to females since the response rate was higher, this does not provide that ADU is comprised mainly of female employees, but may give an insight to a sample size of the workforce. From the findings of the research, it seems that ADU creates a comfortable working environment for their faculty given that the highest response was of 7 to 12 years and above. This also shows that ADU focuses on building loyalty and a feeling of belonging in its working environment.

When asked whether ADU would hire based on culture or background, 26 out of 39 agreed that ADU would not recruit employees due to the culture they belong to, however, 8 out of 39 believe the opposite. Moreover, if the conflict aspects at ADU are discussed, almost half state that they face miscommunications in language, while the other half express the opposite. Additionally, 16 out of 38 declare that there is an awareness of cultural differences in their work environment, however, 11 out of 38 disagree to that. 24 from 39 agree that there are different attitudes towards time and this depends on the culture of the employee, yet 4 respondents disagree. 25 out of 38 also agree that team members are expected to provide different outcomes based on the country they belong to. In addition, 21 respondents reported that they face decision-making issues when in a multicultural team due to different opinions, while 10 state that they do not face such issues.

When asked about conflicts in general, it was observed that half of the respondents faced issues while the other half do not. In open-ended responses, respondents stated that ADU promotes high respect for cultural diversity among faculty and staff and that they are extremely satisfied with their working environment. However, some employees discuss how other team members from ethnic clusters that result in acts of favoritism and that management should focus on diversifying all departments so such risks are eliminated. The majority also states that they feel appreciated at ADU, yet they may leave their current position if they are offered an attractive job somewhere else. This shows that on an individual level, employees at ADU have different opinions towards the actions of the company and this may also be dependent on the culture of the individual and his perception of the environment.

# 6. CONCLUSION & RECOMMENDATIONS

This research discusses the impact of cultural diversity on work team performance in Abu Dhabi University. A survey was used as quantitative data to determine the impact of diversity on employees, this questionnaire focused on general demographics, cultural diversity's impact, and individual reflections. After conducting the analysis, it can be said that there is a dual impact on the level of performance in Abu Dhabi University. A positive and negative correlation between cultural diversity and work team performance can be seen. Employees in ADU seem to be satisfied with the overall working environment and face no issues while working in a multicultural team, the opposite is also true as some employees do face issues and state that cultural clusters are formed which hinder decisions of other team members.

Creating a multicultural work team is very important for the business world nowadays. It acts as a means to improve a corporation's productivity if it is monitored and implemented in the right manner. A diverse culture may increase chances of conflicts, it is the duty of higher management to assure that such cases do not occur by providing training that focuses on dealing and communicating with a multicultural team or guides employees to workshops that deal with team bonding activities and encourage working with members from different cultures. Moreover, diversity should exist in all sectors of a company so that no specific cultural clusters are formed.

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# An Evaluation of Laws and Bills on Surrogacy in India

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#### Abstract

Non regulation of surrogacy business in India paved way to various unethical practices involved in the each step of the procedure. Due to absence of law for regulating surrogacy there are a number of cases where surrogates face exploitation.

An increasing number of surrogacy rackets, legal minutiae and reported incidences of exploitation of surrogates came to be known; there was an urgent urge for regulation of surrogacy process. In order to deal with the situation the Indian govt. attempted to regulate the process so that it ensures the safety for all involve in the process. However the regulation made the process more difficult by imposing a ban.

Indian courts have been known for not dealing comprehensively with the cases and often kept leaving the task for legislature. This paper aims at understanding and critically evaluating the various ICMR guidelines and regulatory bills on surrogacy and its implications on surrogates, intended parents, practitioners and civil society at large thereby suggesting measures to deal will the situation. The review of the above bills and guidelines make it clear that it is extremely necessary to regulate the surrogacy practices in the country to prevent the unethical practices prevailing under it and also to stop the exploitation of the surrogates.

#### Key Words: Surrogacy, ICMR, Surrogacy Regulation Bill

#### **Introduction:**

Many western countries have either ban surrogacy or have allowed it under strict regulations. Countries like German, Austria, France, Switzerland, Sweden, Norway, Italy and Bulgaria have completely prohibited all surrogacy agreements. Surrogacy agreements are against **public policy** in those countries. While those who oppose surrogacy want to put a ban on surrogacy, the supporters wants it to get fully legalized. The Indian Council of Medical Research has laid down guidelines to regulate surrogacy practices in India considering the fact that India has been seen as a major center by childless couples across the world to realize their dream into reality through a child born out of surrogacy. However it remains to be seen whether the guidelines as laid down by ICMR relating to Surrogacy are being practiced and implemented in Principle or not.

