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Comparative Studies on the Absorptivity of Heavy Metals by the Different Zeolitic Materials Developed from *Kankara* Clay

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Abstract:- In this research, the comparative studies of removal of Cu^{2+} and Pb^{2+} ions by low-cost adsorbent such as Zeolites (A, Y and ZSM-5) has been studied. In order to achieve this, the XRD of the zeolites were investigated. The batch experiment employed however, determined the adsorbent dose, contact time, and pH. The impacts of adsorbent dose and contact time on the adsorption of heavy metals were determined from 0.025g- 0.4g and 5-120 minutes respectively while the effects of the pH of the metal ion solutions on removal levels of metal ions by different zeolites used were done between 3.5 and 7.5. Subsequently, sorbent dose, equilibrium time and the optimum pH required for the removal of heavy metals by different zeolites were arrived at. These factors were found to increase with increase in the removal of heavy metals. Adsorption isotherms investigated found out that the experimental data fitted well to Langmuir isotherms. The results showed that Zeolites A, Y and ZSM-5 hold the potential to remove cationic heavy metals species from domestic waste water in the order Zeolites A > Y> ZSM-5.

Keywords:- *Adsorbent, Langmuir Isotherm, Wastewater, Cationic Heavy Metals.*

I. INTRODUCTION

For life to exist, water is one of the most important component that must be available for human existence and survival. Therefore, water polluted and its insufficiency for 3human consumption are major issues that need to be dealt with [1, 2]. These pollutants may arise from municipal and agricultural effluents and as such are capable to harm life forms and environment. The most common toxic metals include: cadmium, manganese, lead, mercury, etc [3]. When these toxic materials are released to the community o living and non-living organisms, they are accumulated into human systems either through direct intake or the food chains and can cause serious health disorders [4]. As such these toxic materials should be in totality avoided from reaching to human dwelling [5]. It has been difficult over the years to establish a method that can be helpful in handling wastewater for the future. However, if these wastes are not recycled, they may have an immediate or long-term negative impacts on human life and human's inhabitant [1]. Nigeria is amongst many developing nations that experiences deadly outcome from exposure to contaminated water, this can largely be attributed to the vast population growth, increasing scarcity of water and insufficient treatment facilities. So this research is needful since wastewater treatment is a defence against this menace.

Currently, there have been several approaches for producing less cost and effective techniques which will bring to a minimal level the quantity of wastewater and enhance the level of quality treated water. Adsorption is becoming a substitute to treatment of wastewater; however, the quest for cheap adsorbents which will intensify metal-binding capacities have been studied [6]. These adsorbents could be of mineral, organic or biological origin, zeolites, industrial byproducts, agricultural wastes, biomass, and polymeric materials [7].

Among these adsorbent, zeolites have been adopted in this research to investigate the effective technology that eliminates the menace caused by toxic metals; their distinctive cation- exchange character that enables the dissolved cations to be extracted by exchanging with cations on exchangeable sites on these surfaces is looked at.

The zeolite adopted by this research eliminates cost and saves energy through synthesizing the adsorbent from *Kankara* kaolin which is a raw material readily available in katsina state, North-Western Nigeria. The process of synthesis will involve alkaline fusion prior to hydrothermal treatment. Consequently, dramatic results are provided for wastewater treatment comparative to those zeolites produced from chemicals or other adsorbent materials like activated carbon which could be expensive and time consuming [2]. The objective of this work is to use *Kankara* clay to develop a low cost adsorbent (zeolite) which will inturn enhance the elimination of these toxic materials from wastewater. The characteristics of the synthesized zeolite will be assessed exposing their different adsorptive behaviours to heavy metals removal by using batch adsorption studies. The study will adopt a model that describes how adsorbates react with

the adsorbents, thus, an equation will be established that correlates the equilibrium data, which will be useful for practical adsorption operation [2].

II. MATERIALS AND METHODS

A. Preparation of Adsorbents

The absorbents were prepared by dissolving 5g of *Kankara* kaolin into 100mL of distilled water. The heavier (coarse) component will settle naturally beneath and the lighter fraction (kaolin) remains as supernatant. The supernatant was allowed to settle into measuring cylinders for 24hours so that the separation of kaolin was enhanced. The process was repeated until enough kaolin samples were available for future experiments. The samples were air dried and kept for further characterization. However, during the calcination, the temperature of dehydroxylation was 600ºC, a temperature lesser than the ones reported in literature [8]. So several zeolites (A, Y and ZSM-5) were synthesized by methods adopted by Kovo (2011)[9] and Ginter, *et al*., (2000) [10] with modifications.

