Extraction Of Humic Acid From Coal And Its Application As Adsorbent For Removal Of Fe +2 , Cu +2 From Aqueous Solution

Section A-Research Paper

EXTRACTION OF HUMIC ACID FROM COAL AND ITS APPLICATION AS ADSORBENT FOR REMOVAL OF FE +2 , CU +2 FROM AQUEOUS SOLUTION

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Abstract

In the present research work Humic Acid extracted from local lignite coal collected from Thar-Sindh, Pakistan has been used as an adsorbent. Adsorption of iron and copper ions was studied at laboratory scale. The effect of contact time, adsorbent dosage, analyte concentration, pH and temperature were studied at room temperature 298.15 K (25°C). The adsorption models Langmuir and Freundlich were applied on the data, maximum adsorption capacity of copper and iron ions is found to be 5.13 mg/g and 2.66 mg/g respectively. Thermodynamic parameters like $\Delta G°$, $\Delta H°$ and $\Delta S°$ have also been determined. These values establish that the adsorption process is favorable in nature.

Keywords: Coal, Humic Acid (HA), Adsorption, Waste water

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Introduction

In recent years, the release of heavy metals has been dramatically increased by many folds, resulting from the continuing growth of urban, industrial and agricultural activities. Sewage sludge, pesticides, metallic ores, fertilizers, municipal waste, and burning fossil fuels are typically the main sources of heavy metal toxicity (Tahoon,et.al; 2020).Contamination levels may further increase due of water bodies due to bioaccumulation and bio magnification processes up to dangerous limit (Paul, D. ET AL.2017).The physicochemical characteristics of water are adversely influenced by increased level of toxic and heavy metals (Zeitoun, M. M., & Mehana, E. E. 2014). Supply of safe water free of harmful contaminants, pathogens is of vital importance for human health (Kumar Reddy, D. H., & Lee, S. M. 2012).

A number of treatment methods like precipitation, neutralization, filtration membranes, exchange of ions, adsorption etc. are exclusively being use depending upon the nature and level of contaminant species(Malik, D. S., et al 2017). However, some of these techniques, such as precipitation and ion exchange, have major disadvantages associated with their high cost, lower performance, high reagent and solvent requirements, and toxic sludge production. (Hirut Gebretsadik, et al 2020). Easy, low-priced and safe cleaning methods for the removal of heavy metals from polluted water are being explored every day.

Adsorption is a mechanism in which atoms, ions or fluid molecules bind to an appropriate interface. This technique creates on the outside of the adsorbent a film of the adsorbate (Wu, Deyi, et al 2008). A variety of materials have been used as adsorbents, such as activated carbon, clays, fly ash, Agri wastes, biomaterials, polymers and composites. (Renu, Agarwal, M., & Singh, K. 2016).Some basic properties necessary for adsorbents used include, such as elevated pollutant concentration reduction capability, high adsorption capacity, environmentally friendly and cost-effective (Al-Rub, F. A., et al 2002).

Humic acid (HA) has been used as a low-cost adsorbent for purifying waste water. Humic acid is the component of soil humus that is frequently applied to fertility-enhancing soil. Humic acid is also present in a number of soils in brown organic matter, as well as in peat, compost, lignite and brown coal. Humic acids have a broad cation exchange potential and carry monovalent and multivalent elements very powerfully (Srivastava, K. C., & Walia, D. S. 1997).

HA's are obtained by alkaline extraction at laboratory temperature from the raw material, lignite, there is no need for additional energy consumption. The preparation of HAs in the laboratory and their use as sorbents in wastewater treatment, with its low cost and low energy consumption, now provides an attractive and inexpensive alternative for the removal of colloidal and dissolved metals (Arslan, G., et al 2010).Carboxylic acids, alcohols, phenols, carbonyls, amides, are the main functional groups found in a sample of HA which may exchange with metallic ions (Erdogan, S., et al 2007). Cu (II) ions have been extracted from waste water by using HA immobilized with sodium alginate (Chen, J. H., et al 2011). Pb(II) from waste water have been extracted by using a natural mineral based adsorbent coated with Humic acid which showed excellent adsorption and regenerative capacity(Lu, M., et al 2019). Carbon and iron-based nanomaterials interacted with HA have been used to remove metallic ions from amphibian water (Tang, W. W., et al 2014). The adsorption kinetics of Cu (II) and Zn (II) from aqueous solution onto Humic Acid have been investigated showing good results (Li, Y., et al 2010).