# Laws on Surrogacy in India

Non regulation of surrogacy business in India paved way to various unethical practices involved in the each step of the procedure. Due to absence of law for regulating surrogacy there are a number of cases where surrogates face exploitation.

An increasing number of surrogacy rackets, legal minutiae and reported incidences of exploitation of surrogates came to be known; there was an urgent urge for regulation of surrogacy process. In order to deal with the situation the Indian govt. attempted to regulate the process so that it ensures the safety for all involve in the process. However the regulation made the process more difficult by imposing a ban.

The ICMR made the first attempt to regulate surrogacy by drafting the National Guidelines for Accreditation, Supervision and Regulation of ART clinics in India. This resulted in formulation of ART Bill 2008, 2010 and 2014 bur were never passed by the parliament. These bills subsequently followed by the Surrogacy (Regulation) Bill of 2016.

# **ICMR Guidelines of 2005**

The ICMR gave Guidelines in  $2005^1$  on Assisted Reproductive Technology. The Law Commission of India submitted  $228^{th}$  report on ART<sup>2</sup> to discuss the need and importance of surrogacy and various steps to control and restructure the surrogacy contracts.

<sup>&</sup>lt;sup>1</sup> National Guidelines for Accrediation, Supervision and Regulation of Art Clinics in India, Indian Council of Medical Research-http://icmr.in/art\_clinincs.htm

<sup>&</sup>lt;sup>2</sup> (Need for Legislation to Regulate Assisted Reproductive Technology Clinics as well as Rights and Obligations of Parties to Surrogacy, "Law Commission, Government of India, Report No. 228. August 2009. http://lawcommissionofindia.nic.in/reports/report228.pdf)

#### The important features of the Bill were as follows:

- The surrogacy contract should contain all the terms and conditions encircling the surrogacy practice.
- It mandates that none of the arrangements should be commercial in nature.
- There should be provision for financial support to the surrogate child in events such as death of the intended parents before the birth of the child or divorce amongst the intended parents and consequent non willingness of them to take the custody of the child.
- The contract should take into consideration the life insurance cover for the surrogate mother.
- In order to ensure the biological relationship either of the commissioning parents should be the donor.
- There should be legal provision to identify the surrogate child as the legitimate child of the intended parents. The need for guardianship and adoption should be waved off.
- Right to privacy of surrogate mother and donor should be protected.
- There should be prohibition on sex-selective surrogacy.
- Abortion cases should be governed under the Medical Termination of Pregnancy Act only.

# **ART (Regulation) Bill 2010**

#### The important features of the Bill were as follows:

- Gays, Lesbians and singles were given legal right to have children through surrogacy.
- The term couple was redefined as two people living together and having physical relationship.
- A surrogate should be woman in the age group of 21-35.
- A surrogate was allowed to have five live births counting her own biological children.
- The number of egg donation by a woman was restricted to six in her life time.
- In case of single man or woman the baby will be entitled to be the legitimate child of his or her.

- An unmarried partners consenting to opt for the surrogate child will be accorded the legal status.
- The intended parents will have to bear the actual cost of surrogacy apart from providing financial help to the surrogate. They may sign the agreement for the same.
- Foreigners were to submit the certificate regarding the surrogacy policy of their country of origin and an undertaking that the child born through surrogacy will be entitled for the citizenship of their country.
- Foreigners were also to provide local guardian for the gestating period of the surrogate.
- ART banks certified by the government were to maintain the record of the potential surrogates along with storing of sperm and eggs and particulars of the donor.
- The private and government ART banks were to be recognized by the state boards. The Board will have the authority to register and record a list of all the IVF clinics along with monitoring their functioning.

The new Visa Rules of 2012 issued by Ministry of Home Affairs specified a number of conditions together with ban on issuing of medical visa for single, unmarried couples, gay and lesbians for commissioning surrogacy in India.

**In 2013** further modifications were done in Assisted Reproductive Technology Regulation Bill to accommodate the suggestions of different Ministries and departments.

#### In 2014

- Homosexuals and single parents were ban from availing surrogacy services in India.
- Commercial surrogacy was banned except for overseas citizens of India (OCI's), people of Indian Origin (PIO's), Non Residencial Indians (NRI's) and even foreigners married to Indian citizen.
- Intended parents were to submit a certificate declaring that the child born through surrogacy is their genetic child.
- It was declared mandatory for Intended parents to accept the custody of the child irrespective of any abnormality.
- Married woman, single woman and divorced woman were allowed to act as surrogate.

