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Production of Modified Zeolites from Rice Husk Ash for Removal of Cadmium from Aqueous Solution

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ABSTRACT: In this study, ZSM-5 zeolite from rice hush ash (RHA) was synthesized and modified to assess the removal of cadmium from aqueous solution using standard methods. Both the synthesized and modified ZSM-5 were characterized using XRD, SEM TEM, FTIR and BET. Presence of silicate in the RHA was confirmed with XRF to contain 86.85% silicate. Batch experiments of the adsorption carried out with specific concentration of cadmium shows that both the synthesized and modified zeolites demonstrated 44% and 78% cadmium ions removal from the simulated solution respectively. The study concluded that synthesized and modified ZSM-5 zeolites are highly efficient adsorbent for heavy metal removal.

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Nigeria is a country filled with resources of nature; for instance, agriculture has a land area of 98.3 million hectares, out of which 79 million hectares are arable (Aransiola *et al.*, 2019). Farming operations result in the generation of a variety of commercial harvests, from where a variety of leftovers, which are content made from biomass containing significant quantities amounts of energy thrown away products after harvest(Aransiola *et al.*, 2019).Rice husk, one of the most abundant agricultural byproducts, is rich in ash if compared to other biomass fuel ashes; it contains 85-98% silica and is very porous and lightweight, with a very high exterior surface area(Bhavornthanayod and Rungrojchaipon, 2009). Rice husk ash (RHA) is a catch-all name for all sorts of ash created by burning rice husks. RHA can be utilized as a low-cost alternative source of amorphous silica in the manufacturing of silicon-based products with industrial and technical applications (Chareonpanich *et al.*, 2004). Rice husk, a low-cost agricultural byproduct, has also been used in the manufacturing of zeolite due to its high silica concentration(Louis *et al.*, 2010). The second naturally occurring element on the earth's surface is silica accounting for around 32% of total volume. Consequently, Silicon is constantly present in the tissues of soil-rooted plants. The majority of the silica on the earth's layer is derived from agricultural or industrial waste(Jesudoss *et al.*, 2018).Many research have revealed that amorphous crystalline silica may be produced using a relatively low-cost source such as rice husk (Pode, 2016).Zeolites are widely used as sorbents in separation operations, in catalytic refinery and petrochemical processes, hence, there is a lot of

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interest in using it to make zeolites(Pode, 2016). Zeolites are water-soluble crystalline aluminosilicates made up of tetrahedral TO_4 units (T = Si or Al) that share oxygen atoms to form atomic-scale pores and pathways (Dey *et al.,* 2013). Zeolites consist of an organized network of micropores and a porous crystalline aluminosilicate framework(Jesudoss *et al.*, 2018). This empirical formula may be used to represent zeolite $M_{n/2}OAl_2O_3xSiO_2yH_2O$, where x is often equal to or larger than 2 because AlO_4 tetrahedral is linked solely to SiO_4 tetrahedral, y is the water present in zeolite vacant seats, and n denotes the cation valence. The framework Si/Al ratio consequently determines the zeolite's ion-exchange capacity, which decreases as the Si/Al ratio increases. Heavy metals, poisonous gases, dyes, and organic pollutants are removed by zeolites, which are particularly effective as gas and water purification systems, isomerization of catalysts, hydrogenation, alkylation, and absorbents (Santasnachok *et al.,* 2015).

Heavy metals are absorbed by plants and subsequently pass via food chains into the bodies of animals and humans, damaging their health and vital processes (Burakov *et al.*, 2018). Due to their toxicity and non-degradability, heavy metals found in waste from industrial operations, insecticides, fertilizers, mining, and energy utilization processes are among the most dangerous contaminants to humans. When exposed to heavy metals in water for an extended period of time, it affects respiratory system and destroys the liver, kidneys, and olfactory sense in humans. The most well-known dangerous heavy metal contaminants in wastewater include chromium, iron, nickel, zinc, cadmium, arsenic, lead, mercury ions, and others, which must be removed using correct methods before water may be recycled or reused. Several treatment technologies, such as chemical precipitation, membrane filtration, phyto-extraction, ion exchange, reverse osmosis, carbon adsorption, electro dialysis, co- precipitation, and adsorption have been used to remove metals from heavy metal contaminated water (Zhao *et al*., 2016). The aforementioned strategies, on the other hand, they're not financially feasible for small and medium-sized enterprises in rural or undeveloped locations.