The present study has been carried out to determine the adsorption potential of indigenous coal based Humic acid extracted via alkaline process, for the removal of heavy metals ions ,Iron (Fe^{+2}) and copper (Cu^{+2}) from aqueous solution. To ascertain optimum conditions for the elimination of heavy metal ions, effect of various factors i.e. sorbent dosage, pH, contact time, preliminary metal ion concentration and temperature have been studied through batch experiments. Langmuir and Freundlich models have been applied to data to study nature of the process. Thermodynamic parameters have also been determined.

Materials and methods
Adsorbent preparation

10 g lignite coal sample is wetted in 100 mL extracting solution, prepared by mixing 15g sodium pyrophosphate and 7g sodium hydroxide in distilled water. The mixture is heated with continuous stirring at (40 ± 5) °C on hot plate for 4 hours. After complete extraction, HCl is added to adjust pH between 1-2. The beaker is put for some time in order to settle down the brownish layer. When brown layer has settled down, solution is filtered off and residue is collected which is Humic acid.
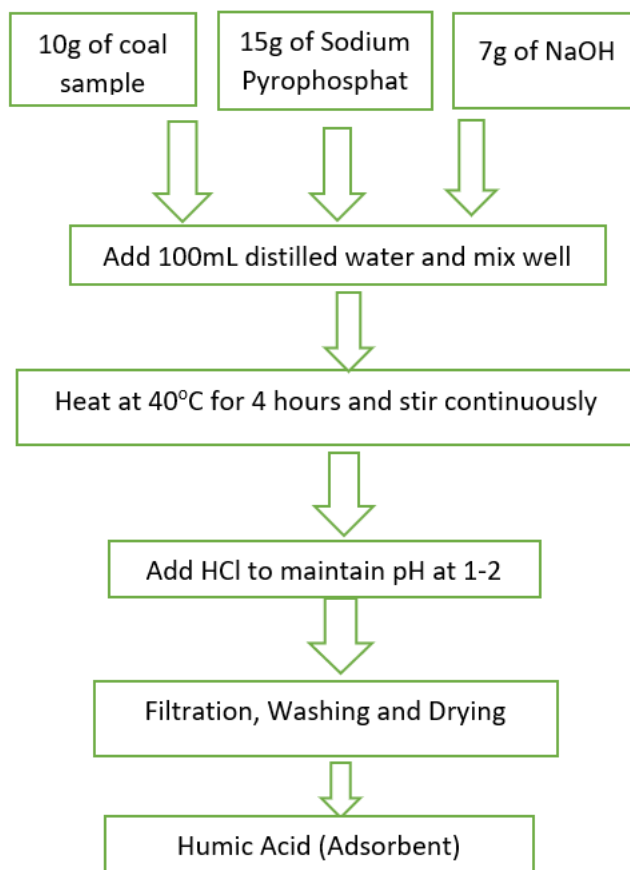
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Figure 1. Flow sheet of HA Preparation

Adsorbent Characterization
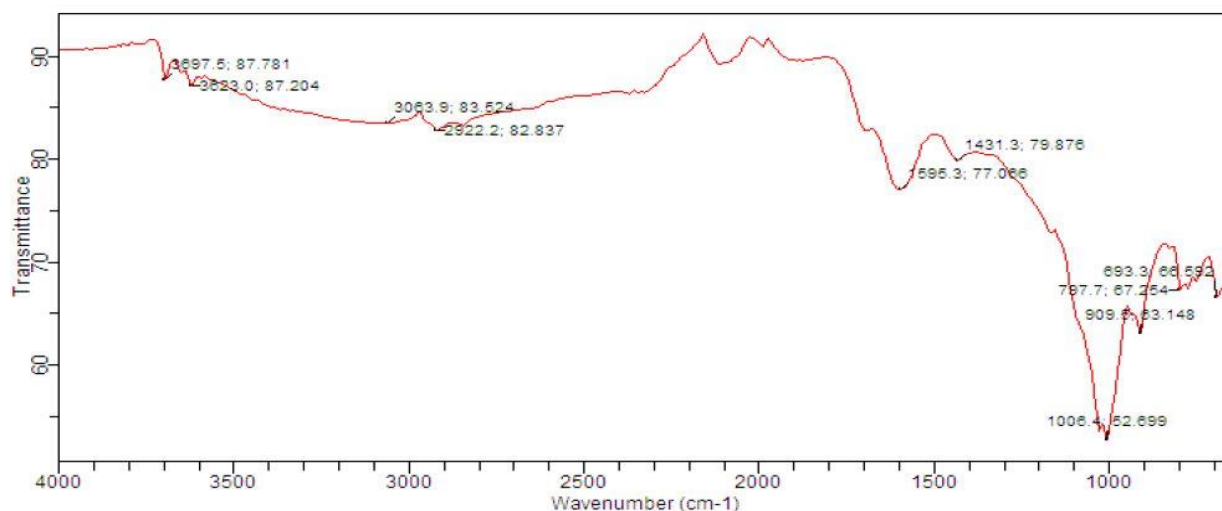## FTIR spectra for Humic acid

