Studies on the Removal of Cu(II) from Aqueous Solutions using Modified *Acacia nilotica* Leaf

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In this work, sustainable and biodegradable *Acacia nilotica* leaf (AN) was chemically modified to remove Cu(II) from aqueous solutions, which is considered a versatile approach to clean contaminated aquatic environments. Zinc chloride-modified *Acacia nilotica* leaf (ZAN) was characterized by scanning electron microscopy (SEM) and other physico-chemical parameters like pH_{ZPC}. The aim was to assess the efficiency and mechanism of adsorption on *Acacia nilotica via* isotherm models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Harkin-Jura, and Frenkel-Halsey-Hill), kinetic models, and thermodynamic parameters. To optimize the removal efficiency, parameters such as effect of initial concentration, effect of pH, dosage, initial concentration, and contact time were studied by batch and column methods. Desorption studies illustrated that about 73% of the metal ions could be removed using 0.2N HCl. The results of the present investigation indicated that ZAN has a high potential for the removal of Cu(II) from aqueous solutions, and the resultant data can serve as a base line for designing treatment plants on an industrial scale.

Keywords: Acacia nilotica; Copper(II); Batch; Column; Adsorption; Desorption; Isotherms; Kinetics; Thermodynamics; Binary metal; Wastewater

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INTRODUCTION

There are large amounts of heavy metals released into the environment. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. Unlike organic pollutants, heavy metals are essentially non-biodegradable and accumulate in living organisms. Metals such as Cd, Hg, Ag, Cr(VI), and Pb are extremely toxic to living beings; others, such as Cu, Zn, Mn, