Project report
(BSCC3151)

On

Development of wheat straw derived zeolites for bioremediation of oil

Submitted in partial fulfilment of the Requirement for the degree of B.Sc. (Hons.) Chemistry

Submitted by

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19SBAS1020003

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CERTIFICATE

This is to certify that the Project entitled "**DEVELOPMENT OF WHEAT STRAW DERIVED ZEOLITES FOR BIOREMEDIATION OF OIL**" submitted in partial fulfilment for the award of the Degree of **BSc. (CHEMISTRY)** from GALGOTIAS UNIVERSITY, GREATER NOIDA, is a record of research work carried out by **MS. MANISHA** under my guidance and supervision.

All the help and assistance received during the course of this investigation have been duly acknowledged.

Tripti Bhatnagar

Dated : 31/05/2022
Place : Noida
No : CBPL2022/108

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CERTIFICATE

This is to Certify that **Ms. Manisha** has carried out her project work entitled "Development of wheat straw derived Zeolites for Bioremediation of oil" under my supervision. This work is fit for submission for the award of bachelor degree in Chemistry.

(Signature)	**(Signature)**
Dr. Arvind Kumar Jain	**Dr. Pinki Chakraborty**
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Greater Noida	**Greater Noida**

CANDIDATE DECLARATION

I hereby declare that the dissertation entitled "**Development of wheat straw derived Zeolites for Bioremediation of oil**" submitted by me in partial fulfilment for the degree of B.Sc. (Hons.) in Chemistry to the Division of Chemistry, School of Basic and Applied Sciences, Galgotias University, Greater Noida, Uttar Pradesh, India, is my original work. It has not been submitted to any other Universities for the award of diploma or degree.

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Completing a task is never one-man effort, but it is often result of Invaluable contribution of number of individuals in direct or indirect manner.

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I submit my deep sense of gratitude to Dr. A. K. Jain, Dean, SBAS, Galgotias University and all other faculty members for encouraging me to work with determination and guiding me with my academics.

On a personal note, I have no words to express my abundant inexplicable affectionate gratitude to my parent for their catalytic role and all my loved ones whose patience and support has been an invaluable source of strength.

Manisha

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List of Abbreviations

S.No.	Abbreviations	Full form
1.	RHA	Rice Husk Ash
2.	WHA	Wheat Husk Ash
3.	CFA	Coal fly ash
4.	PAC	Post Activated Carbon
5	GAC	Granular Activated Carbon

Abstract

The rapid growth of industrialization and the ever-emerging new technologies have increased concerns about innovative emerging ideas of waste utilization and cost reduction. One of the ways is in the industrial sector to utilize & process rice husk, wheat husk or straw (lignocellulosic biomass) for production of a useful cost-effective material like zeolite. Zeolite is a superb adsorbent material which has been synthesized from inorganic as well as organic waste such as natural clay, fly ash, wheat husk ash, bagasse, rice husk, etc. Zeolites have great commercial value and thus in the present project zeolite have been synthesized from lignocellulosic waste like wheat straw and rice husk since these wastes are widely available and inexpensive. In this research optimization of zeolites production was done using different acids & bases. The zeolites thus produced were then analyzed for their oil bioremediation properties. The results showed that zeolites adsorbed different kinds of oil in a very efficient and effective way.

Key words = Zeolite, Rice Husk, Wheat straw, Lignocellulosic waste, Bioremediation

1.0 INTRODUCTION

Zeolite comes from the Greek word which refers to minerals that absorb water on heating [1]. Zeolites have crystalline structure made up of silica, aluminium and oxygen. They form a 3D cage like structure with cavities or channels whereby alkali/alkali earth metals and water molecules reside. They are also known as molecular sieves due to their similar pore size structure. According to researchers, rice husk (RHA) contains 90-99% silicon dioxide, which may be an inexpensive supply for a few industries to use as a stuff [2-4]. Zeolites are found naturally and can also be synthesize in laboratories. Natural zeolite like chabazite, phillibite, stilbite, natrolite etc. are non- porous and are mainly found in volcanic origin and in sedimentary rocks origin. $M_{2/n}:Al_2O_3:xSiO_2:YH_2O$, is the general of zeolite where M stands for the metal ion layered framework. In reference to US geological survey, there are almost 40 types of zeolites of sedimentary and volcanic origin. Synthetic zeolites are designed by scientists for specific purposes for example ZSM (petroleum catalyst), Zeolite A (for laundry and detergents purposes) etc. Synthetic zeolites are porous and have high exchange capacity than natural zeolites

poses for example ZSM (petroleum catalyst), Zeolite A (for laundry and detergents purposes) etc. Because of their layered porous structure, zeolites have a wide range of applications: charged alkali and alkali earth monovalent (i.e., Na^+, K^+, etc.) and divalent ion (i.e., Ca^{2+}) and (OH) groups. The Si/Al quantitative relationship in zeolites controls their action capability and attraction of cations that live at intervals between their channels and pores because these molecules are easily modified by cations and molecules from their environment. Husk materials release a large amount of silica and therefore can be viewed as a potential alternative source of silica. [5]. There is a good vary of potential mineral structure because the network is extended in 3 dimensions based on AlO_4 and SiO_4 tetrahedral that may share 1,2, or 3gas atoms every.

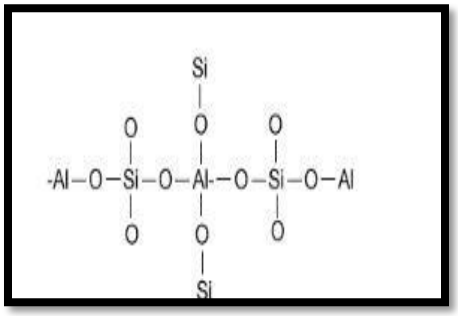


Fig: 1 Basic structure of Zeolite. [1]

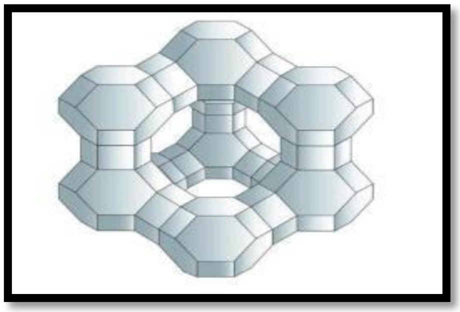


Fig: 2 Crystalline structure of Zeolite [1]

Their widely recognized microporous structure results from this specific structural characteristic. Due to their large pores and adsorption characteristics, Zeolites are important ion exchangers with useful applications in a variety of industries as well as waste water treatment plants, animal feed additives, catalysis, nuclear waste, agriculture, and organic chemistry applications. [6].

1.1 <u>Types of Zeolites</u>

All these zeolites have different physical and chemical properties. The easily tunable and flexible structure with diversified chemical composition are the main reasons for the primary differences. Particle density, cation selectivity, molecular pore size are few of the properties that can vary with zeolite. Numerous natural and synthetic zeolites have unique structure and pore sizes from approximately 3 Å to approximately 8 Å. Some of the commercial zeolite types are A, beta, mordenite, Y, ZSM-5.

The main differences between natural and synthetic zeolites are given below

- Most of the synthetic zeolites are produced from energy consuming chemicals and natural zeolites from natural ore found inside the earth crust.
- Two common synthetic zeolites have silica to alumina ratio of 1 : 1 and clinoptilolite (clino) have 5 :1 ratio.
- Unlike synthetic zeolites natural zeolites do not degrade in mildly acid environment. Most commonly, the ‘clino’ zeolite is broadly accepted for use in the agricultural industry, for soil amendment and as food additive.

1.2 <u>Lignocellulosic waste</u>

Lignocellulosic waste refers plants dry matter (Biomass). It is a renewable carbon resource and present in a very large amount on earth. [7] Lignocellulosic waste includes woods, rice and wheat straw sugarcane bagasse etc. Lignocellulosic waste contain a large quantity of silica for example rice husk have 75% silica. Rice, wheat production are widespread. However, it additionally generates a large amount of non- meals biomass, primarily within the kind of husk, straw. Traditionally, it has been treated as a waste and moreover, burning of these contribute to air pollution, creating a public health hazard. Similarly, rice_husk is an abundant agricultural waste used as a fuel in rice processing industries because it is a renewable energy source with efficient energy content of 12–18 MJ kg^{-1} and high transport cost.

Black residue produced from husk materials contain about 15% carbon and the remainder of silica during burning. This review shows an efficient way which reduces the scope of air and water pollution. Moreover, the rice husk can also be used as an alternative source of silicon.

Thus, despite the fact that Rice husk & wheat straw have been mostly ignored and simply burned, these lignocellulosic materials are likely to have significant utility [8] . To synthesize zeolites fly ash is being used. Rice husk ash contains 92-95% silica, wheat husk ash contains 74.28% silica, and silica is used for the preparation of zeolites [9-11]. So, this kind of lignocellulosic waste is an excellent source of silica the synthesis of zeolites. This process can be cost effective and helps us to minimize the problem of organic waste disposal.

Every year million of tons of lignocellulosic waste are generated by forestry and agricultural practices in India. Investigations are made to synthesize zeolite from waste materials which have high content of silica for example sludge of paper industry waste, lignocellulosic waste etc. Obtaining silica from lignocellulosic waste for zeolite production is a great achievement because it is renewable resource, cost effective and can be available at world wide and at low cost.

Fig: 3 (Lignocellulosic waste) [11]

1.3 Bioremediation

Bioremediation is a combination of the two words "bio", meaning to live and remediation means solve a problem. Bio carriers have been developed to immobilize natural hydrocarbon-degrading microorganism the usage of porous substances which includes activated carbon and zeolites to facilitate crude oil clean up. The outstanding physical and chemical properties of these materials makes them extraordinarily helpful in a very type of agricultural, environmental, manufacturing and industrial processes.

In situ and ex situ are the two basic methods of bioremediation.[12] In situ Bioremediation uses a biological system to treat contaminants in the same location. Ex situ bioremediation treats contaminants in a different location than the original site. Factors that influence bioremediation are nutrient availability, pH, temperature, and moisture content.

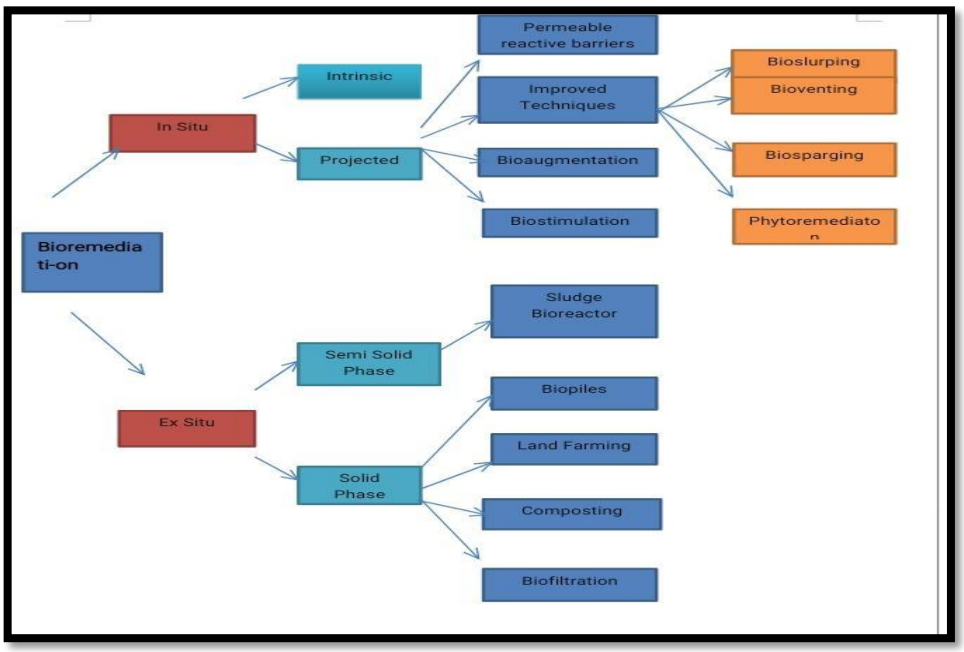


Fig : 4 (Different bioremediation strategies) [12]

Zeolites are crystalline hydrous physical and chemical properties that act as molecular sieves, replacement the constituent cations with loss and adsorption of water and other molecules without changing the structures. Oil recovery from crude oil due to petrochemical products and soil pollution has become a major problem worldwide. Bioremediation is generally recognized as a cost-effective option when comparing available removal techniques.

The layered structure also provides adsorption property which helps in physical adhesion of the polluting chemicals onto a solid surface. A wide range of materials used for water remediation include activated carbon, bentonite, peat, sand, coal, fiberglass, polypropylene, amberlite, organoclay, and attapulgite [13]. Remediation technology for petroleum hydrocarbon contaminated ground water by the use of activated carbon has been compared and the results reveal that PAC as better effective remediation power than GAC (granular activated carbon) and therefore its use is recommended [14-15] .

2.0 LITERATURE REVIEW

Zeolites are very important for many industrial, environmental and agricultural practices. Zeolites are hydrated alum inosilicates and are found naturally and can also be synthesized in laboratories for different approaches. Till date approximately 200 zeolites are synthesized in laboratories by slow crystallization method and new methods are found to synthesize zeolites which are cost effective and raw material can easily available to achieve this approach researchers are found source of silica from agriculture or plants. There are millions of tons agricultural waste which have no use are burnt every year which cause air pollution, global warming etc. Use of both rice and wheat husk ash has been explicitly reviewed and their uses in construction, catalysis, medical, food and agriculture have been documented systematically in this review.

Bioremediation is the process of cleaning contaminated areas with living organisms. Microorganisms and plants. Use of organisms for conversion and reduction Converting pollutants to non-toxic substances is an environmentally friendly process that does this. Do not adversely affect the environment or living things. Bioremediation is the best applications of zeolite synthesis. This is a more environmentally friendly approach.

Presence of silica in agricultural waste material

- ### Rice husk as a source of silica

Rice husks are a by-product of the rice milling and amount for 20% of the total weight of rice. Rice husks' most important inorganic component is silica. . Upon extraction, inhalation can cause severe respiratory illness . Therefore, it is important to recover and recycle high quality materials as they can not only extract promising resources but also be very beneficial to the environment. Rice husks are high in silica and can be used to make many products that use silica .[16-17]

- ### Wheat straw as a source of silica

Wheat husk is a most common agricultural waste that contains silica in a sufficient amount. The wheat straw ash treated with sodium hydroxide and heat at 320 ^{0} C for 1 hour then acidified by carbon dioxide or sulphur dioxide. The sample were termed as Ash silica CO_2 and Ash silica SO_2 according to their treatment process.

- **Use of lignocellulosic waste for biofuel and chemical production**

Lignocellulosic biomass is one of the most appealing renewable resources for manufacturing biofuels and chemicals. The low conversion rate and poor selectivity to desired items, on the other hand, remain issues [18]. As a result, scientists have recently concentrated their efforts on developing heterogeneous catalysts for the thermochemical conversion of such material. The technology presented here can create both bio-oil and hydrogen-rich gas. The mesoporous, metal oxide, and supported metal catalyst architectures of zeolite are discussed in connection to their catalytic performance in the processes indicated.

- **Synthesis of zeolite from clay and fly ash**

The climate friendly zeolites is a mineral manufactured from inorganic waste such as clay ,fly ash, rice husk ash [19] .CFA(coal fly ash) a by-product is produced in industries as a large amount of solid wastes. It contains polycyclic aromatic hydrocarbons, silica heavy metal and other toxic substances.[20] . CFA pollute , land , air and also very hazardous. Hence CFA can be used for the synthesis of zeolite.

Fig : 5 (Zeolites synthesis)[19]

- **Presence of silica in agricultural waste materials**

Silica found in agricultural waste rice husk , wheat husk are the agricultural wastes that contains, silica which is used to synthesize zeolites. The percentage of silica varies between 98- 36% [21]. Agriculture waste are very effective source of silica because they are environmental friendly as well as cost effective.

3.0 Material and Methods

3.1 Preparation of phosphate buffer

Materials used

Salts Used: Na_2HPO_4, $Na_2H_2PO_4$, distilled water, weighing balance , beakers etc.

Procedure

For phosphate buffer preparation, at first 50 ml of 0.1 M solutions of both the Acid and base salts (NaH_2PO_4 & Na_2HPO_4) resp. were made i.e. 0.78 gm & 0.71gm were weighed resp. Then then the pH meter with electrode instrument was used. At first, with the standard, the pH was calibrated then the base solution is taken and pH meter electrode was dipped in it and then the acid was added to the base solution drop-wise and the reading was observed for pH. When the required pH of 7 is reached, mixing was stopped and the buffer was prepared that can be used or stored for future experiments.

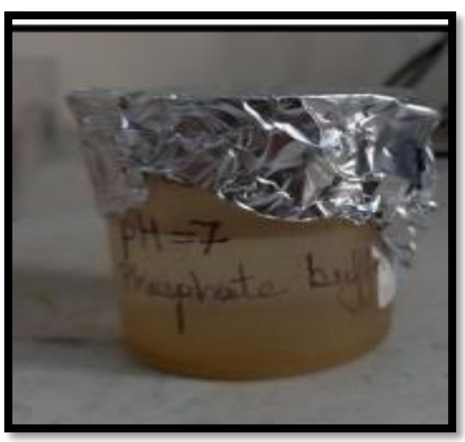


Fig: 6 (Phosphate buffer having pH of 7)

3.2 Preparation of zeolite

Experimental plan

The research work will be divided into three stages.

STAGE 1

Preparation of Ash from lignocellulosic wastes

The first stage involved the preliminary studies of the lignocellulosic wastes Which include the physical examination of the samples, collection of samples and burning of samples to ash.

1. Wheat straw
2. Rice Husk

STAGE 2

Silica prepared from ash material

Different lignocellulosic waste ash were taken and were treated NaOH, KOH, HCl, H_2SO_4 for conversion to Silica .

10g of the ash was placed in a round bottom flask (250ml).Take 3N NaOH in 1:7 ratio i.e. 12g NaOH and 100ml distilled water pour the NaOH solution into the round bottom flask containing the ash sample. Gently heat the mixture at 80-90^{0}C for 30minutes .Remove the sample from the heating mantle and allow it cool at room temperature. The sample was filtered using what man filter paper to remove the unburned carbon impurities. Clean filtrate solution obtained is a mixture of sodium silicate solution $SiO_2 + NaO \rightarrow Na_2SiO_3 + H_2O$.

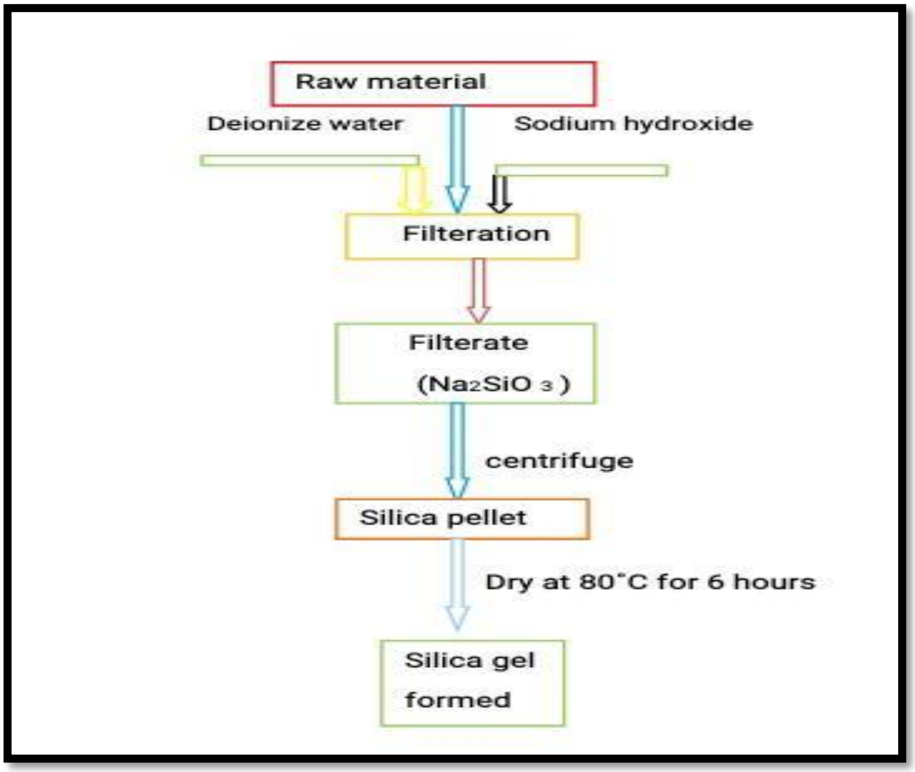


Fig : 7 (Flowchart – Extraction of silica from lignocellulosic waste)

The solution is further concentrated in over for 90minutes at 100-150^{0}c. The final concentrated solution is a gelatinous sodium silicate and its quantity is measured by using weighing balance. The concentrated solution was then placed in 200ml beaker and 12N concentrated sulphuric acid was added to the solution until the solution become acidic pH 3-4. Silica is separated out from the solution and sodium sulphate is obtained as a byproduct. Little amount of distilled water was added to reduce the high exothermic temperature of 85^{0}C and the solution is kept for 30 minutes. $Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O$. The silica gel formed is aged for over night. 50ml of distilled water was added to the silica formed and then placed Into (rubber) and centrifuge for 15minutes at 3000 rpm. After centrifuging the supernatant is discarded and the gel is transferred Into beaker and dried at 80^0 for6hours. Silica product is obtained and percentage yield is measured.

STAGE 3

Zeolites from silica

Separately in two beakers, 6.6g of sodium hydroxide (NaOH)was dissolved in 55ml distilled water and 8.0 g SiO_2 was dissolved in 55ml distilled water. The NaOH solution is to be added to SiO_2 solution along with constant stirring until a clear solution is obtained (solution A).

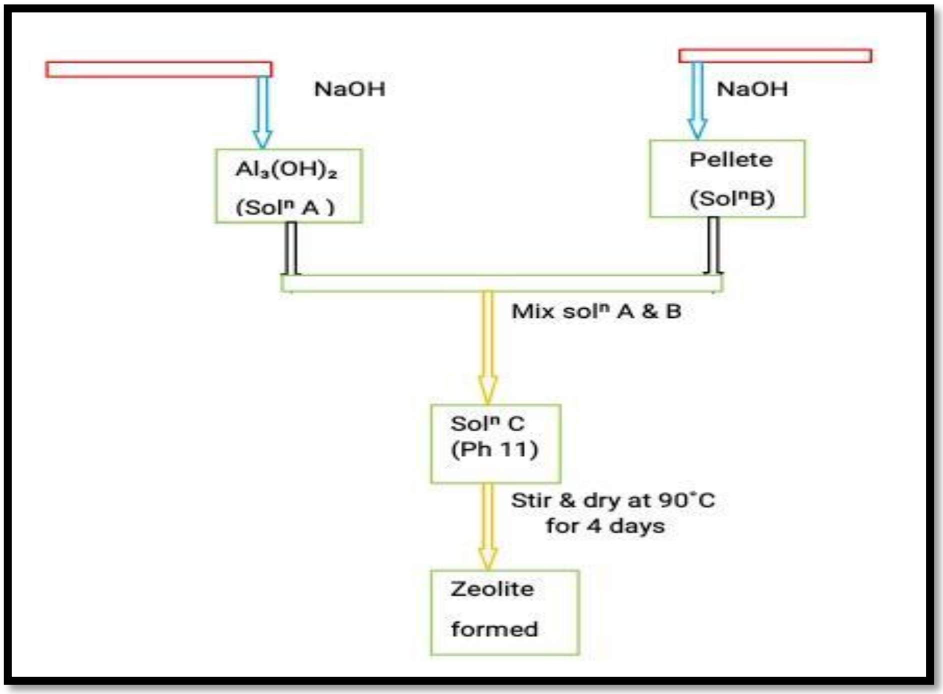
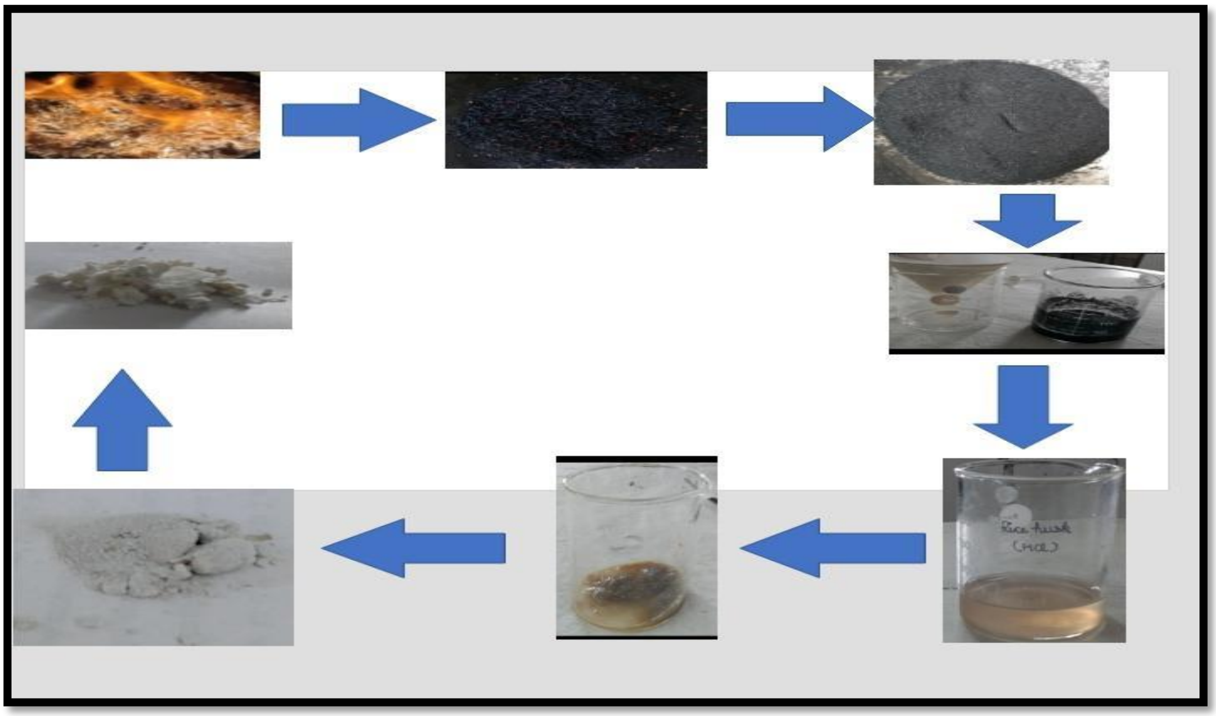


Fig: 8 (Flowchart- Synthesis of Zeolite from silica)

6.6g NaOH solution and 3.3g $Al_2(OH)_3$ solution were prepared in 55ml distilled water. Added the NaOH solution to $Al_2(OH)_3$ solution and stirred until a clear solution Is obtained (solution B). Solution A and solution B were added together and pH was adjusted to 11 using pH meter and the solution was stirred for 1hour at room temperature using electric stirrer. The solution was kept at 90^0C for 4days.The solid material/powder obtained was washed again using distilled water to reduce the pH to 8 and finally the sample is dried in oven for 6 hours at 100^0c. The final product formed is zeolite.

Burning of husk Ash Filtration



Silica and zeolite Concentrated sodium silicate

Fig : 9 (Preparation of zeolite)

<u>STAGE 4</u>

<u>Bioremediation of oil using zeolite</u>

Take a pre – weighted falcon tube . Add 1ml engine oil , waste oil . Then add 0.5 g of zeolite crystals and keep in Incubation for 24 – 48 hrs. After incubation centrifuge the tube (remove pellet having zeolite. And take the weight of zeolite. Put the whole liquid in a glass petri plate that has been pre-weighted . Take weight of oil residues.

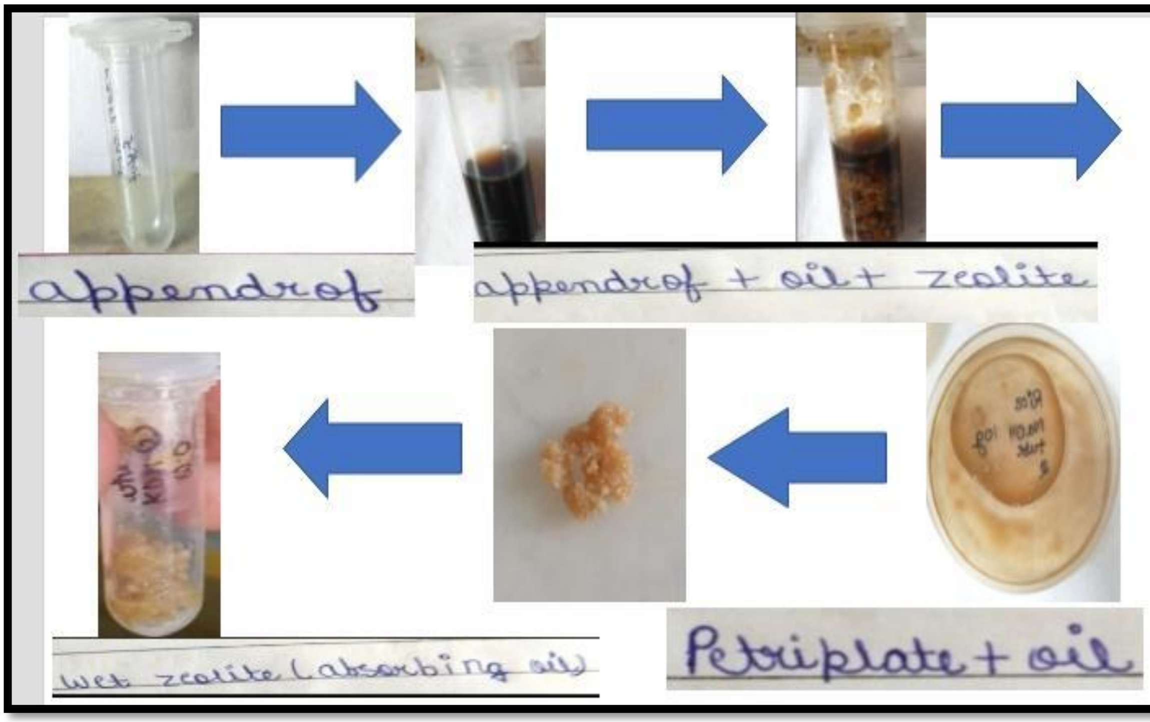


Fig : 10 (Bioremediation of oil)

4.0 Result and Discussion

The present research project involved the production of Zeolites from lignocellulosic wastes. Initially, the samples of rice husk and wheat straw (Fig.11 and 12) were collected from farmers. The waste was then dried in incubator at 60˚C for 24 hours. After that .they were incinerated separately in an iron utensil and were converted into ash form .

Fig: 11 (Rice Husk)

Fig : 12 (Wheat Husk)

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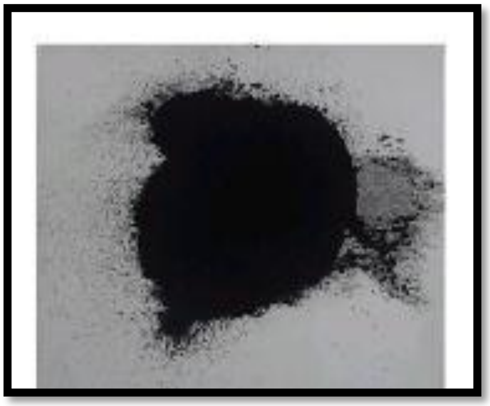

Fig : 13 (Rice Husk Ash)

Fig : 14 (Wheat Husk Ash)

Observation Table:

Table 1: A comparative data of wheat straw ash to Zeolite production

S.No	Use alkali or acid	Use of wheat husk ash	Silica obtained from wheat	Zeolite
1	NaOH	10g	3.0g	12g
2	KOH	10g	3.3g	8.96g
3	HCl	10g	0.21g	3.80g
4	H2SO4	10g	0.28g	5.61g

Table 2: A comparative data of Rice Husk ash to Zeolite production

S.No	Use alkali or acid	Use rice husk ash	Silica obtained from rice	Zeolite
1	NaOH	10g	3.3g	12.74g
2	KOH	10g	5g	12.87g
3	HCl	10g	0.18g	3.28g
4	H2SO4	10g	0.17g	5.14g

The mixture was initially heated and after heating it was filtered. The filtrate again was heated at 100˚C for 90 minutes and after that Sulphuric acid was added till the pH 3-4 of the solution was obtained. The solutions were left over the night. Next day 50ml distilled water was added to each solution and centrifuged for 15 minutes at 3000rpm. After centrifuge, pellet and supernatant layer are separated. Pellet was dried at 80˚C for 6 days. After this silica is obtained.

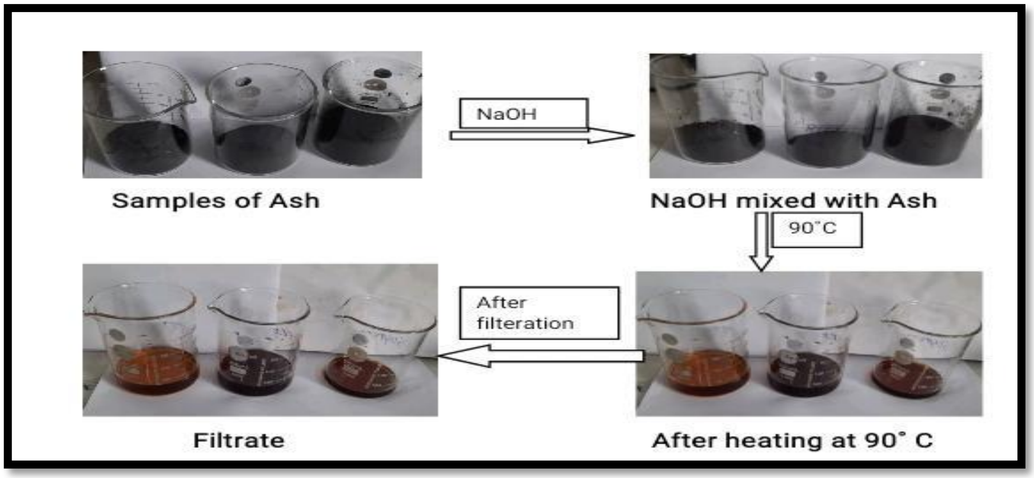

Fig :15 (Process of extraction of silica from ash)

Fig:16 (Silica after dry)

For the next step of zeolite formation, two separate solutions are prepared of Sodium Hydroxide and Aluminum Hydroxide respectively in separate beakers. Both solution A and solution B were mixed with each other to make a “solution C”. Adjustment of the pH 11 of the solution was done by adding Sulphuric acid. This solution was incubated for 4 days at 90^0C. After which final product zeolite is obtained.

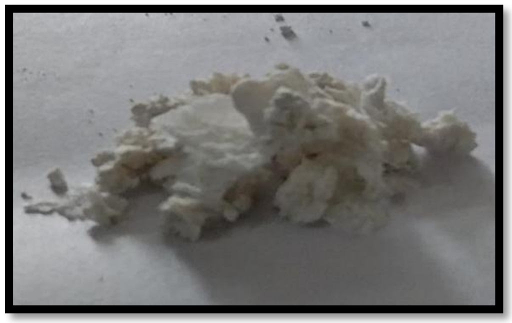

Fig : 17 (Zeolite crystal)

BIOREMEDIATION/ ADSORPTION OF OIL WASTE BY ZEOLITES PRODUCED

The Zeolites thus prepared were then tested for bioremediation of oil. The Zeolites were produced using two different Bases or alkali (KOH and NaOH) and two acids (HCl and H_2SO_4).

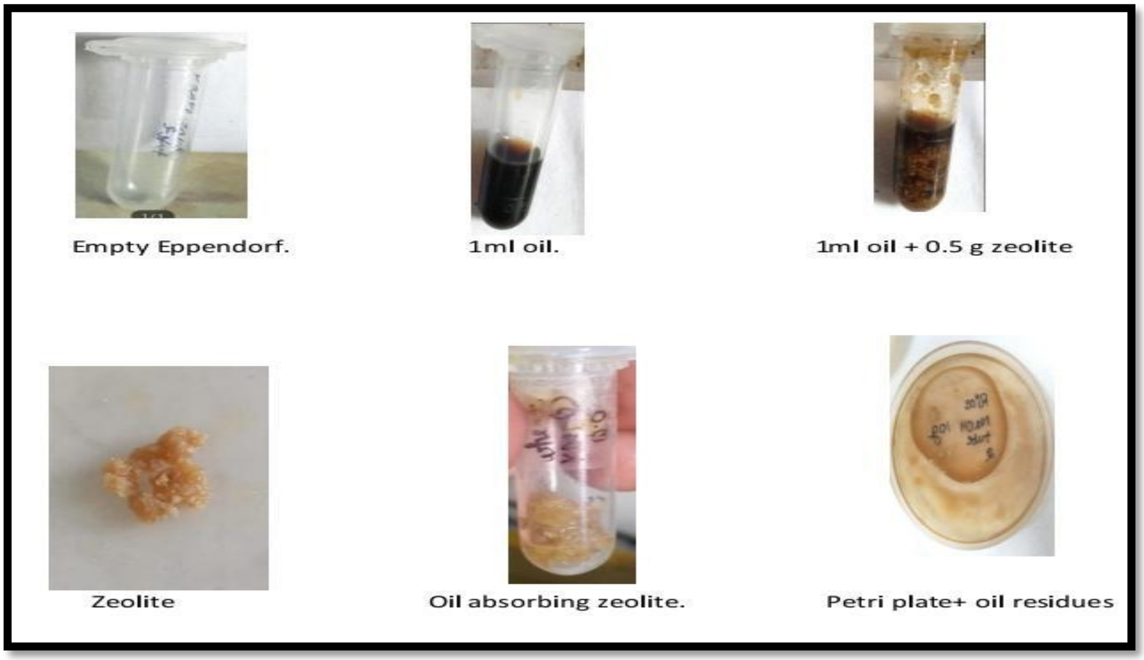

Fig : 18 (Bioremediation of oil (Waste Engine oil)

Adsorption /Bioremediation of waste engine oil by zeolite produced from Wheat straw ash using Sodium hydroxide.

- Weight of empty Eppendorf – 0.91g
- Weight of Eppendorf + 1g engine oil – 1.91g
- Weight of Eppendorf + 1g engine oil+ 0.5 g zeolite – 2.41g
- Keep in incubation for 24-48 hrs. at room temperature.

  After incubation the tube and remove the excess oil by centrifugation and tapping out of the extra oil into a petriplate.

  The zeolite present in the oil bound state was removed after 48 hours from the tube and weighed = 1.04 gm.

Thus, oil adsorbed by the 0.5 gm of zeolites

Initial weight of Zeolite = 0.5g (Z1)

Final weight of Zeolite = 1.04g (Z2)

Therefore, Oil adsorbed = (Z2 – Z1) = (1.04 – 0.5)g = 0.54 g

Thus, Zeolites can adsorb the same amount of engine oil as compared to their weight.

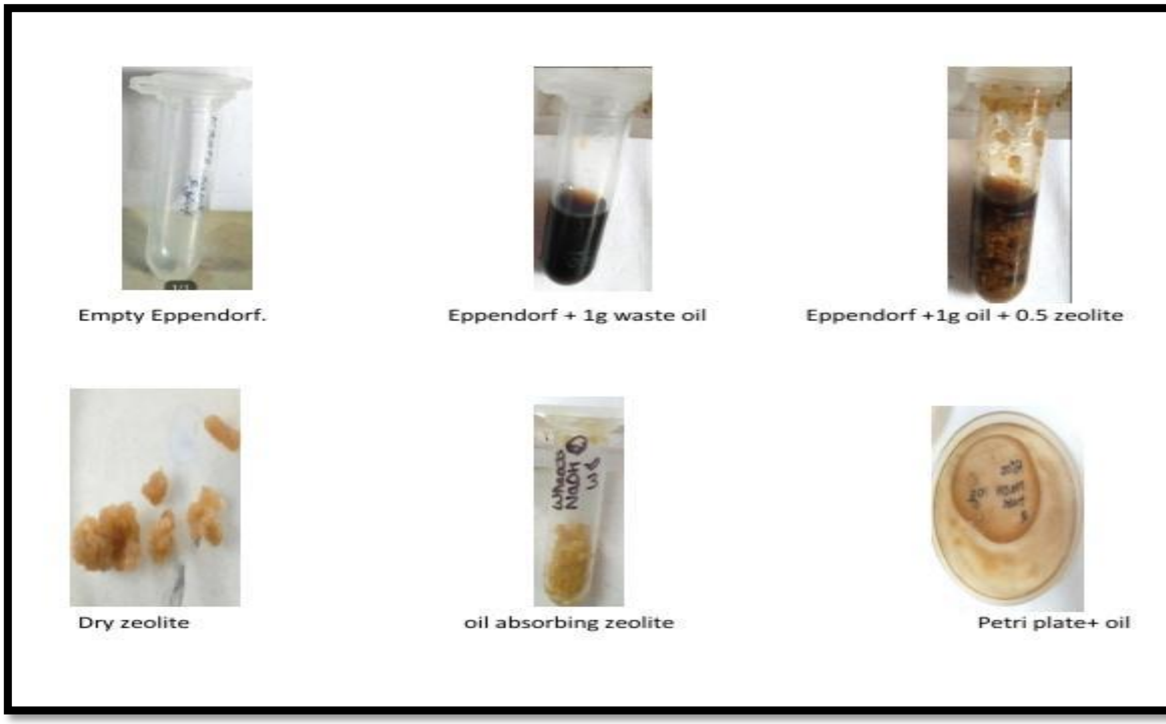

Fig : 19 (Bioremediation/ adsorption of oil (waste cooking oil)

Adsorption /Bioremediation of waste cooking oil by zeolite produced from Wheat straw ash using Sodium hydroxide.

- Weight of empty Eppendorf – 0.91g
- Weight of Eppendorf + 1g engine oil – 1.91g
- Weight of Eppendorf + 1g engine oil+ 0.5 g zeolite – 2.41g
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  The zeolite present in the oil bound state was removed after 48 hours from the tube and weighed = 0.93 gm.

Thus, oil adsorbed by the 0.5 gm of zeolites

Initial weight of Zeolite = 0.5gm (Z1)

Final weight of Zeolite = 0.93 (Z2)

Therefore, Oil adsorbed = Z2 – Z1 = 0.93 – 0.5 =0.43 gm

Thus, Zeolites can adsorb almost similar amount of engine oil as compared to their own weight.

SIMILARLY, all the other zeolites produced from wheat straw ash and rice straw ash using both acids and bases were used to test their Oil adsorbing capacity to analyze and optimize which zeolites would be best utilized for oil bioremediation. The Table 3, given below depicts the weight of oil adsorbed by the different zeolites after 24 hours and 48 hours of incubation. The calculations were done as given above.

S. No.	Treatment used for zeolite production	Weight of waste engine oil adsorbed on the Zeolites produced from Wheat Straw ash (in gm) (Z2-Z1)	
		After 24 hours	After 48 hours
1	Sodium Hydroxide (NaOH)	**0.54**	0.43
2	Potassium Hydroxide (KOH)	0.35	**0.56**
3	Hydrochloric acid (HCl)	**0.63**	**0.67**
4	Sulphuric acid (H_2SO_4)	**0.69**	0.49

Table 3 :Weight of Waste Engine oil adsorbed by Zeolites produced from Wheat Straw ash (in gm)

In the above table it is clearly seen that when zeolites produced from wheat straw ash are used for adsorption of waste engine oil than the zeolites developed using HCl provide the maximum adsorption and retain 0.63 gm and 0.67 gm respectively after 24 and 48 hours of incubation.

S. No.	Treatment used for zeolite production	Weight of waste cooking oil adsorbed on the Zeolites produced from Wheat Straw ash (in gm) (Z2-Z1)	
		After 24 hours	After 48 hours
1	Sodium Hydroxide (NaOH)	0.43	0.47
2	Potassium Hydroxide (KOH)	0.55	**0.74**
3	Hydrochloric acid (HCl)	0.52	**0.62**
4	Sulphuric acid (H_2SO_4)	0.45	**0.51**

Table 4. Weight of waste cooking oil adsorbed by Zeolites produced from Wheat Straw ash (in 'g')

In the above table it is clearly seen that when zeolites produced from wheat straw ash are used for adsorption of waste cooking oil than the zeolites developed using KOH provide the maximum adsorption and retain 0.55 gm and 0.74gm respectively after 24 and 48 hours of incubation.