Figure 2. FT-IR spectrum of humic acid

FT-IR spectrum of humic acid shown in Fig 2 has been recorded in range 4,000-600cm^{-1}. The sample shows absorbance at 3600 cm^{-1} indicating the O-H stretching of alcohols/or phenols as well as N-H stretching of amines/or amides. The weaker absorption at 2822 cm^{-1} indicate the presence of C–H stretching of methyl and methylene groups (Das, T.,et al 2015). The absorbance at 1595 cm^{-1} band indicates the contribution of the C = C stretch (aromatic ring) and 1431 cm^{-1} shows characteristic band of COO- groups. The absorbance at 909cm^{-1} and 747 cm^{-1} indicates aromatic C-H out of plane deformation of aromatic structure with O-substituted benzene ring, mono-substituted benzene ring, and condensed ring systems. The peak at 1006 cm^{-1} depicts the stretching of ethers

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(C-O-C) (Zara, M., et al 2017). All these functional groups are present in Humic Acid structure which indicate that material extracted from coal through alkaline extraction resembles to that of humic acid.
Batch Experiments

Batch Experiments are conducted to remove iron and copper ions from waste solution. The parameters like adsorbent dose, pH, contact time, Initial metal ions concentration have been optimized at 298.15K (25°C).
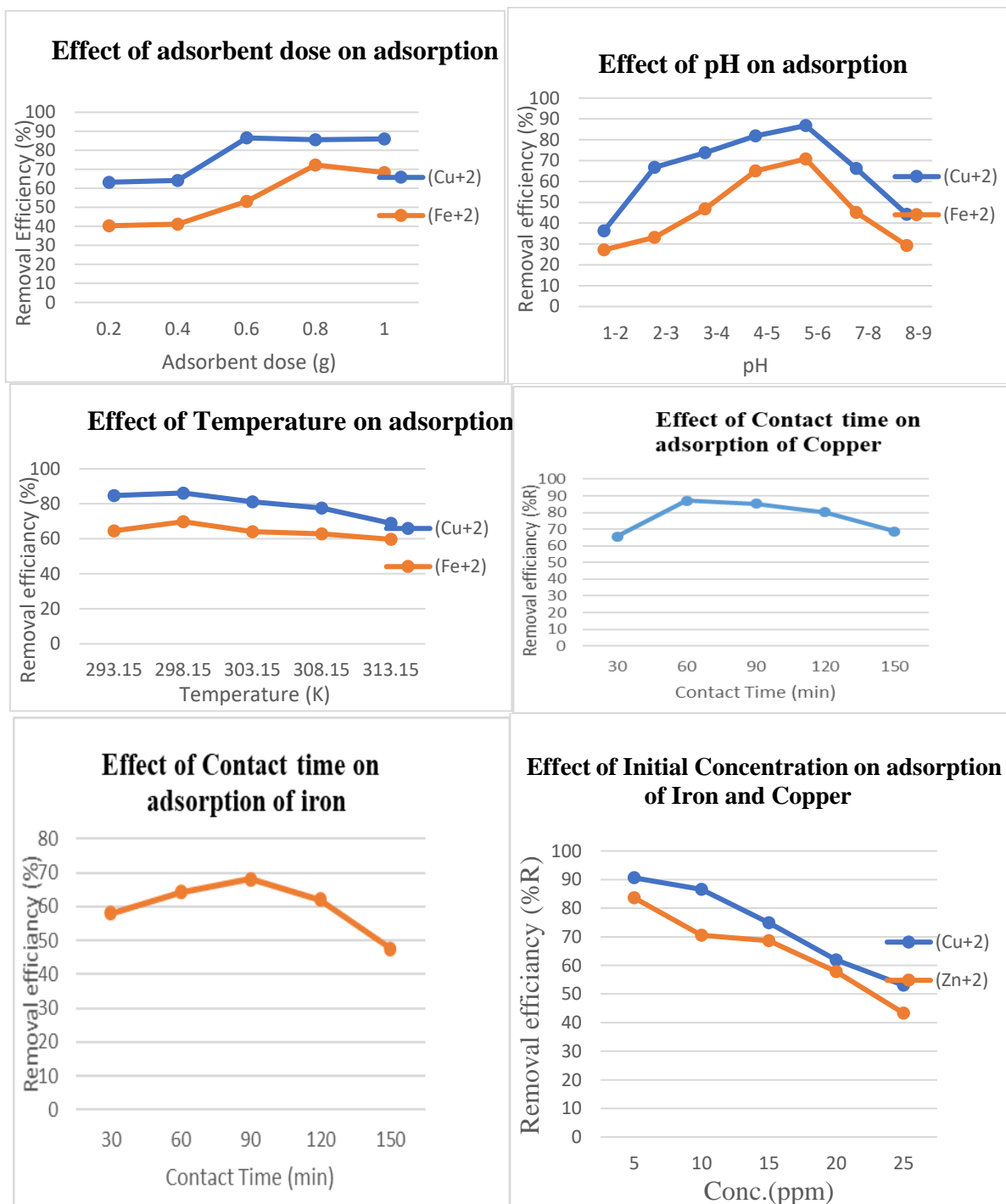

Figure 3. Optimization of parameters: (a) Effect of Adsorbent dose, (b) Effect of pH, (c) Effect of Temperature, (d) Effect of Contact time, (e) Effect of Initial concentration

RESULTS AND DISCUSSION
Process Optimization
Factors affecting adsorption of copper and iron ion on humic acid have been optimized by batch experiments. Different doses of the adsorbent (0.2,

0.4, 0.6, 0.8 and 1.0 g) are used to find the optimum dose required to adsorb maximum concentration of ions. The results of effect of adsorbent dosage have been presented in (Figure 3a). It can be noted that sorption process speeds up with increase in

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adsorbent dose and decrease after attaining optimum dose, i.e. 0.6 g for Cu^{+2} and 0.8 for Fe^{+2}.Commonly, the removal efficiency increases by increasing the amount of adsorbent dosage, due to the increasing number of accessible active sites of adsorbent. However, with rise in adsorbent dose, there is less proportionate increase in adsorption, resulting from many sites remaining unsaturated during the adsorption. Thus, with increasing adsorbent dose, the amount of adsorbate adsorbed per unit mass of adsorbent is reduced (Gorzin, F., & Bahri Rasht Abadi, M. 2017).

The effect of pH change on adsorption of iron and copper ions have been investigated in the range 1–9 and presented in the (Figure 3b). The study shows that the maximum adsorption occurs at pH 5-6. The plot of pH vs. removal efficiency show a decreasing trend towards adsorption of Cu^{+2} and Fe^{+2} ions after pH 5-6. It shows that iron and copper removal is favored at moderate pH values due to the deprotonation of functional groups that reduces repulsion forces and increases the attraction between metal ions and functional active sites of adsorbent. Though, at low pH the protonated active sites numbers increase and cause a great repulsion with positive charged metal ions that greatly reduces the adsorption capacity of the adsorbent. At very high pH values, several complexes between metal species and OH groups formed that block the large numbers of adsorbent active sites and reduce their adsorption capacity (Tahoon, M. A., et al 2020).

The effects of temperature change on adsorption of iron and copper ions have been studied in the range 293.15K to 313.15K i.e. (20°C-40°C) and shown in (Figure 3c). The study show that the maximum adsorption occurs at 298.15K i.e. 25°C. The plot of Temperature vs. removal efficiency shows a decreasing trend towards adsorption of Cu^{+2} and Fe^{+2} ions after 25°C.At high temperature, the removal efficiency decrease. This is because with increasing temperature, the attractive forces