B. Characterisation of the Adsorbents

The raw sample and the synthetics products were identified by XRD machine model X'pert Pro by Philips adopting standard operating procedures.

➢ *Preparation of Stock Solutions*

Stock solutions of copper nitrate and zinc nitrate were made in a volume of up to 1000mg/cm^3 in high density polyethylene containers.

➢ *Preparation of Standard Solutions of Zn^{2+} and Cu^{2+} (Synthetic Wastewater)*

In preparing the concentrated solution of copper and Zinc ions, methods adopted by APHA, 2005 were used. Specifically, 1.599g of zinc nitrate was dissolved in a mixture of 200cm^3 of distilled water and 10 cm^3 of concentrated HNO_3. Deionised water was added to make up to the 1000mL mark to be used for further analysis. 20cm^3 portion of the stock solution was further diluted to 1000mL using deionised water which was used for the further analysis. Similarly, 1.599g of synthetic copper nitrate was prepared by dissolving in distilled water, 10cm^3 of concentrated HNO_3 was then added and the solution diluted to 1000 cm^3 mark using distilled water. Working solution was prepared as described in the procedures of zinc.

➢ *Investigation of Adsorption Potentials of Zeolites A, Y and ZSM-5 from Kankara Clay*

In investigating the adsorption potentials of heavy metals from synthetic wastewater by zeolites (A, Y and ZSM-5), the effects of adsorbent dose, contact time, and pH on the percentage removal of Zn^{2+} and Cu^{2+} were examined. These measurements were in compliance with those adopted by the 'Standard Methods for the Examination of Water and Wastewater' [11].

- *Effect of adsorbent dose on the adsorption of Zn^{2+} and Cu^{2+} onto zeolitess*

The effect of adsorbent dose on percentage removal of metal ions by varying zeolite dose in the range of 0.025 to 0.4g were studied. Separate masses of adsorbents (ranging from 0.025 to 0.4g of zeolites) were put into 5 beakers each containing 50cm^3 of metal solution of initial concentration of 20mg/cm^3. The solutions were agitated at a fixed stirring rate of 200rpm with an adsorbent time of 20mins at room temperature (25± 3ºC) and a fixed pH of 6.0. The final concentration was determined by Absorption spectrophotometer and the percentage removal of Zn^{2+} and Cu^{2+} for each zeolites obtained.

- *Effect of contact time on the adsorption of Cu^{2+} and Zn^{2+} onto Zeolites*

The effect of contact time on removal of Cu^{2+} and Zn^{2+} was studied. A gram of the adsorbent materials (Zeolites A, Y, and ZSM-5) was taken into 5 separate beakers each containing 50mL of metal solution at an initial concentration of 0.02mg/cm^3. The mixtures were shaken at constant stirring speed of 180rpm for differing time period from 20 - 120 minutes at a constant pH of 6. The final concentration of each solution was determined by Atomic Absorption Spectrophotometer, and the percentage Zn^{2+}/Cu^{2+} for each zeolites was then determined.

- *Effect of pH on the adsorption of Zn^{2+} and Cu^{2+}onto Adsorbents*

The effect of pH on adsorption of Cu^{2+} and Zn^{2+} was studied. However, 1.0g each of the adsorbents (Zeolites A, Y, and ZSM-5) was taken into 5 beakers each containing 50cm^3 of metal solution at an initial concentration of 0.02mg/cm^3. The mixture were shaken at a constant stirring speed of 180rpm for fixed period of 20 minutes and at room temperature (25± 3ºC). The pH of the metal ion solution was varied from 3.5- 7.5 by addition of Copper nitrate and zinc nitrate before the experiment. The final pH after adsorption of metal ions by each zeolites was evaluated by Atomic Absorption Spectrophotometer, and the percentage removal of Zn^{2+}/Cu^{2+} by each zeolites was then determined.

C. Adsorption Capacity Test

The adsorption capacity test for zeolites A, Y and ZSM-5 as adsorbents for Zn^{2+} was carried out in a manner that 50cm^3 of the already prepared solution of Zn ions which contained 0.02mg/ cm^3 of Zn^{2+} was each taken into five seperate beakers containing known masses of 0.025g, 0.05g, 0.01g, 0.02g and 0.4g of the adsorbents added to the solution, particularly at a constant pH across. The solution was stirred at 180 rpm at 30 min for which equilibrium was achieved. The supernatant of the mixture was then filtered using whatman filter paper. The determination of Zn was done by atomic absorption spectrophotometer. Similarly, the procedure was followed in determination of adsorption

capacity of adsorbents for Cu^{2+}. The amount of metal solute removed at equilibrium was computed thus,

$$q_{e=(C_o - C_e)\frac{m}{V}} \quad (1)$$

Equation 1 presents the amount of metal solute removed at equilibrium.

where, m (g) is the mass of adsorbent; V (cm^3) the volume of adsorbate; C_0 and C_e (mg/ cm^3) are the initial and equilibrium metal concentrations (single-component) in the liquid phase, respectively.

The percentage of Cu^{2+} and Zn^{2+} removed, R (%) from the solution was calculated using equation (2)

$$R = 100\ \frac{(Co-Ct)}{Co} \quad (2)$$

III. RESULTS

A. *Characterisation of Zeolites (A, Y and ZSM-5) as adsorbent*

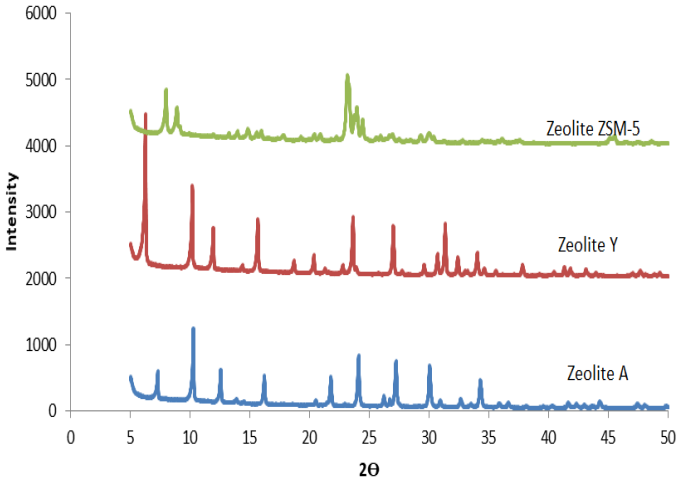

Fig 1:- XRD pattern of synthesized zeolites A, Y and ZSM-5 from kankara metakaolin

The figure above confirms that the material used for adsorbent are zeolite synthesized from kankara metakaolin and have XRD pattern typical of Zeolites A, Y and ZSM-5 as reported somewhere in our work. It is interesting to note that the metakaolin obtained was very reactive and facilitated prompt transformation into zeolitic materials. However, the zeolites obtained did not present any impurities, however, this is evident with the characteristic peak at 2θ values of 7.2°, 10°, 12.6°, 16.2°, 21.8°, 24°, 26.2°, 27.2°, 30°, 30.9°, 31.1°, 32.6°, 33.4° and 34.3° which is typical of zeolite A as was reported previously by Treacy and Higgins [12] and in one of our research works. Zeolite Y peaks at Bragg's angle of about 6, 10, 12, 16, 19, 20, 24, 27, 31 and 32˚which conforms with the findings in literature [13]. Similarly, zeolite ZSM-5 in the figure 1 has 7°, 8°, 9° 23°, 24° and 25° as characteristic peaks which corresponds to Kovo's (2011) [9] research.

➢ *Batch Adsorption Studies*

The adsorption studies will be discussed based on these parameters as effect of pH, effect of contact time and effect of amount of sorbent

B. *Effect of pH*

From the study, it is seen that the removal of metal ions decreases with acidity of the solution [14]. However, as the pH increases, more negatively charged surfaces become available, thereby enhancing a greater metal uptake. Figure 2 shows that increasing pH of the solution further from 3.5 causes prompt removal of metal ions until equilibrium pH is reached. It follows that the percentage removal of metal ions when equilibrium is reached is; 95.5% of Cu^{2+} is removed by zeolite *A* when the pH of solution is 5.5, also zeolite *Y* removes 95% of Cu^{2+} at pH 5.5 and 65% of Cu^{2+} is removed by ZSM-5 at pH 5.5. The pH at which removal of Zn^{2+} ions is at maximum is also 5.5 except for zeolite *Y* which is 4. However, 94% of Zn^{2+} is removed by zeolite *A*, 93% by zeolite *Y* and 62% by zeolite *ZSM-5* respectively. This can be explained further that as the pH increases, more of the metal ions which are positively charged in mixture were adsorbed on the negative surfaces of the zeolites. This enhances the percentage removal of the metal ions.

However, as the pH is increased above 5.5, the adsorptive capacities of Cu^{2+} and Zn^{2+} ions increases but at slower rate. This is as a result of the competitive adsorption between hydrogen ion and metal cation. This is in conformity with the works carried out by Hashen, (2007); Periasamy and Namasivayam (2010) [15, 16].

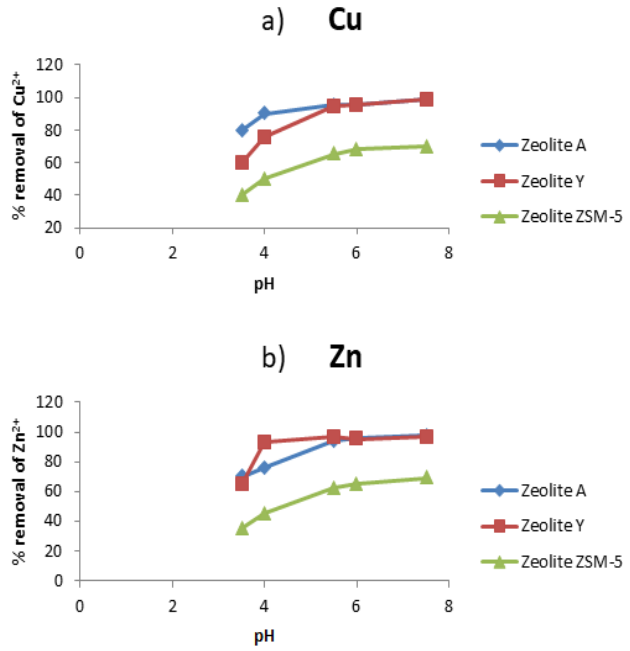

Fig 2:- Effects of pH on (a) copper removal for Zeolites A, Y and ZSM-5 at 27± 2 °C. (b) Zinc removal for Zeolites A, Y and ZSM-5 at 27± 2 °C.

C. Effect of contact time on the adsorption of Cu^{2+} and Zn^{2+} onto Zeolites (A, Y and ZSM-5)

The effect of contact time on the removal of Cu^{2+} and Zn^{2+} onto different Zeolites is studied. It is observed from Figure 3 that as the contact time of the different zeolites each in metal ions solution increases from (5- 120) minutes, the removal percentages of Cu^{2+} and Zn^{2+} increase. In the initial period of adsorption, the removal of metal ions was rapid, this is evident to the availability of removal sites by the zeolites. However, as the metal ions become filled up into zeolites pores/ sites, the process tends slower. In order words, as equilibrium contact time reaches 30 minutes, zeolite A removed 97.7% and 99% of Cu^{2+} and Zn^{2+} respectively. The removal of Cu^{2+} and Zn^{2+} ions onto zeolites Y and ZSM-5 at equilibrium are; 93% removal of Cu^{2+} at 15 minutes contact time; 90% removal of Cu^{2+} at contact time of 60 minutes. Zeolite Y removed 97% Zn^{2+} ions at equilibrium contact time of 10 minutes whereas 87% of Zn^{2+} is removed by zeolite ZSM-5 respectively. Increasing the contact time further than the contact times listed above for each zeolites result to no significant effect on adsorption. At this stage, adsorption is maximum, this observation is similar to one by Saeedeh *et al.*,

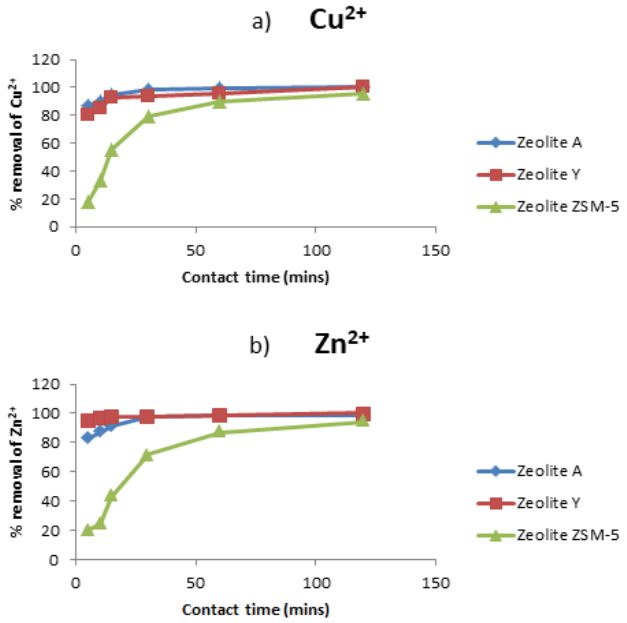

Fig 3:- Effect of contact time on (a) Copper removal for Zeolites A, Y and ZSM-5 at 27 ±2 ºC. (b) Zinc removal for Zeolites A, Y and ZSM-5 at 27 ±2 ºC.

D. Effect of sorbent dose on adsorption of Cu^{2+} and Zn^{2+}

Figure 4 shows the effect of the sorbent dose on the uptake of Cu^{2+} and Zn^{2+}. Three zeolites were investigated as adsorbents for the removal of metal ions in synthetic wastewater. The adsorbent (Zeolites A, Y and ZSM-5) dose was in each case for each adsorbent varied between 0.025g to 0.4g in 50 cm^3 corresponding to 0.5 g/ cm^3 to 8 g/ cm^3 in a batch adsorption process. In each case, increase in adsorbent dose prompted the increase in percentage (%) removal of Cu^{2+} and Zn^{2+}.

The maximum percentage removal of Cu^{2+} using Zeolites A, Y and ZSM-5 are; 97%, 93% and 90.4% at adsorbent doses of 0.1g (2g/ cm^3) for both zeolite A and zeolite Y and 0.2g (4g/cm^3) for zeolite ZSM-5 respectively. Similarly, the maximum percentage removal of Zn^{2+} onto zeolites A, Y and ZSM-5 are; 92%, 97% and 97% all at adsorbent dose of 0.1g (2g/ cm^3).

It is evident that for the Cu^{2+} metal ions, zeolites A had a higher percentage removal of than zeolites Y and ZSM-5, but that was not the case for Zn^{2+} ions removal. Zeolites Y and ZSM-5 had a higher removal. The optimum % removal of metal ions by zeolites is found to be in the adsorbent dosage of between 0.1g – 0.2g (2g/ cm^3 – 4g/ cm^3). Beyond these, the increase in percentage removal of the metal ions was found to be relatively small or insignificant, this findings agrees with Adie *et al.*, (2012)[18]. The variation in sorption capacities between various adsorbents could be related to the type and concentration of surface group responsible for the adsorption of metal ions from solution [19, 18]. Thus, the phenomenon of increase in % removal of metal ion (Cu^{2+}/ Zn^{2+}) with increase in adsorbent dosage, more surface area is available for adsorption due to increase in active sites or due to conglomeration of zeolites at higher doses.

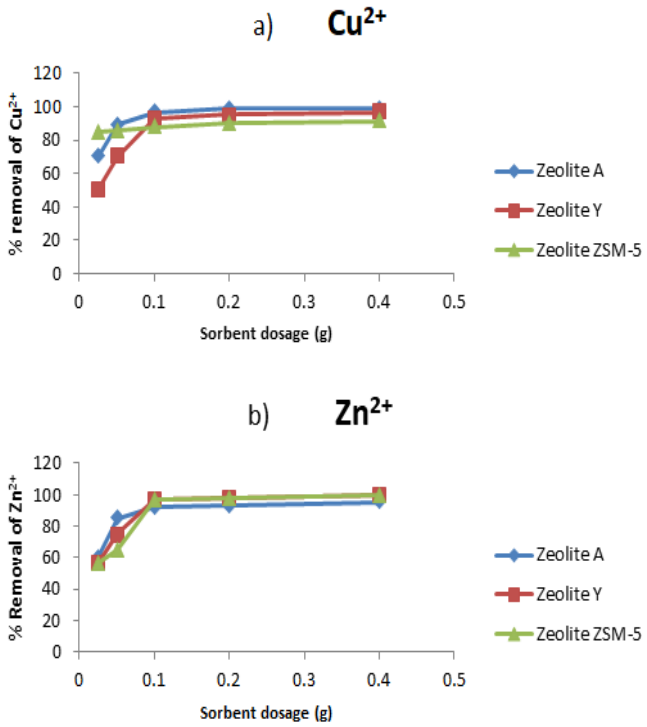

Fig 4:- Effect of Sorbent dose on (a) Copper removal for Zeolites A, Y and ZSM-5 at 27 ±2 ºC. (b) Zinc removal for Zeolites A, Y and ZSM-5 at 27 ±2 ºC.