- A woman could act as surrogate only once in her lifetime and there should be a gap of two years within the live births.
- A child born through Indian egg or sperm donation was not to be entitled for the citizenship rights.
- The Supreme Court was criticized for their failure to regulate surrogacy practice.

The Bill contained details of all ART clinics and ART banks, nature and type of services etc. The govt. however ignored this and the other recommendations<sup>3</sup>, <sup>4</sup>.

# Surrogacy (Regulation) Bill 2016

The Surrogacy Regulation Bill was finalized by the panel headed by External Minister Sushma Swaraj and had received its clearance by the cabinet. The bill had proposed radical changes from the situation where it was a booming business under medical tourism to banning of commercial surrogacy altogether. The 228th report of Law Commission of India also recommended prohibiting commercial surrogacy and allowing altruistic surrogacy to the Indian citizen through proper legal bindings.

The regulation was streamlined through establishing National Surrogacy Board at the Central Level and State Surrogacy Boards at state level along with Appropriate Authorities at Union Territories.

#### The important features of the Bill were as follows:

- Legally wedded Indian couple who have been married at least for five years with either of them with proven history of fertility or related issues.
- The age of husband must be 26 to 55 and the wife's age must be between 23 to 50 years of age.
- Registration of Art Clinic is mandatory.

<sup>&</sup>lt;sup>3</sup> <u>http://blog.indiansurrogacylaw.com/wp-content/uploads/2014/10/Surrogacy-Bill-2014.pdf</u>

https://www.prsindia.org/uploads/media/draft/Draft%20Assisted%20Reproductive%20Technology%20(Regulation)%20Bill,%202014.pdf

- Complete ban on commercial surrogacy. Clinic can charge for rendering their services bur under no circumstances a surrogate mother can be paid except the medical expenses.
- Overseas Indians, foreigners, unmarried couples, single parents, live-in-partners and gay couples are barred from commissioning surrogacy.
- Only close relatives can offer surrogacy services to the eligible couple.
- The surrogate should be married with her own children and can act as a surrogate only once in her life time.
- Undertaking of commercial surrogacy, abandoning the surrogate child, exploitation of surrogate mother, selling and import of human embryo have all been categorized as violation and shall be punishable with imprisonment for a term not less than 10 years and a fine up to 10 lakh.
- All the clinics will have to maintain their records for a minimum period of 25 years.
- The surrogate child will have the same rights of as that of a biological child.
- It also made illegal for medical practitioners to employ procedures that hurts the surrogate mother and the baby's physical and mental health<sup>5</sup>,

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<sup>6</sup>http://www.thehansindia.com/posts/index/Hans-Classroom/2016-10-07/New-SurrogacyBill-2016/257578

<sup>7</sup> http://www.sify.com/news/motherhood-and-morality-india-debates-the-surrogacy-bill-newscolumns-qi3llOejbhijg.

<sup>8</sup>https://www.indiatoday.in/education-today/gk-current-affairs/story/surrogacy-bill-337358-2016-08-26

<sup>9</sup> Ravi Malavika- 31<sup>st</sup> August 2016- https://feminisminindia.com/2016/08/31/critical-analysissurrogacy-regulation-bill-2016/

<sup>&</sup>lt;sup>5</sup>https://www.prsindia.org/uploads/media/Surrogacy/Surrogacy%20(Regulation)%20Bill,%20201 6.pdf

# The Surrogacy (Regulation) Bill 2019

The Bill seeks to ban commercial surrogacy in our country. It provides for constitution of surrogacy board at state and national level and to regulate non atonement of the child by the intended parents under any circumstances.

- The Bill prohibits commercial surrogacy but allows for altruistic surrogacy.
- It prohibits live-in-partners, homosexuals, foreigners and single parents from using surrogacy service.
- The National Surrogacy Board (NSB) and the State Surrogacy Boards (SSB) should be constituted respectively.
- Only surrogacy clinics registered under the Surrogacy (Regulation) Act, 2019 will be able to perform procedures related to surrogacy.
- A married woman between the ages of 25 and 35 who has a child of her own can be a surrogate or can help in surrogacy by donating her egg.
- The surrogate mother needs to be a close relative of the intending couple and can become a surrogate only once in her lifetime
- A woman cannot become a surrogate mother by providing her own gametes (unfertilised eggs).
- The intending couple should have a 'certificate of essentiality' mentioning that either or both members of the couple suffer from infertility and a 'certificate of eligibility' to proof that the couple has been married for at least five years issued by the appropriate authority.
- The couple should be Indian citizens and married for at least five years
- The age of the wife must be in the age group of 23-50, and the age of the husband in the age group of 26-55.
- They should not have any surviving child (biological, adopted or surrogate)
- Insurance coverage for a period of 16 months covering postpartum delivery complications should be provided for the surrogate.