between adsorbent surface and metal ions are weakened and the thickness of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the adsorbent surface to the solution phase, which results in a decrease in adsorption as temperature increases (Horsfall Jnr, M., & Spiff, A. I. 2005).(Figure 3d) shows the graphical representation of contact time studies taken during batch experiments. The Equilibrium is established after 60 min with removal efficiency 85.3% for Cu^{+2} and 90 min with removal efficiency 68.2% for Fe^{+2}.After 60 and 90 min removal of copper and iron decrease respectively. The reason is that the entire adsorption process takes place in two phases. First is a rapid uptake phase in which the exponential rate of adsorption is observed due to the availability of surplus binding sites and high concentration gradient. The second phase is comparatively slower, in which equilibrium is achieved due to the exhaustion of binding sites and low concentration gradient. The initial faster and higher uptake rates of metal ions are found to be significant and humic acid qualifies as a potential and efficient adsorbent for the removal of heavy metals from groundwater (Manirethan, V., et al 2019).

The effect of metal ion concentration has been studied at varying initial concentration (5–25 mg/L) while keeping all the other parameters unchanged. Figure 3e indicates the effect of initial concentration on adsorption of Cu^{+2} and Fe^{+2} ions. It can be noted that adsorption is higher at lower concentrations and vice versa. Maximum adsorption is noted at 10 mg/L with gradual decrease in sorption capacity up to 25 mg/L. This could be because at higher concentrations, as more ions are competing for the available binding sites, the rate of adsorption decreased, resulting in lower adsorption percentage (Pandey, A., et al 2007). Optimized conditions derived through batch mode experiments are summarized in (Table 1).

Table 1: Optimized parameters for Copper and Iron ions adsorption

Parameter	Adsorbent dose (g)	pH	Contact Time (min)	Concentration(ppm)	Temperature (K)
Copper	0.6	5-6	60	10	298.15
Iron	0.8	5-6	90	10	298.15

Adsorption models

Adsorption isotherms explain the nature of adsorption of the adsorbate on the surface of adsorbent. It provides information about the equilibrium established between the solute and the adsorbent. Here we will describe the Langmuir and Freundlich isotherms according to experimental data taken through batch experiments.

Langmuir model

$Ce/qe = 1/q_ob + Ce/q_e$ (Langmuir equation)

The Langmuir isotherm (Figure 4a and 4b) was constructed by plotting the data between 1/Cf and 1/Q. A straight-line having correlation coefficient (R^2) 0.593 for Cu^{+2} and 0.449 for Fe^{+2} which is an indicator of mild favorability of the adsorption process (Ho 2003).

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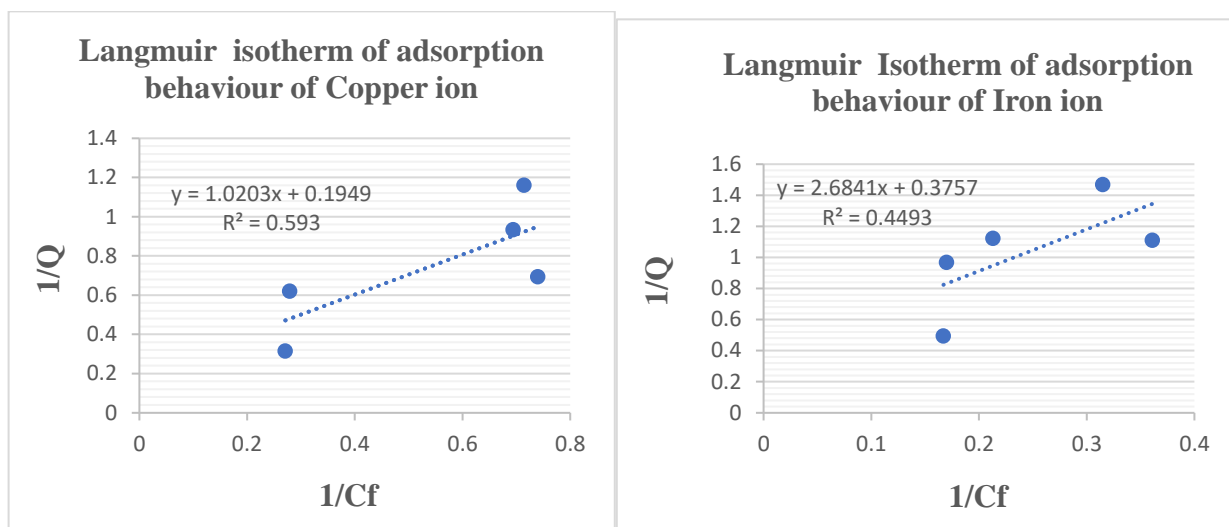
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Figure 4: Langmuir Isotherm graph (a) Langmuir isotherm graph for Cu^{+2} (b) Langmuir isotherm graph for Fe^{+2}

