Development of Coal Fly Ash Based Zeolite-Alginate Composite and Removal of Heavy Metals from Synthetic Solution

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Abstract

In the present study Coal Fly Ash (CFA) has been used in the preparation of zeolitic material which was further processed to prepare alginate- zeolite composite material in the form of beads. The material was characterized, SEM, and FT-IR to study minerals and their internal morphology. The adsorption parameters were optimized at room temperature to determine adsorption capacity of the adsorbent for heavy metal cations of Cu and Zn in synthetic solution. Application of Langmuir and Freundlich isotherms revealed that the adsorption process is physio- chemical in nature. The kinetics study show that the adsorption of Cu and Zn cations follow Pseudo First order kinetics. Thermodynamics values show that the process is feasible and endothermic in nature.

Key Words: *Coal Fly Ash, Composite material, Adsorption, Heavy metals*

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Introduction

Fly ash is fine particulates driven out from the coal terminated boilers. The measure of coal fly ash as waste discharged by the power plants and processing units has been expanding throughout the world. Reusing of coal fly ash has turned into an expanding worry because of expanding landfill expenses. The fly ash now increasingly being used in the manufacturing of Portland cement, agricultural sector and water treatment.

Coal fly ash is converted into the zeolites to decrease the landfills and giving high worth items. It has been studied that the aqueous combinations of zeolites with soluble media activate the poisonous metals [1]. These zeolites have a capacity of removing Cr (III) from the waste water. Zeolites has large capacity for the removal of Cr (III) than virgin fly ash because of the high corrosive killing limit and cation trade limit of zeolite. The intensity of removing chromium by the fly ash based zeolites reached to 100% only because of precipitation of Cr $(OH)_3$ [2]. Vinassae and bagasse fly ash used as adsorbent material for increasing the removal efficiency by decreasing their chemical oxygen demand (COD) and also by their adsorbent dose, shaking time and by setting their contact time [3]. The adsorption of lead by the formation of bio mixture globule composites through the sol-gel bed by adding shapeless silica into the calcium particles cross connected alginate. This process required less effort with biocompatibility and recyclability [4]. Nano fiber layer with fly ash used for the removal of VOCs form the air and other waste pollutants by the electrospinning capacity [5]. Mesoporous high surface activated carbon zeolites (Z-AC) used with enhanced NaOH capacity for the removal of methylene blue recognized as best adsorbent for the colors expulsion [6]. The treatment of fly ash with KOH produced K-H Zeolites for the take up of Cs^+. This treatment also include alginate gel polymer for the removal of cesium [7]. The treatment of zeolite with NaOH used for the removal of lead. This treatment leads to the zeolite Na-P1[8]. Zeolite and alginate complexes created for the evacuation of natural and inorganic mixes like zinc and toluene[9]. Nitrates, sulfates and zinc removed from the wastewater by the biopolymer alginate/clinoptilolite-rich tuff pellets by the process *adsorption by adding Fe(III) and Ca (II) chlorides [10]. MWCNT- fortified alginate gel based adsorbent used for the removal of cesium and strontium by enhancing their surface territory and sorption limit[11]. The treatment of coal fly ash with alkali produce modified fly ash used for the removal of Aluminum, Nickle, Lead, Zinc and Manganese in the acid mine drainage (AMD).This is the chemisorption and adsorbent can be recovered and reused [12]. Expulsion of methylene blue from watery materials through adsorption at pH 6.75 [13]. Synthetic treatment of Zeolite used for the removal of NO_X, SO_X, mercury and other cations from the air [14]. The adsorption through fly ash also used in paper industry for the adsorption of dark color in various concentration [15]. Different forms of fly ashes used for the different types of Zeolites like Hydroxysodalite, NaPI with high content of Ca and X Zeolite with high substance of Al. Potentially these Zeolites many times higher than simple fly ash [18]. Zeolites prepared from the sonochemical treatment to replace the fusion based treatment in order to anticipated the energy demand [19]. Na-PI zeolite prepared from different techniques which has high surface area six times greater than simple zeolites [20]. Zeolite A and X by product of zeolite soda lite prepared by changing temperature and crystallization conditions [21]. For the expulsion of Indigo Carmine and Orange 16 iron oxide Nano composites used as an agent [22]. Coagulants base Zeolites from fly ash by leaching hydrochloric acid used for wastewater treatment. Addition of calcium ion enhanced their ability [23]. Alginate-Ca CO_3 composite beads used for the removal of cadmium ions from waste solution [24].*

Material and Methods

Reagents and Chemicals

Synthesis of coal fly ash based Zeolite-Alginate Composite and its adsorption studies required various reagents like HCl, HNO_3, Na_2CO_3, NH_4Cl, NaOH, $CaCl_2$, Cu and Zn metal ions standard solutions and sodium alginate have been used.

Preparation of Zeolite material

Coal fly ash and Sodium Hydroxide was taken in a crucible in a suitable amount and fused at 600^OC for 2 hours. Then added distilled water and mixed it then again placed in a furnace for Hydrothermal treatment at 80^OC for 24 hours. After this *filtered the solution with 2-3 washings and dried them. Zeolite material is obtained.*

Preparation of Zeolite-Alginate composite

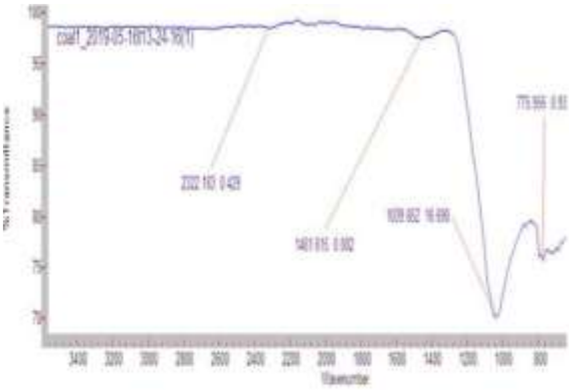
2g of sodium alginate was taken and dissolved in 100 mL of water to make 2% solution. Placed the beaker on the hot plate for 3-4 hours with constant stirring. After that added 2g of Zeolite and stirred again for 2 hours. After making gel like solution then beads were formed with dropper in a 1000mLbeaker having 1M $CaCl_2$ solution. Filter the beads by placing a large filter paper and dried them in electric oven maintained at 60 ^{0}C for 24 hours and characterized by using FT-IR and Scanning Electron Microscopy (SEM) and then are used as adsorbent.

Result and Discussion

Characterization of Adsorbent

FT-IR analysis

FT-IR is useful to determine the functional groups present in the materials. The change in intensity and shift in peaks position gives information about the zeolitic and composite material. Figure (1 & 2) show FT-IR spectra of CFA based zeolites and its alginate composite material.it can be observed that there are changes in the intensity and shifts of peak position in both the spectra. Zeolitic and composite materials show similar spectra at some places like peaks at 1461.61cm^{-1}(1) and 1421.00cm^{-1}(2) indicated the C-H bonding.in the same way peaks at 2322.78cm^{-1}(2) and 2322.18cm^{-1}(1) show the O=C=O group. There are some points at which different peaks show different behaviors like at 3320.32cm^{-1} (2) showed N-H stretching this indicates the presence of secondary amine but this peak is not present in the zeolite spectra (1). The composite spectra also show very sharp peak at1618.38cm^{-1} indicating the strong C=C stretching.[2]



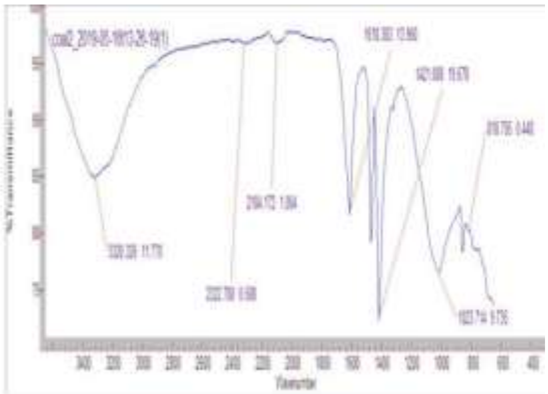


Fig. 1. FT-IR of zeolite material material.