- A child born out of a surrogacy procedure will be deemed to be *the biological child of the intending couple*
- An abortion of the surrogate child requires the written consent of the surrogate mother and the authorization of the appropriate authority
- Abandoning, exploiting or disowning a surrogate child will be induced with penalty such as imprisonment up to 10 years and a fine up to 10 lakh rupees<sup>10,11</sup>.

# Criticism

A critical evaluation of these guidelines needs to be undertaken to understand the reality.

In the light of the government initiatives like the Artificial Reproductive Technology which is in practice today, it throws lights on the critical facts like absence of documentation of the procedure, no standardization of the drugs used, insufficient information for patients about the side-effects of the drugs used, and no limits to the number of times a woman may be asked to go through the surrogacy procedure. The agents along with doctors do not disclose the fact that a successful cycle need not lead to a baby being born.

The process of regulating ART began in 1999 in India. Commercial surrogacy was legalized in India in the year 2002 but there were no guidelines then. The National Guidelines for the Accreditation, Supervision and Regulation of ART Clinics in India was approved in 2005. The bill promoted medical tourism and took steps to regulate surrogacy for growing number of intended parents from abroad. The issue of increasing number of women becoming donor is not taken care off. However the bill was viewed as a positive move towards regulating the surrogacy business since there were no legal bindings the rules were not implemented strictly.

A close inspection of the **ART Bill, 2008** which draws from the **ICMR guidelines of 2005** which was propagated in regulating surrogacy and protecting the intended parents from unethical

<sup>&</sup>lt;sup>10</sup> https://www.insightsonindia.com/2019/08/06/surrogacy-regulation-bill-2019/

<sup>&</sup>lt;sup>11</sup> https://indianexpress.com/article/explained/explained-key-provisions-of-the-bill-to-regulatesurrogacy-5896417/ retrieved on 29<sup>th</sup> October 2019)

practices involved in the process exhibits it did not play any role in protecting the surrogates from the risks and the dangers of these reproductive technologies. The guidelines of ICMR had specified no norms relating to the conduct of doctors and the medical support staff in terms of entering into financial transactions with prospective surrogate couples.

The need to regulate surrogacy was realized in the wake controversies arising out of Baby Manji's birth in the year 2008. The intended parents from Japan avail the surrogacy services in India but got divorced before the birth of the baby. The mother refused to accept the child and the father was denied the custody on the account that he couldn't adopt the child legally as the Indian law did not approve of single man's adoption. Finally the custody was given to the paternal grandmother of the baby by the Supreme Court of India. Thus the need to legalize and regulate surrogacy was desperately felt<sup>12</sup>.

In an another inconsistent case of surrogacy opted by German couple as the German law did not recognize the validity of surrogacy agreement to accept parenthood, nationality and citizenship issues. Consequently it did not allow the children to be German citizens. Thus the twins were rendered stateless and parentless<sup>13</sup>. To avoid the foreseeable legal hurdle of immigration process, the couple approached the Gujarat High Court for permitting their surrogate children to carry Indian passport.

Indian courts have been known for not dealing comprehensively with the cases and often kept leaving the task for legislature.

The 228<sup>th</sup> report of Law Commission in 2009 brought focus on the exploitative nature of surrogacy and thus pleaded for legalization and regulation of surrogacy in India. It also recommended to prohibit commercial surrogacy and permit for altruistic surrogacy for Indian nationals only.

<sup>&</sup>lt;sup>12</sup><u>http://www.indiacourts.in/Baby-Manji-Yamada-vs-union</u> 0f India-ANR\_3bc98bbb-8224-442c-90b9-7d1531137762

<sup>&</sup>lt;sup>13</sup> <u>https://writingsurrogacy.wordpress.com/tag/jan-balaz-vs-anand-muncipality/</u>

In 2010 a gay couple, Dan Goldberg and Arnon Angel from Israel were stranded for over three months to carry their twins born to a surrogate in Mumbai as they were refused paternal test by the Jerusalem Family Court to initiate citizenship process. Goldberg and his twin baby boys returned to Israel in May 2010 after being granted Israel passports<sup>14</sup>.