The application of agricultural byproducts for heavy metal removal or bio-sorption is emerging as a novel waste water treatment option for small and medium-sized businesses(Santasnachok *et al.,* 2015). Recently, the importance of using low-cost materials with good selectivity as prospective sorbents has been emphasized (Zhao *et al.,* 2016). Zeolites have received a lot of attention because of their capacity to remove heavy metal ions from aqueous solutions through the ion exchange phenomena *(*Panneerselvam *et al.*, 2009).

This research is aimed at synthesizing ZSM-5 zeolite from agricultural wastes and modifying the synthesized ZSM-5 with an acid with the aim of assessing the efficiency of the zeolites in adsorbing heavy metals from polluted water.

MATERIALS AND METHODS

Sample Collection and Pretreatment: The rice husk for the production of zeolites was obtained at a local rice milling industry in Ede, Osun state, Nigeria. Figure 1 shows a sample of the rice husk collected at the location. The sample was pretreated with 3M hydrochloric acid before carbonization via open burning. All the chemicals utilized in this project were of analytical standard.

Fig 1: Sample of Rice Husk

*Synthesis of ZSM-5 Zeolite:*ZSM-5 is typically prepared at high temperature and high pressure in a Teflon coated autoclave and can be prepared using varying rations of SiO_2 and Al containing compounds. There are many ways to synthesize ZSM-5; a common method to synthesize is an aqueous solution of silica, sodium aluminate, sodium hydroxide, and tetrapropylammonium bromide are combined in appropriate rations:

$$SiO_2 + NaAlO_2 + NaOH + N(CH_2CH_2CH_3)_4Br + H_2O \rightarrow ZSM\text{-}5 + analcime + alpha\text{-}quartz$$

The carbonized product was calcined at 600 °C for 4 h at 5 °C/min in a furnace. At the end of the calcination, rice husk ash (RHA) was obtained and characterized. ZSM-5 zeolite was synthesizedusing hydrothermal method. First and foremost, a slurry of silica was obtained when 9.92 g of prepared RHA was dissolved in 51.6 g of water and stirred vigorously. A solution of 0.624 g of aluminum hydroxide and 1.44 g of sodium hydroxide was slowly added to the slurry to form a precursor gel, which for 45 minutes, the mixture was briskly mixed. The resulting mixture was then hydrothermally treated for 72 h at 150 °C in a Teflon walled stainless steel autoclave. The precipitate was washed severally with purified water until it reached a pH of 7. It was oven driedat 90 °C overnight and heated for 5 h in a furnace at 550 °C at a heating system rate of 1 °C/min.The Na-form of the zeolite was formed with use of NaOH, and the constant ion exchange with dilute excess of 1 M NH_4NO_3 transformed to the H-form of the Na-ZSM-5 zeolite. At a rate of 10 mL per gram of zeolite, the NH_4NO_3 solution was added. The water, ammonia, and ammonium nitrate were then removed by filtering, washing, drying at 80°C overnight, and calcining at 550°C for 5 hours(Jesudoss *et al.*, 2018). The ZSM-5 zeolite obtained after calcination was analyzed using XRF, XRD, FTIR, SEM and BET.

*Modification of ZSM-5 Zeolite:*Four grams of ZSM-5 zeolite and 0.385 g of phosphoric acid were mixed in 40 mL of distilled water. The mixture was rapidly agitated for 3 h at 60 °C before being steamed to dryness in a 120 °C air oven. The zeolite treated with phosphoric acid was allowed to react with 30 mL of dilute $NaHCO_3$ solution for 3 h at 60 °C with vigorous shaking to yield the disodium form C of a PNa^{2-} -ZSM-5 zeolite. Before usage, it was cleaned with water, and then dried overnight in a 120° air oven. The improved ZSM-5 zeolite was examined with XRD, FTIR, SEM, and BET.

Adsorption Studies: Batch experiments of the adsorption were carried out with 25 -100 mg/L standard solution of the cadmium ion. Approximately 0.3 g of modified ZSM-5 ofthe sample was combined with 100 mL of each modeled solution of water, and the resultant solution was stirred for 20 minutes on a rotary shaker set to 100 rpm. The combination was then filtered using No.1 (18.5 cm) whatman filter paper, and the amount absorbed was measured using an Atomic absorption spectrophotometer (AAS) to assess the adsorbent's efficiency.

Equation (1) expresses the percentage removal as:

$$\% \text{ removal} = \frac{C_0 - C_f}{C_0} X100 \qquad (1)$$

Where C_0 and C_f are the initial and final adsorbate concentrations in solution, respectively.

RESULT AND DISCUSSION

*Elemental Composition of RHA:*The elemental composition of the RHA used in this research was characterized using XRF as shown in Table 1. The result showed that the RHA was composed of 86.85% silica, 3.67% alumina which is similar to some of the results already reported in literatures(Ajima and Iguchi, 2009). Santasnachok *et al*,reported 91.5% silica and 2.27% alumina to be constituent of RHA. Similarly, Dey *et al*., 2013 reported that silica and alumina content of RHA to be 95.54% and 0.78% respectively. Considering the result obtained in this study, it could be deduced that RHA obtained at a rice milling industry in Ede North area of Osun state is a good silica source for the zeolite synthesis and other applications.

Table 1: Elemental Composition of Rice Husk Ash (RHA)

Symbol	Conc. (ppm)	Content (weight %)
Al	2832.5	3.67
Si	59189.6	86.85
P	937.1	1.47
S	1373.4	2.35
K	2805.5	2.32
Ca	867.1	0.77
Mn	163.5	0.15
Fe	734.7	0.72
Ni	18.0	0.02
Cu	24.9	0.02
Zn	134.0	0.11
Pb	84.4	0.06
W	199.7	0.17
Rb	85.7	0.06
Mo	152.6	0.16
Sb	624.3	0.58

*XRD Analysis of ZSM-5 and Modified ZSM-5 Zeolites:*Figures 2 and 3 illustrate the XRD structures of zeolites synthesized and modified zeolites, respectively.

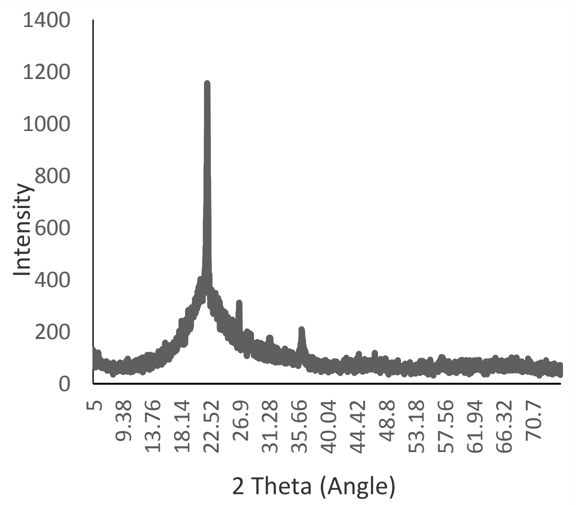

Fig 2: XRD pattern of the synthesized ZSM-5 zeolite

The materials' powder X-ray Diffraction (PXRD) patterns have been identified at room temperature using CuKα (= 1.5406) radiation at a beam voltage of 40Kv and a beam current of 45mA on a Rigaku ultima IV equipment. Continuous scans in a 2-range of 5-75º were used to obtain a wide angle pattern to validate the phase of the zeolite. X-ray diffraction pattern with the peaks at 2θ angle of 22.64º, 27.58º, 36.76º, matched very well with those reported in literatures. The XRD results revealed that the crystallinity of ZSM-5 is determined by the ratio of SiO_2/Al_2O_3 ration (Panpa & Jinawath, 2009). On the other hand, the pattern obtained by continuous scans of the modified ZSM-5 zeolite in a 2θ range of 5-75º showed that there is no structural degradation during modification as shown in Figure 3. The diffraction peak observed at 2θ of 23.2º showed that there is amorphous phase which will aid the surface area for the adsorption process.

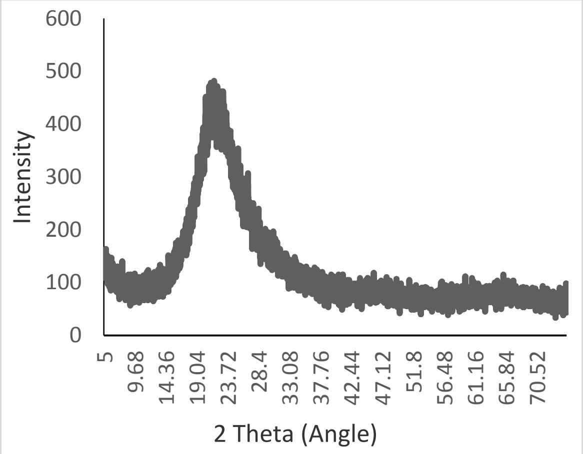

Fig 3: XRD pattern of the synthesized and modified ZSM-5 zeolite

*Morphologies of the Zeolite:*Scanning electron microscopy (SEM) was used to analyze the surface morphologies of the zeolites using a Teneo Low Vacuum Scanning Electron Microscope (LVSEM) with a Schottky emitter at an accelerating voltage of 2.00 kV and a beam current of 0.001 nA (100 PA). The morphology of the ZSM-5 zeolite observed at magnifications of 50µm, 100µm and 200µm are shown in Figures 4a, 4b and 4c respectively. The ZSM-5 synthesized show an organized irregular form morphology with a large particle length of about 50µm.

According to the SEM pictures, ZSM-5 exhibits a sheet-like shape. In addition, their proportions are not consistent, which is typical of systems with no templates(Jesudoss *et al.*, 2018). Furthermore, the inside of the silica and aluminum molecules grew, which resulted in an excellent ZSM-5 framework crystalline sheet and fiber-like morphological arrangement.

The morphology of the modified ZSM-5 zeolite observed at magnifications of 50µm, 100µm and 300µm are shown in Figures5a, 5b and 5c respectively. The modification could have prevented structural degradation of the synthesized zeolite(Panneerselvam *et al.*, 2009). It can be seen from the plate that the modified zeolite revealed the presence of smooth shaped-crystals in the zeolite framework.

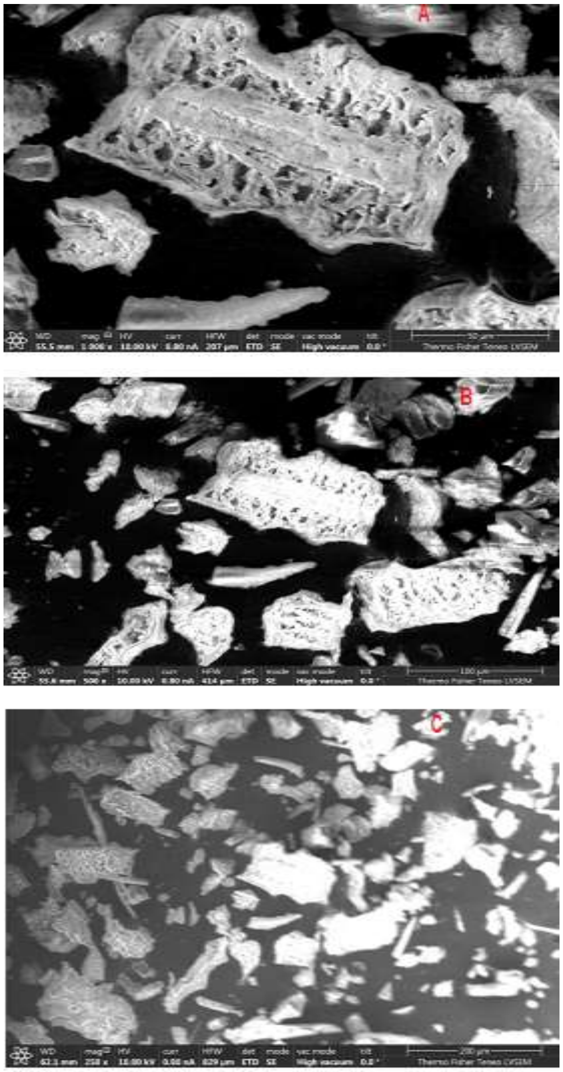

Fig4: SEM Images of ZSM-5 zeolite at (a) 50 µm (b) 100 µm (c) 200 µm

*FTIR analysis***:** For the initial synthesis, infrared spectroscopy was used to identify the ZSM-5 formation. The Fourier transform infrared spectrum of the produced ZSM-5 zeolite material are in the 4000-400 cm^{-1} region. The spectra clearly showed the characteristic absorption bands at 3462.34, 3350.46, 2006.04, 1639.55, 1101.39, 796.63, 468.72 cm^{-1} in the

ZSM-5 zeolite, distinct tetrahedral and framework atom vibrations were given. The distinctive band of 3462.34cm^{-1} is because of hydrogen connected Si-OH groups in the zeolite framework, while a wide peak of about 3350.46cm^{-1} is due to Al-OH inside the zeolite structure. The Hydroxyl vibrations mode of the remaining H_2O molecules in the zeolite voids are responsible for the band at 1639.55. T-O-T (T= Si, Al) framework vibrations are responsible for the peaks between 400 and 1101.39 cm^{-1}

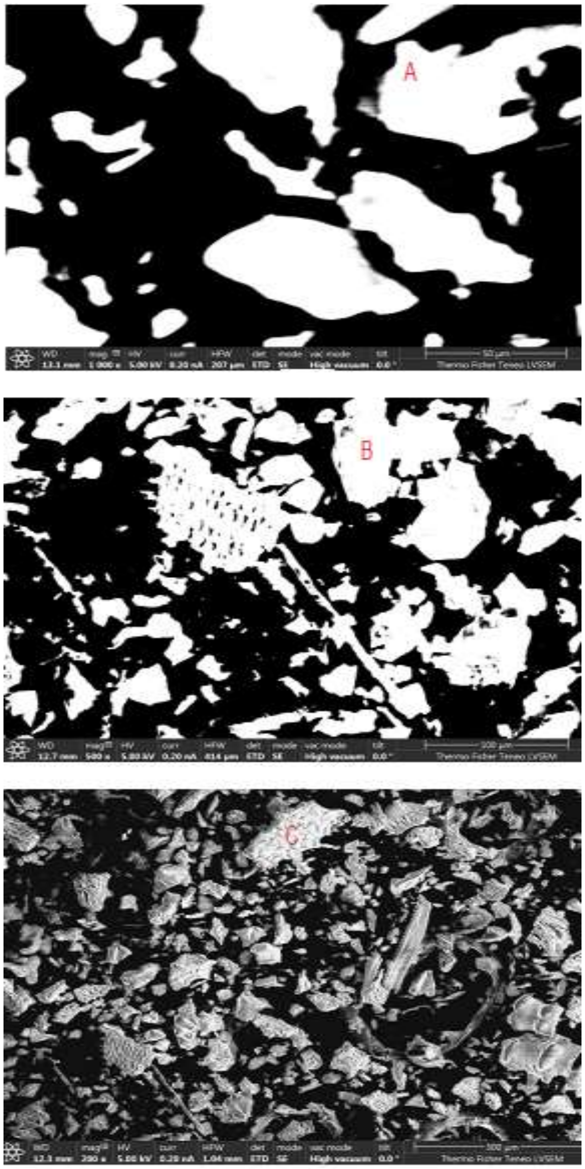

Fig5: SEM images of Modified ZSM-5 zeolite at (a) 50 µm (b) 100 µm (c) 300 µm

Bending inside vibrations techniques of (Si, Al) O_4 ZSM-5 tetrahedral zeolites cause the bands at 1101.39 and 468.72cm^{-1}, which are indifferent to the framework structure (Jesudoss *et al.*, 2018). Figures 6 and 7 show the FTIR spectrum for both synthesized and modified zeolite respectively exhibit similar IR spectroscopic features. There are only minor differences between the spectra. The FTIR spectra of the modified ZSM-5 zeolite samples are obtained in the range 4000-400 cm^{-1} where it revealed distinct bands of absorption at 3462.34, 3271.38, 2353.23, 2000.25, 1888.37, 1770.71, 1633.76, 1504.53, 1101.39, 794.7, 617.24, 470.65 cm^{-1}in the modified zeolite, distinct vibrations of tetrahedral and framework atoms were assigned. The P-H vibration mode of the phosphoric acid utilized in the zeolite alteration is responsible for the distinctive band of 3271.28.

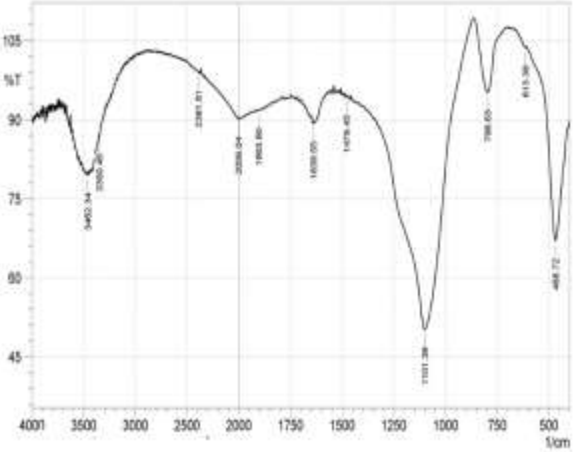

Fig 6: FTIR Analysis of Synthesized ZSM-5 Zeolite

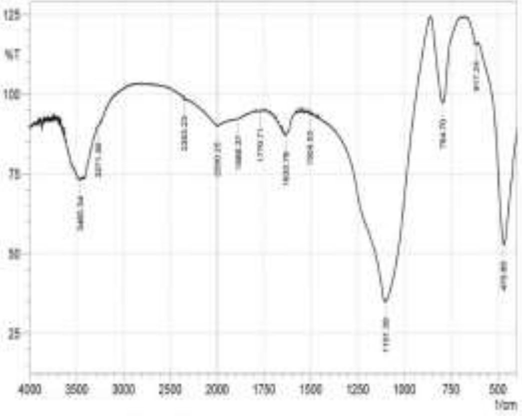

Fig 7: FTIR of the Modified ZSM-5Zeolite

*Determination of Surface Area of the Zeolite:*Nitrogen sorption isotherms were measured using a Quanta chrome Autosorb IQ2 device at 77K with nitrogen gas as the adsorbate. Before the measurement, the materials were degassed at 150 ^{0}C for 6 h (10 ^{0}C/min heating rate) in helium. From the desorption data of the isotherms, the surface areas were computed using the Brunauer-Emmette Teller (BET) technique, and the pore size distributions were determined using the

Barret-Joyner Halenda (BJH) method. Figure 8 depicts the surface areas of the samples calculated using nitrogen adsorption/desorption isotherms. According to IUPAC categorization, the two samples showed type III isotherms with upward absorption with P/P_0 = 0.2 and a hysteresis loop between P/P_0 = 0.6 and P/P_0 = 1. The micro porosity structure of ZSM-5 and modified ZSM-5 may be responsible for the hysteresis loops in the adsorption-desorption isotherms at varying relative pressures. The existence of microspores is indicated by linkage in the smallcomparativecompression zone (Jesudoss *et a*l., 2018). The textural features of synthesized as well as improved ZSM-5 zeolites shown in Table 2. The textural mesoporosity of the crystals was acquired when the isotherms' hysteresis loop appeared at greater relative pressure. The addition of phosphoric acid to the synthesized zeolite improves the surface area from 13 to 33 m^2g^{-1}, pore width from 3 to 12 nm, and pore volume from 0.1 to 0.2 ccg^{-1}, resulting in improved metal ion absorption from the simulated aqueous solution of the adsorbate.

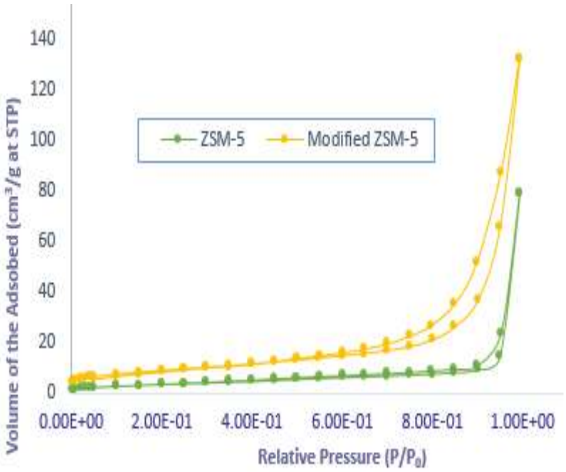

Fig 8: The BET Nitrogen Adsorption/Desorption Isotherms of Synthesized ZSM-5 Zeolites and the Modified ZSM-5 Zeolites.

Table 2: Textural Parameters of ZSM-5 Zeolite and the Modified ZSM-5 Zeolite

Sample	**Surface area (m^2g^{-1})**	**Pore volume (ccg^{-1})**	**Pore diameter (nm)**
ZSM-5	13	0.13	3.4
Modified ZSM-5	33	0.21	12.2

*Adsorption of Cd Metal by the Zeolites:*The Table of results obtained from the AAS analysis showing the adsorption performance of the synthesized ZSM-5zeolite adsorbent dosage for 0.3g/100ml adsorbate of different concentrations at 20 mins is shown in Table 3. It was observed that the adsorbent was effective in the metal removal. The relatively low adsorption rate in the removal of cadmium ions using the synthesized ZSM-5 zeolites could be attributed to the low surface area. However, the modified ZSM-5 zeolites shown in Table 4 revealed that the adsorbent is more effective in the removal of the cadmium ions from the aqueous solution. For instance, the adsorption of cadmium ions was observed to be between 28-60 % with the synthesized zeolite while the modified zeolite shows adsorption between 51-78 %.This could be attributed to the increase in the surface area of the adsorbent which enables pores spaces to be open, thereby giving easy access to more active sites of the adsorbents for adsorption. The phosphoric acid used in the modification help in washing off the impurities on the pore spaces. Based on these observations, it was concluded that the modified ZSM-5 has better adsorption performance compare to the synthesized zeolites.

Table 3: Table of Results Displaying the Adsorption Performance of the Synthesized ZSM-5 Zeolite

Metal	C_o(ppm)	C_t(ppm)	% Removal
Cd^{2+}	0.025	0.014	44
	0.050	0.020	60
	0.075	0.052	31
	0.10	0.072	28

Table 4: Table of Results Displaying the Adsorption Performance of the Modified ZSM-5 Zeolite

Ions	C_0(ppm)	C_t(ppm)	% Removal
Cd^{2+}	0.025	0.008	68
	0.050	0.011	78
	0.075	0.033	56
	0.10	0.049	51

Conclusion: This study was carried out to investigate the possibility of RHA as a silica source for ZSM-5 zeolite synthesis. It went further to modifying the synthesized zeolite, examining the effectiveness of both the synthesized and modified zeolite in adsorbing cadmium ion from the simulated wastewater. Both the synthesized and modified ZSM-5 zeolites are highly efficient adsorbent for heavy metal removal but the modified ZSM-5 zeolite showed a better adsorption capacity.

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