Fig. 2. FT-IR of Composite

SEM analysis

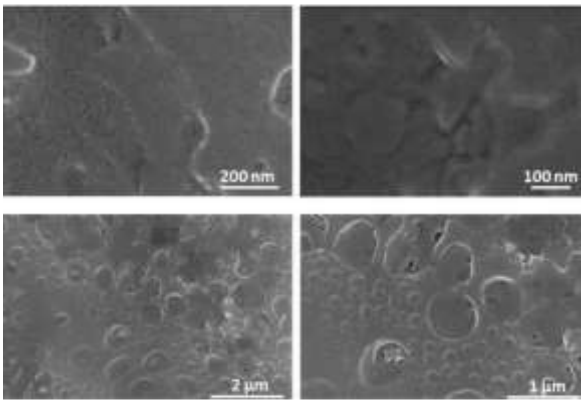


Fig. 3. Zeolite Material

The SEM images of Zeolites shoed micro pseudo sphere like features agglomerated with each other having spherical spaces. The image ranged in 100nm in size.

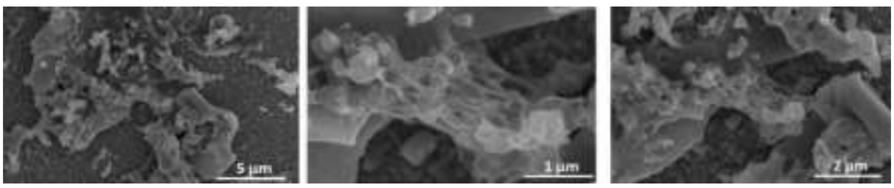


Fig. 4. Zeolite-Alginate Composites

The images showed two type of morphology beads and flake like structure covering the entire beads connected with each other in a compact layer with regular spaces. These images ranged in size 1µm.