**The 2010 ART bill** didn't become law due to numerous short comings. The bill permitted surrogacy for single parents but restricted the foreigners and homosexuals. The surrogate's rights had not been taken care off in the bill. Due to absence of law there were numerous cases of exploitation of surrogates.

In **2012** the **draft** banned only those foreigners from hiring surrogacy services whose country of origin didn't recognized commercial surrogacy. The ban on commercial surrogacy paved its way to springing of surrogacy hubs in other neighboring south Asian nations like Nepal, Thailand, Vietnam and Cambodia. The 2013 ban on "gay surrogacy" witnessed shifting of all such cases to Nepal. With tightening of law, the surrogates were persuaded by the clinics to go to Nepal for delivery and earn extra amount of 50 thousand. Many clinics also shifted their complete operations to Nepal by setting a base. More than a dozen of Indian and Thai clinics were already operating there. Since Nepal had no law by than except that the surrogate shouldn't be a Nepali citizen the open border policy of two countries facilitated the process smoothly. Thus it emerged as an offshore surrogacy hub where the impregnate surrogates were smuggled from India for the purpose of deliveries.

The Draft Assisted Reproduction Technology (Regulation ) Bill, 2014 aimed at regulating the mushrooming ART business and addressed various ethical and social issues. The bill as the title suggests should had regulated the ART industry and safeguard the interest of stakeholders involved in the process. However a close observation of the Bill suggests that that it was more inclined towards promoting the interest of the private practitioners and service providers and failed in its duty to protect the safety and the well being of the surrogates and the children born.

<sup>&</sup>lt;sup>14</sup> <u>http://archive.indianexpress.com/news/israeli-gay-couple-to-take-surrogate-twins-</u> home/624650/questionnaires

Thus the bill built a capitalist approach to the whole concept of ART rather than a well-being approach<sup>15</sup>.

In **2015** the surrogacy got banned for foreign nationals. Since then it has been surrounded by more controversies and is being debated on various ethical and moral grounds. The dark reality came into headlines soon after the outbreak of massive earthquake in Nepal in April 2015 when the Indian surrogates were stranded and the Israeli intended fathers along with their surrogate babies were airlifted abandoning the surrogates behind in the quake affected country. But as Pandey<sup>16</sup> rightly mentioned that media failed to report that that the surrogates were stucked in Kathmandu due to the ban which pushed them outside their country to earn their living. The ban resulted in underground operations through shifting its base which made surrogates more vulnerable.

In the aftermath of earthquake, the Nepali cabinet gave a serious thought to the issue and by September 2015 surrogacy was declared illegal in Nepal<sup>17</sup>. When the governments ban people find other destinations to continue and in fact it makes surrogates more vulnerable in third world country. The ban in India and Nepal shifted the intended parents to far riskier places like Cambodia where there is serious lack of medical facilities. On November 3<sup>rd</sup> 2016 the government of Cambodia absolutely banned the surrogacy<sup>18</sup>.

<sup>16</sup> Pande, Amrita. (2016). Is the prohibitory approach, adopted by the Surrogacy (Regulation) Bill 2016, really the best way to protect the rights of surrogates and their children in India?http://himalmag.com/surrogacy-bill-india-women-rights-labour/--Surrogacy Bill's issteps-

<sup>17</sup> Hodge Sarah and Rao Mohan. (2016). Public Health and Private Wealth; Stem Cells, Surrogates, and Other Strategic Bodies.Oxford University Press.

<sup>18</sup><u>http://www.theatlantic.com/health/archive/2016/05/dwindling-options-for-surrogacy-abroad/484688/</u>

<sup>&</sup>lt;sup>15</sup> http://racolblegal.com/A Critical Analysis of the Draft Assisted Reproductive Technologies (Regulation) Bill and Rules, 2014

The ban of surrogacy in India, Nepal, Bangkok, Thailand and other parts of the globe triggered the unregulated baby business in Cambodia. After the Southeast Asian countries restricted the foreigners from carrying surrogacy in their country following various legal battles, exploitation of the surrogate and the scandals surrounding it a large number of surrogacy centers started sprawling in Cambodia. The availability of cheap medical facility and no law except guy and single parent led to emerging of Combodia as an attraction for Medical Tourism from the year 2015 onwards. But the base at Cambodia had its own concern as they were not well equipped with their medical infrastructure to deal with huge pressure. The clinics were set up in Cambodia and the surrogates were from India and Thailand.