The Langmuir constants, i.e. q_{max} (maximum sorption capacity) and b (affinity of adsorption) were calculated from slope and intercept of the isotherm. The values of R^2 are far away from unity which is an indication that the absorption process of Cu^{+2}/Fe^{+2} is slightly physical in nature. The value of the Langmuir constant "b" should be greater than 0 and less than 1 (Zahid et al; 2017). In this case values are closer to zero hence only mild physical adsorption takes place for Fe^{+2} and Cu^{+2}. The values are shown in (Table 2).

Table 2: Langmuir constants calculated from Langmuir isotherm

Adsorbate	Slope	Intercept	q_{max}(mg/g)	b	R^2
Cu^{+2}	1.0203	0.1949	5.130	0.191	0.593
Fe^{+2}	2.6841	0.3757	2.661	0.139	0.449

Freundlich model

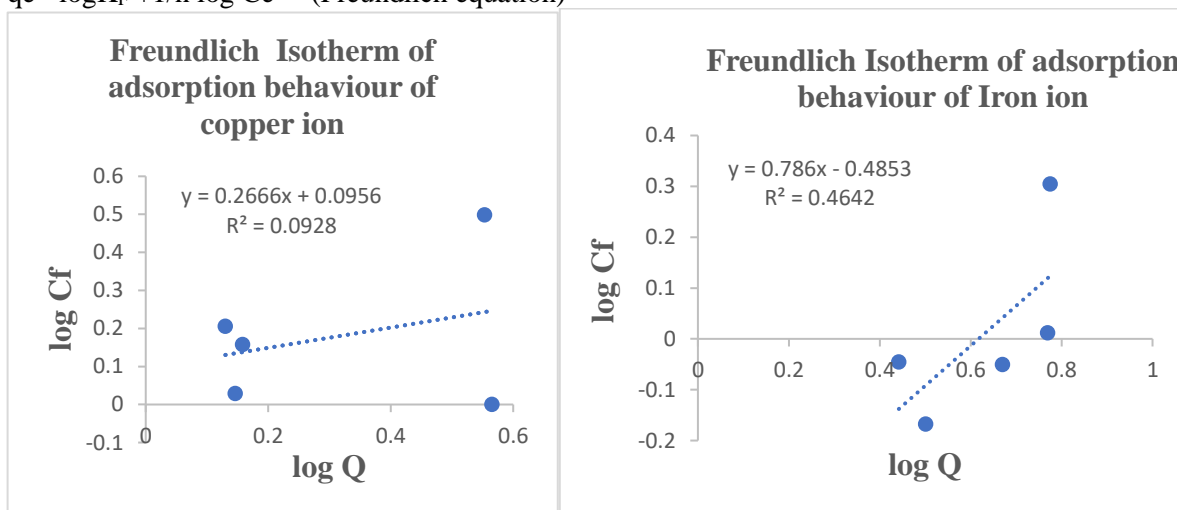Log qe =logK$_F$ +1/n log Ce   (Freundlich equation)

Figure 5: Freundlich Isotherm graph (a) Freundlich isotherm graph for Cu^{+2} (b) Freundlich isotherm graph for Fe^{+2}

The adsorption both physisorption and chemisorption is better explained by the Freundlich model. The required isotherm is constructed by plotting logq vs. logCf (Figure5a and 5b). The values of co-relation coefficient R^2 for both Cu^{+2}/Fe^{+2} are less than 1, hence the absorption process is physical in nature. There may be a weaker bonding between adsorbent and adsorbate molecule. The values of Freundlich constant should be greater than 1 and less than 10.It shows physico-chemical adsorption. (Table 3) shows that Freundlich isotherm is favorable for Cu^{+2} n=3.759

than for Fe^{+2} n=0.272, hence Cu^{+2} observes Physio-Chemical adsorption and Fe^{+2} mostly undergoes

Physical adsorption (Ho and Wang, 2008). The values are shown in Table 3.