Parameter optimization by AAS

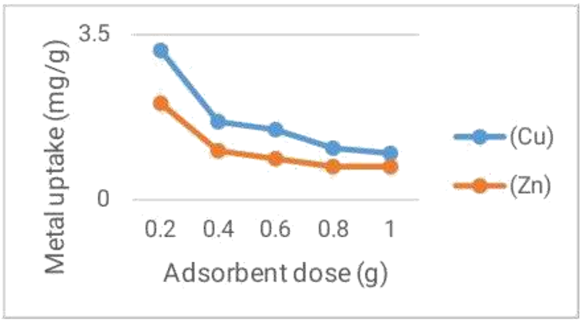


Fig. 5. Effect of Adsorbent dose on the metal uptake of Cu and Zn ions

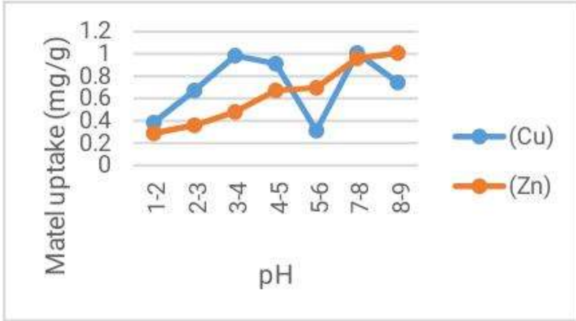


Fig. 6. Effect of pH on the metal uptake of Cu and Zn ions

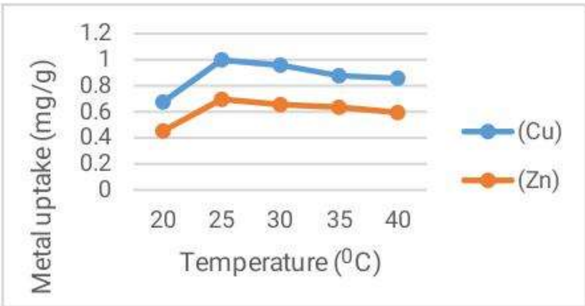


Fig. 7. Effect of Temperature on the metal uptake of Cu and Zn ions

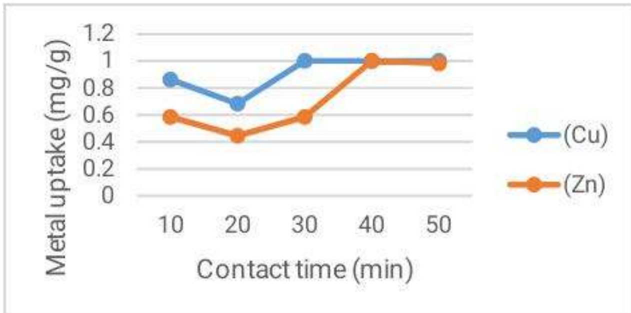


Fig. 8. Effect of Contact Time on the metal uptake of Cu and Zn

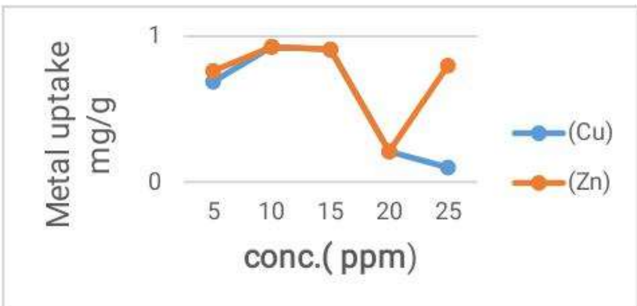


Fig. 9. Effect of Concentration on the metal uptake of Cu and Zn

Effect of Adsorbent dose

Study on the effect of the composites amount for the removal of Cu and Zn is *important to check the efficiency of the adsorbent for metal uptake and for percentage removal. The influence of the composite varying from 0.2g to 1.0g. Metal uptake trend decreasing as the amount of adsorbent increasing g both in the case of Cu and Zn as shown in the fig. 5. The maximum removal efficiency for Cu and Zn was observed at 93.5% and 66.3% respectively. [10]*

Effect of pH

The pH factor greatly influenced the solution internal bonding and other reactions with heavy metals. Figures shows the working of fly ash adsorbent for the removal of metal ion in case of pH. These studies showed that Cu showed the normal behavior like with increasing pH there was an increasing trend in the metal uptake but it sudden showed a depth at pH 5-6 as same in the case of removal efficiency. This sudden behavior as due to the pH moving towards the neutral point and again start increasing almost all the Cu is removed as shown in the fig. 6. On the other hand Zn showed normal behavior in case of metal uptake and removal efficiency as they are increasing with increasing pH. [12]

Effect of Temperature

The adsorption of Cu and Zn ions also greatly influenced by temperature. Figure shows that Cu and Zn uptake is 0.98 and 0.68mg/m at 25^{O}C respectively. The removal efficiency also shows the same behavior at 25^{O}C in the case of both. However further increasing temperature results to decrease in the metal uptake efficiency so 25^{O}C is the equilibrium point as shown in the fig. 7. According to the studies ion on the adsorbent surface and removal.

Effect of Contact Time

Contact time is the important to check the competence of adsorbent in the minor time limit. Shaking time gives a significant factor in the proper interaction of the adsorbent with the metal ions. Fly ash adsorbent showed their maximum capacity for the metal ions at the maximum time 0 mins as almost all the Cu and Zn ions was adsorbed. As the mechanism of solute transfer to the adsorbent was through diffusion process. As the concentration gradient between the solute and the active pore sites is large hence the rate of adsorption of Cu and Zn ions are faster as shown in the fig. 8. At the initial stage the rate of diffusion is slow due to the low *pore diffusion but gradually increasing with increasing time.*

Effect of Concentration

Metal ion adsorption is strongly affected by its concentration in aqueous solution while maintaining the adsorbent concentration to 1g.In start it shows increase in the adsorption of both Cu and Zn ion by increasing concentration but then showed a sudden depth at 25ppm and then moved in a normal trend both in the case of metal uptake as shown in the fig. 9.

Isotherm models

Langmuir Isotherm

Langmuir adsorption isotherm explain the process of adsorption occurring at the specific homogeneous sites of adsorbent adsorption energies with no interaction between the solute molecules and finally equilibrium point is reached. The Langmuir isotherm is given by the formula.