Some Doctors preferred Ukraine over Cambodia as the laws there were better defined. It didn't affect the business in India as a large number of clinics continue their operation in association with Ukraine based infertility clinics. The experience and the expertise of the doctors still attract the foreigners who facilitate it with their tie up in other country with extra cost<sup>19</sup>.

The **2016 bill** instead of providing regulation led to ban on surrogacy. The bill excluded the widowed, the divorced, single parents, couples in live-in-relationships and even LGBT+ community. But by the time bill got passed we already witness Bollywood icons like Karan Johar and Tushar Kapoor fulfilling their dream of single parenthood. The bill failed at tackling larger social, psychological, emotional and economic issues that continue to affect the well being of the surrogate mother and the child.It is the basic fundamental right and allows everyone to have their legal biological child. Not allowing unmarried and singles the assistance of surrogacy is pure prejudice against them<sup>20</sup>. By shifting it from commercial to altruism will have its own consequences such as exploitation of surrogate by the family member and also it would be

<sup>20</sup> 'Surrogacy Bill violation of privacy rights'http://www.thehindu.com/news/national/%E2%80%98Surrogacy-Bill-violative-ofprivacy-rights%E2%80%99/article16437493.ece

<sup>&</sup>lt;sup>19</sup> Bhowmick, Nilanjana. (2016). "After Nepal, Indian surrogacy clinics move to Cambodia". http://www.aljazeera.com/indepth/features/2016/06/nepal-indian-surrogacy-clinics-move-cambodia-160614112517994.html.

difficult to find a family member who will agree to provide her services for pure altruistic reason. Indeed commercial surrogacy may not be exploitative; it required stringent regulation rather a ban. Putting a ban may not solve the issue as in the country like India where we are still striving for gender equality; even altruistic surrogacy can put the surrogates at the higher risk of exploitation. Just removing the commercial aspect will not do away the chances of exploitation<sup>21</sup>.

**The 2019 bill** has ignored the suggestions of ICMR guidelines for regulating ART clinics and thus there is a serious doubt whether it will be successful in achieving its goal. The bill got passed in Lok Sabha and now Rajya Sabha proposed to send it to the same parliamentary panel again.

Limiting the surrogates to be close relative will cause an acute dearth and unavailability of the surrogate and will in no way curb the exploitation of the women. Altruistic surrogacy may lead to unwanted pressure on women in the family to act as surrogate.

Limiting the eligibility to five years to avail surrogacy is not in harmony with one year period defined by WHO and the ART Bill of 2014. This may reduce the hope of parenthood for many.

There is no justification behind curtailing the compensation for surrogate mother who will undergo the hardship for the period of gestation. It has overlooked various ethical concerns and fails to explain which type of surrogacy will be suitable or obstruct the autonomy of the potential surrogates<sup>22</sup>.

There is no provision for medical facilities after birth. It doesn't take into account the long term medical problem which may arise for e.g. post-partum depression or any other physical, emotional, mental and psychological implications<sup>23</sup>.

<sup>&</sup>lt;sup>21</sup> Saxena, Saumya. (2016). Exposition of Surrogacy Rules in India: criticism of the Surrogacy Bill,2016, <u>http://blog.ipleaders.in/surrogacy-rules-in -india/</u>

<sup>&</sup>lt;sup>22</sup> Shukla, Spriha (2018); The Surrogacy Bill: A much-needed reform that fails the test-Dec 2018; www.orfonline.org

<sup>&</sup>lt;sup>23</sup> http://thewire.in/64656/why-the-government-needs-to-rethink-the-surrogacy-bill

The ban on commercial surrogacy for gay couple in 2012 got extended to ban of surrogacy for everyone except 'Alturistic surrogacy' where a female close relative or family member agrees to carry a child for an Indian heterosexual couple.

## Conclusion

The review of the above bills and guidelines make it clear that it is extremely necessary to regulate the surrogacy practices in the country to prevent the unethical practices prevailing under it and also to stop the exploitation of the surrogates. Also it is pertinent to make legal provisions bendable so that ART can be used positively rather than being operated under the shades of unethical practices as our practitioners have already established their base in neighboring countries. Imposing a complete ban may not serve the purpose as many genuine couples will be deprived from fulfilling their dream of parenthood.