E. Adsorption Isotherm

Langmuir isotherm was adopted in this study. Its equation assumes that the assumptions that maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface, provided the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface [20]. The Langmuir isotherm is defined as:

$$Qe = (bQmCe)/(1 + bCe) \quad (3)$$

and in linearized form is:

$$Ce/Qe = (Ce/Qm) + 1/(bQm) \quad (4)$$

where *Qm* and *b* are Langmuir constants related to the sorption capacity, and sorption energy, respectively. *Ce* is the equilibrium concentration in mg/cm^3 and *Qe* is the amount of adsorbate adsorbed per unit weight of adsorbent *(mg/g)*. The plot of *Ce/ Qe* against *Ce* as shown in figures 5 and 6 present the adsorption of copper and zinc ions onto different zeolites which give a straight line. It is clear that the linear fit fairly well and this enables the applicability of the Langmuir model which requires that the maximum adsorption corresponding to the removal of Cu^{2+} and Zn^{2+} ions onto the zeolites surfaces.

The Langmuir isotherm constants and their correlation coefficients R^2 are listed in Table 1 which shows that the experimental data fitted better to the Langmuir equation, and as such is suitable for the analysis of kinetics. This type of observation was also stated by Omar (2011)[2]. Consequently, the removal process of metal ions on synthetic zeolites (A, Y and ZSM-5) follow the Langmuir isotherm model, where the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the sorption of the next ion. This explains a similar relationship using activated carbon obtained from different raw materials were used as adsorbents [21, 22]

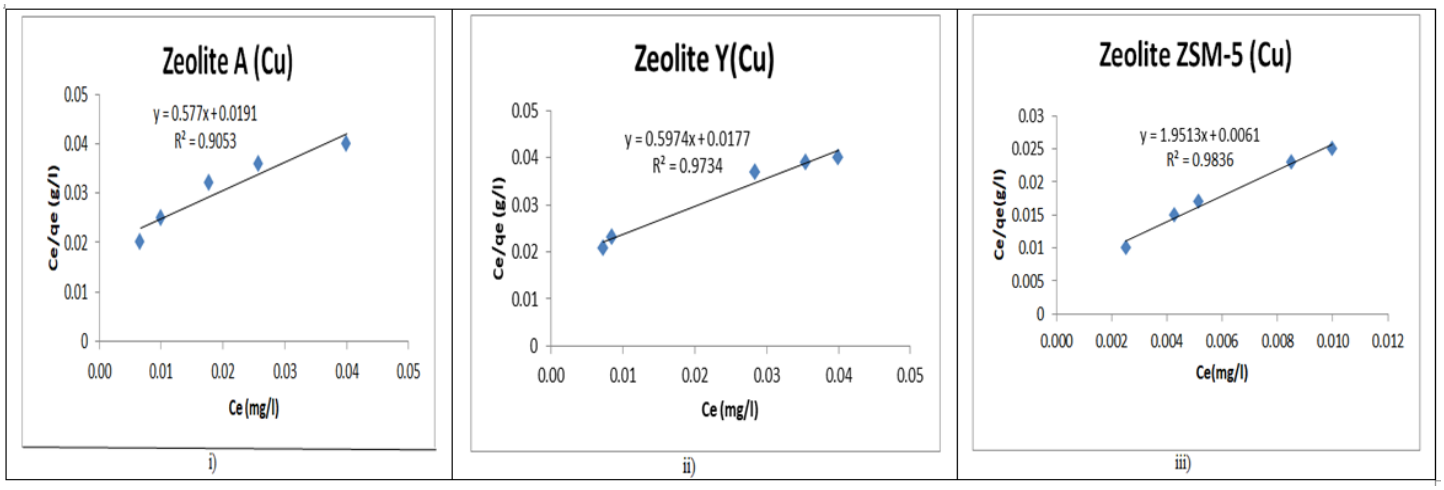

Figure 5. Langmuir plot of i) Zeolite A for copper removal at 27 ±2 ºC ii) Zeolite Y for copper removal at 27 ±2 ºC iii) Zeolite ZSM-5 for copper removal at 27 ±2 ºC

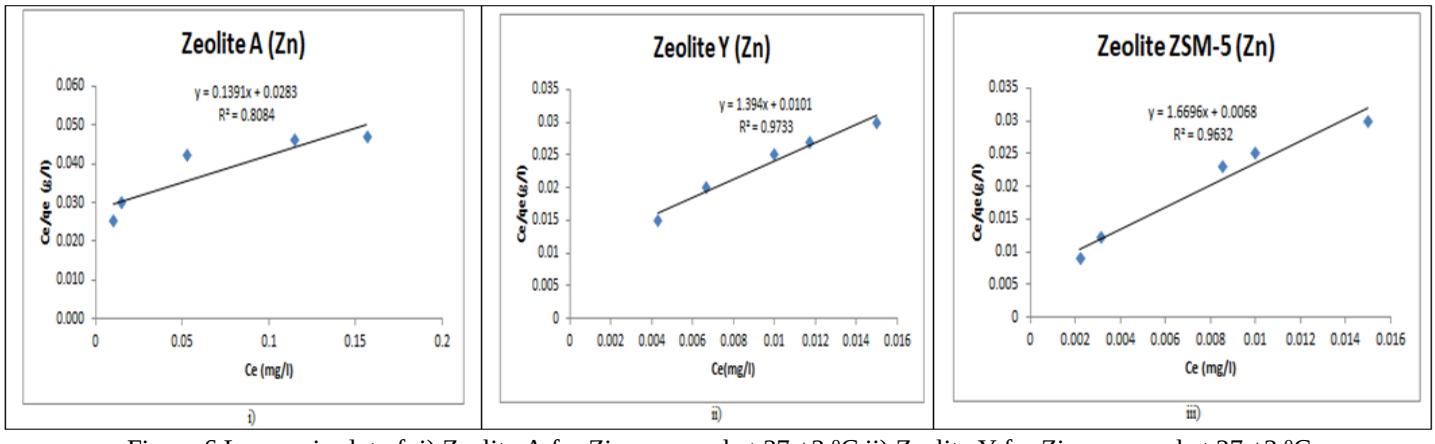

Figure 6 Langmuir plot of i) Zeolite A for Zinc removal at 27 ±2 ºC ii) Zeolite Y for Zinc removal at 27 ±2 ºC iii) Zeolite ZSM-5 Zinc removal at 27 ±2 ºC

Heavy metals	Adsorbent (Zeolites)	Langmuir constant		R^2
		B	q_m	
Cu	A	0.577	0.0191	0.9053
	Y	0.5974	0.0177	0.9734
	ZSM-5	0.9836	0.0061	0.9836
Zn	A	0.8084	0.0283	0.8084
	Y	0.9733	0.0101	0.9733
	ZSM-5	0.9632	0.0068	0.9632

Table1:- Langmuir constants for the adsorption of Cu(II) and Zn(II) ions onto Zeolites A, Y and ZSM-5

Table 1 presents the Langmuir adsorption constants and correlation coefficients (R^2). It is revealed from the data that Langmuir adsorption was best for the Cu^{2+} ions adsorption onto zeolites Y and ZSM-5 with R^2 of 0.9734 and 0.9836. Similarly, the Langmuir adsorption best for adsorption of Zn^{2+} ions onto zeolites Y and ZSM-5 with R^2 were 0.9733 and 0.9632 respectively. These values fall within the value presented by Mulu 2013[(23)] in his work. However, this does not hold for adsorption of Cu^{2+} and Zn^{2+} onto zeolite A which had their R^2 values of 0.9053 and 0.8084 (Table 1) instead. Neverthless, the adsorption was feasible. The features essentially gotten from Langmuir adsorption isotherm predict the affinity between the sorbate and sorbent using a dimensionless constant called separation factor or equilibrium parameters.

IV. CONCLUSION

Low cost adsorbents like zeolites made from kankara kaolin are effective for the removal of Cu^{2+} and Zn^{2+} ions from aqueous solutions. The batch method was employed; however, parameters such as pH, sorbent dose and contact time were studied at ambient temperature of 27°± 2°C. The parameters investigated showed that increase in pH, contact time and adsorbent dose increased the percentage of adsorption or removal of metal ions. Finally, the Langmuir isotherm used fitted well with the experimental data obtained. However, it was established that the Zeolite A had higher monolayer adsorption capacity than Zeolites Y and ZSM-5.

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