Equation.١ $C_e/q_e = 1/q_o b + C_e/q_e$

Where q_e is the amount of the adsorbate in equilibrium in milligram per gram, C_e is the equilibrium concentration of adsorbent, b is the Langmuir isotherm constant q_o is the maximum theoretical adsorption capacity. the separation factor R_L that predict the shape of the isotherm and feasibility of the adsorption process.[9]

Equation.٢ $R_L = 1/1+bC_O$

When $R_L > 1$ adsorption process is unfavorable and it is linear when $R_L= 1$ and process is favorable when $R_L < 1$.

This isotherm was obtained by plotting $1/C_f$ vs. $1/q$. straight line was obtained having a correlation coefficient for Cu is 0.8485 and for Zn is 0.8049 as these values are somehow close to 1 this indicates that the adsorption process is favorable. R_L value of copper is smaller than 1 as this process is favorable for Cu but not for Zn as the R_L value is higher than 1 as in the fig. 10 and fig. 11.[22]

Table 1. Langmuir Constant

Adsorbate	Intercept	Q_{max}	Slope	b	R^2
Cu	0.2969	3.36	0.5763	0.515	0.8485

Zn	-0.8091	-1.235	9.3855	-0.086	0.8049

The value of the Langmuir constant b should not be less than 1 and greater than 10 but in this case vales are less than 1 so only physical adsorption takes place. So this experiment reveals that adsorption process is physical in nature.[13]

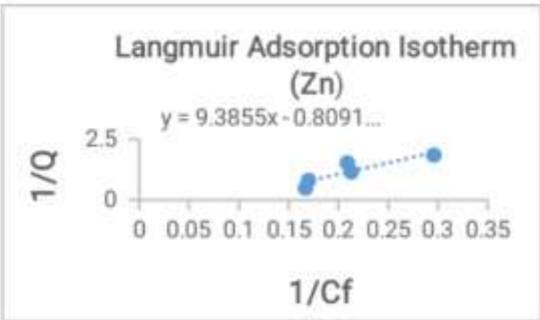


Fig. 10. Langmuir Adsorption Isotherm of Zn

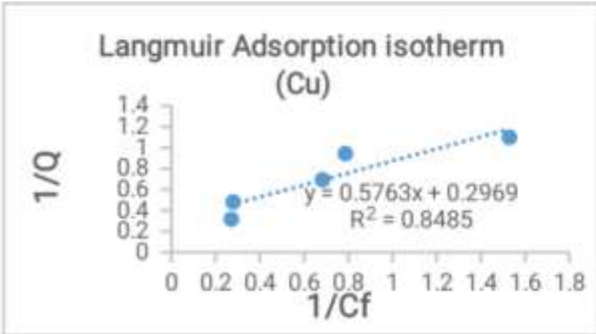


Fig. 11. Langmuir Adsorption Isotherm of Cu

Freundlich model

The adsorption of the heterogeneous metals are determined by the Freundlich isotherm model applied on the metals having multilayered structure.

***Equation.* ٣** $$\log q_e = \log K_F + 1/n \log C_e$$

Where q_e the adsorbent adsorbed is the Freundlich constant relates to the adsorption capacity. K_F and n are the freundlich constant.

Figure shows the relationship between $\log C_f$ and logQ. The correlation coefficient are 0.1918 for Cu and 0.531 for Zn which are somehow close to 1 indicates that process parameters somehow preferable for Freundlich model but the n value shows that Freundlich isotherm is only favorable for Cu in case of physical adsorption but for Zn chemical adsorptions takes place as shown in the fig .12 and 13.[13]