S. No.	Treatment used for zeolite production	Weight of Waste Engine oil adsorbed on the Zeolites produced from Rice Husk ash (in gm) (Z2-Z1)	
		After 24 hours	After 48 hours
1	Sodium Hydroxide (NaOH)	0.41	0.51
2	Potassium Hydroxide (KOH)	0.36	**0.63**
3	Hydrochloric acid (HCl)	0.57	0.5
4	Sulphuric acid (H_2SO_4)	0.42	0.31

Table5. Weight of Waste Engine oil adsorbed by Zeolites produced from Rice Husk ash (in 'g')

In the above table it is clearly seen that when zeolites produced from wheat straw ash are used for adsorption of Waste cooking oil than the zeolites developed using KOH provide the maximum adsorption and retain 0.63gm respectively after 48 hours of incubation.

S. No.	Treatment used for zeolite production	Weight of waste cooking oil adsorbed on the Zeolites produced from Rice Husk ash (in gm) (Z2-Z1)	
		After 24 hours	After 48 hours
1	Sodium Hydroxide (NaOH)	0.41	0.45
2	Potassium Hydroxide (KOH)	0.48	**0.74**
3	Hydrochloric acid (HCl)	**0.58**	**0.60**
4	Sulphuric acid (H_2SO_4)	**0.6**	0.32

Table6. Weight of Waste Cooking oil adsorbed by Zeolites produced from Rice Husk ash (in 'g')

In the above table it is clearly seen that when zeolites produced from wheat straw ash are used for adsorption of waste cooking oil than the zeolites developed using KOH provide the maximum adsorption and retain 48 hours of incubation. While zeolite produced using HCl also gave a high adsorption efficiency of 0.58g and 0.60g after 24 and 48 hours of incubation.

DISCUSSION

Zeolites are derived from aluminosilicates layered structures which exists both naturally and can also be produced synthetically using organic as well as other inorganic materials. The three-dimensional structure with pores consisting of silicon, aluminium and oxygen ions and the arrangement can be described as silicon ions are neutrally-loaded in the crystal structure and the aluminium ions having one more positive charge is responsible for creating negative charge areas to exist within the structure and for charge balance, cation such as (Na+, K+…) or proton (H+) is placed in the pores as a counter-ions. In the crystal structure, altering the ratio between aluminium and silicon can have an impact on the pore size as well as the counter-ion amount. Mostly, natural zeolites contain aluminium and are hydrophilic as well as hydrophobic in nature. These materials form a good absorbent for polar substances (e.g. water and water-soluble substances) and also for nonpolar substances like gases, oils etc.

Hydrophobic zeolites are manufactured in the form of crystals with mostly the diameter of (1 µm to 1 mm). Synthetic zeolites are expensive compared to natural zeolites and are oftenly used as hydrophobic zeolites or zeolite catalysts. The use of wate materials like wheat straw or rice husk or other lignocellulosic waste as explained in this study opens up the scope for new methodologies by which zeolite synthesis can be made cost effective if they are produced from waste material. Most of the present research on zeolites are focussed on the production of zeolites as efficient and cost-effective materials used for oil spillage adsorption. Till date, this aspect of zeolite science has received little attention since adsorption has been highly studied using activated carbon and microorganisms and needs more investigative research works. Nowadays, different types of zeolites produced from wheat straw ash and rice husk ash are also being tested in numerous replicated laboratory analyses for their ability to adsorb waste engine oil as well as waste cooking oil. The relationship between weight of zeolite and weight of oil adsorption was different for different zeolites.

In the present project it was clearly proved that zeolites developed from wheat straw ash and rice husk ash can be very easily be used to effectively adsorb waste oils when the zeolites are incubated with different types of oils for different interval of time. The best adsorption capacity of 0.50-0.74gm oil was found when 0.5 gm of Zeolites produced from wheat straw and Rice straw ash were used. These were developed using KOH and HCl. Thus, it is clearly seen in Table 3 to Table -6 that Zeolites can adsorb oil to a ratio equal to or even more then their own weight.

Thus, the hypothesis has been proved that zeolites developed from lignocellulosic or biological materials can be utilised as well adsorptive terrestrial oil spills in oil refinery plants, during road accidents, beach spillage accidents from oil tankers and spills at petrol stations as an effective remedy for oil-contaminated soils. The contaminated zeolites can then be ignited or heated to remove the oil impurities bound to it and the energy emitted due to combustion of the zeolite oil mixture further can be a source for electrical power generation. after which, the ignited mix could be reused in subsequent oil spills. Various organic and inorganic materials have been applied as sorbents for oil spill clean-up like minerals like alumina, silica, zeolite, clay, alumina-phosphate, and mesoporous adsorbents. They are also considered as one of the most promising solutions for oil spill clean-up due to their simplicity and high efficiency [22] and such perspectives provide potential for development of environmentally-friendly and sustainable 'green' technology for remediation of oil spills

It is well known that materials suitable as an oil spill sorbents should possess certain characteristics like oleophilicity, hydrophobicity, high uptake, retention capacity and biodegradability and should also be inexpensive and available in large quantities.

Thus, production of large amount of zeolites from lignocellulosic waste could very well be used for Bioremediation and sorption of oil from soil or water. The process would also be cost effective as well as functionally very efficient and effective.

5.0 Conclusion

We used lignocellulosic waste material for the preparation of zeolites because it is low cost or no cost raw material and can easily available at world wide level everywhere. Developing Countries like India don't have proper waste disposal or waste management for this type of waste. Lignocellulosic biomass attracts flies which are responsible for spreading many types of diseases. According to a 2014 report by IARI (Indian Agricultural Research Institute), in 2008-09 country generated 620 million tone crop residues, of which 60% was paddy straw, 22% wheat straw. In this research, wheat straw ash and rice husk ash and were used in the production of different zeolites. Chemical method and thermal method are used for the extraction of silica from lignocellulosic waste. This process of extraction of silica is cost Effective and also helps to minimize the waste. Bioremediation is an eco-friendly process use to bioremediation of oil using zeolite. We used waste materials which are easily available and cost effective or no cost (waste material) for the synthesis of zeolites. Rice husk and ash are also used in the manufacturing and synthesis of new materials like fuel, fertilizer, and substrate, as well as for making activated carbon, pet food, fibre, silica and silicon compounds, and bricks. Steel, cement, and construction industries also use Rice husk ash. Heavy metals are removed from wastewater using rice husk as an adsorbent. Rice husk is readily available and inexpensive in rice-producing countries, which is an added bonus to its use. It is a greener approach.

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