Table 3: Freundlich constants calculated from Freundlich isotherm

Adsorbate	Slope (1/n)	Intercept (Logk_f)	kf	n	R^2
Cu^{+2}	0.2660	0.0956	1.246	3.759	0.092
Fe^{+2}	0.786	-0.4853	0.327	0.272	0.4642

Thermodynamic Parameters
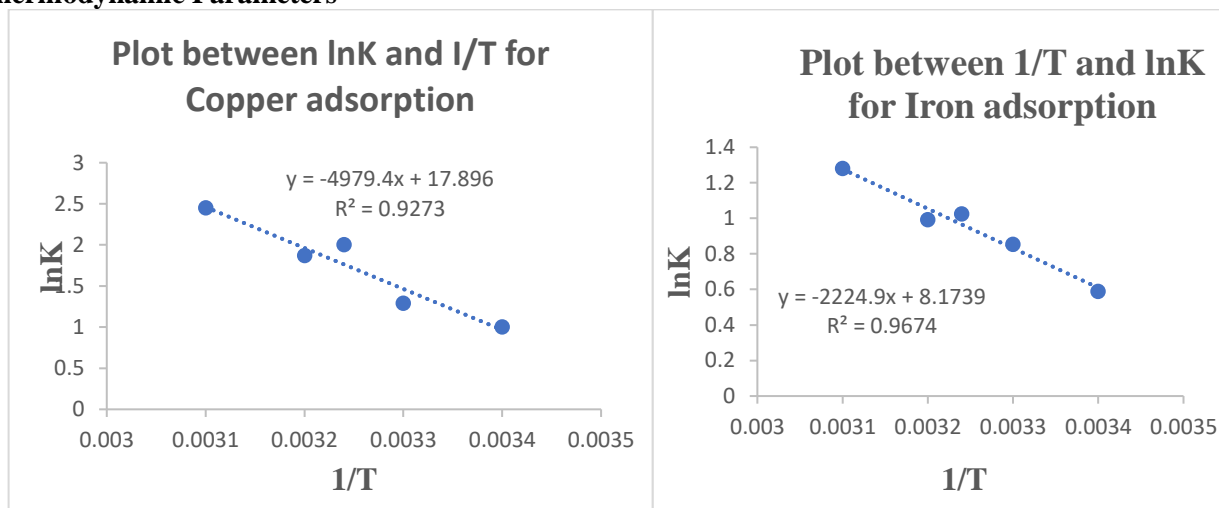

Figure 6: Thermodynamic parameters (a) Plot between lnk and 1/T for Cu^{+2} adsorption (b) Plot between lnk and 1/T for Fe^{+2} adsorption

Thermodynamic parameters, the standard enthalpy change (ΔH^0), standard entropy change (ΔS^0) and standard Gibbs free energy (ΔG^0) of adsorption, have been determined at room temperature (298.15 K). The values of thermodynamic constants are listed in (Table 4 & 5). The values of ΔS^0 (kj/mol K) and ΔH^0 (kj/mol) are calculated from the slope

and intercept of the graph (Figure 6a & 6b). Values of thermodynamic parameters show that the adsorption process is feasible and endothermic in nature with minor randomness at the adsorbent-adsorbate interface (Vadivelan and Kumar 2005, Zahid et al 2015)

Table 4: Thermodynamic constants of the adsorption of Cu^{+2} at various temperatures

Temperature (K)	ΔG^0 (kJ/mol)	Slope (ΔH^0)kJ/molK	Intercept (ΔS^0)kJ/mol	R^2
293.15	-2.62			
298.15	-3.20			
303.15	-4.71	-4979.4	17.896	0.9273
308.15	-5.13			
313.15	-6.38			

Table 5: Thermodynamic constants of the adsorption of Fe^{+2} at various temperatures

Temperature (K)	ΔG^0 (kJ/mol)	Slope (ΔH^0)kJ/molK	Intercept (ΔS^0)kJ/mol	R^2
293.15	-1.43			
298.15	-2.11			
303.15	-2.49	-2224.9	8.1739	0.9674
308.15	-2.62			
313.15	-3.33			

Conclusions

The adsorption of copper and iron ions from aqueous solution on to humic acid adsorbent have been investigated. The results show that sorption of

copper and iron ions is a feasible process with very encouraging recovery of the iron and copper under study. It can be inferred from the study that humic acid extracted from indigenous coal may be a cost-

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effective alternative for waste water treatment especially for heavy metals elimination.

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