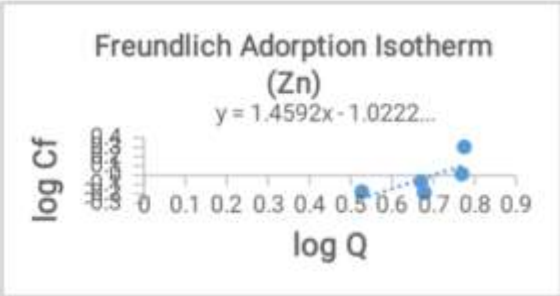


Fig. 12. Freundlich Adsorption Isotherm of Zn

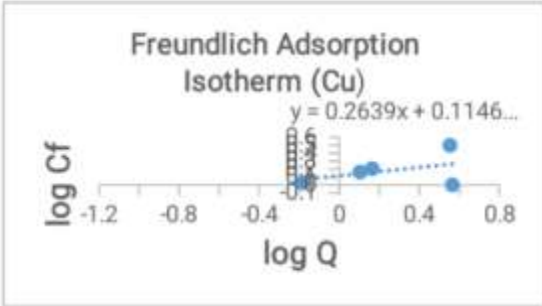


Fig. 13. Freundlich Adsorption Isotherm of Cu

Kinetics models

Pseudo first order kinetics model showed the binding of the metal ion to the only one adsorption side on the adsorbent. Pseudo first order kinetic equation are described as:

Equation. Σ $\log(q_e - q_t) = \log q_e - K_1 t/2.303$

By plotting a graph between log $(q_e - q_t)$ *and t gives the values of* q_e *and* k_1

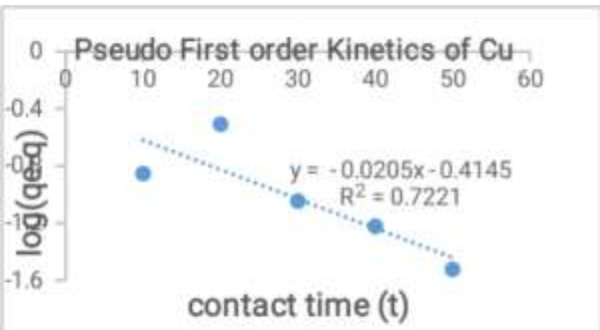


Fig. 14. Pseudo First order kinetic of Cu

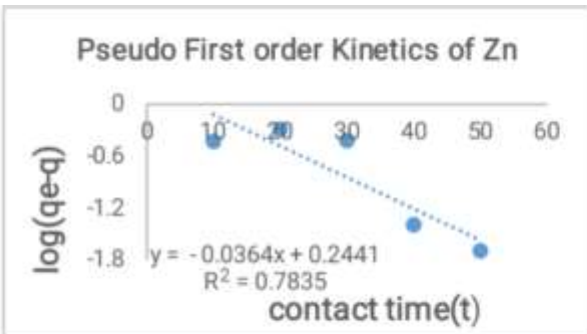


Fig. 15. Pseudo Second order kinetic of Zn

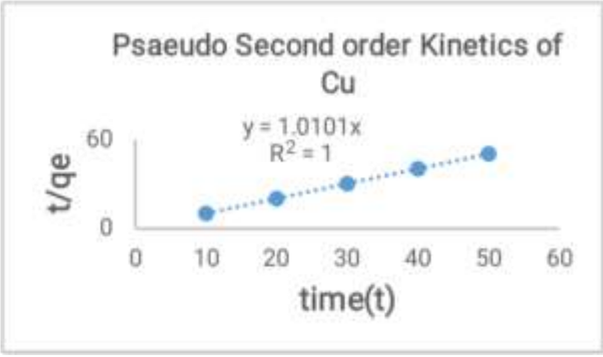


Fig. 16. Pseudo Second order Kinetics of Cu

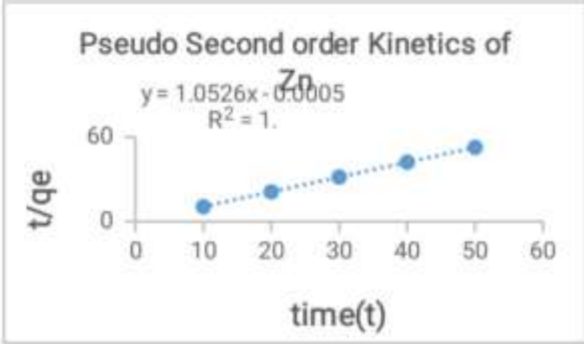


Fig. 17. Pseudo Second order kinetics of Zn

Pseudo second order rate equation

Equation. $\circ$ $t/q = 1/K_2q_e{}^2 + t/q_e$

By plotting a graph between t/q and t gives a straight line and the values of q_e and K_2 can be determined by slope and intercept as shown in the fig.14,15,16 and 17. The correlation coeffient for both the Cu and Zn is 1 shows that adsorption process follow pseudo first order kinetics.[19]

Thermodynamics Parameters

Thermodynamics parameters like Gibbs free energyΔG^0, Standard Enthalpy change ΔH^0 and Entropy changeΔS^0 can be determined from the adsorption of Cu and Zn shown in the table. 2. Data can be determined from the graph plotted between lnK and 1/T shown in the fig. 18 ad 19. ΔH^0 and ΔS^0 can be determined from the slope and intercept.[5] The values of thermodynamics parameters showed that the process is endothermic and adsorption process is feasible.

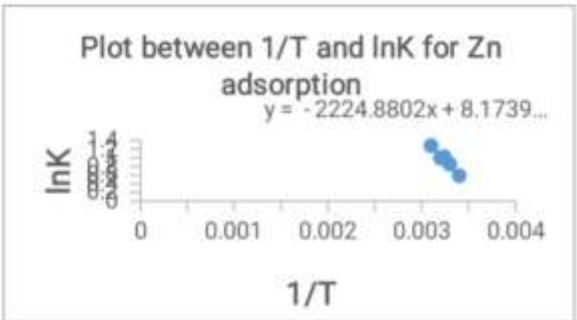


Fig. 18. Plot between 1/T and lnK for Zn adsorption

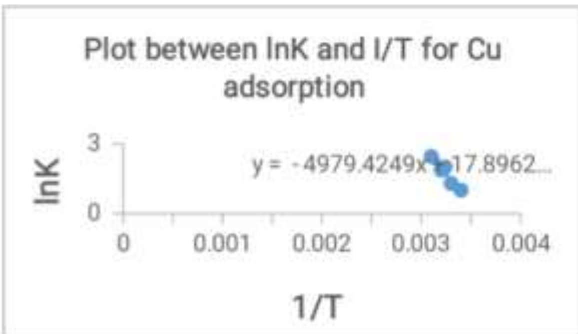


Fig. 19. Plot between 1/T and lnK for Cu adsorption

Table 2: Thermodynamics constant for the adsorption of Cu and Zn

Metal ion	Temperature (K)	ΔGo (kj/mol)	Slope (ΔH/R)	Intercept (ΔS/R)	ΔS^O (kj/mol)	ΔH^O (kj/mol)
Copper	293	-2437.73	-4979	17.896	0.15	-41.395
	298	-3200.15				
	303	-4713.12				
	308	-5131.60				
	313	-6381.24				
Zinc	293	-1433.83	-2224.9	8.1739	0.068	-18.497
	298	-2115.91				
	303	-2498.46				
	308	-2623.95				
	313	-3331.17				

Conclusions

The aim of this research work was to investigate the adsorption behavior of heavy metals Cu and Zn on Zeolite-Alginate composite materials. After converting coal fly ash into the zeolitic material and then transforming it to Zeolite-Alginate composite by treatment with sodium Alginate. The composite material was characterized by SEM analysis and by FTIR spectra to identify the different changes in bonding and morphology. The influence of various parameters (initial concentration, pH, temperature, contact time and Adsorbent dose) was studied and calculated the metal uptake and Percentage and analyzed through Atomic Adsorption Spectrometer. Isotherm models were applied,. Langmuir isotherm model explains the physical nature of adsorption process and Freundlich isotherm confirms the physico- chemical nature of the process. Adsorption Kinetics shows that the process follows Pseudo First order Kinetics. Thermodynamics parameters shows that the process is exothermic in nature.

It is further concluded that the material developed is a good adsorbent for heavy metal ions especially for Cu and Zn. The process may be applied for other heavy metals ions too. The process is economical and environmentally friendly.

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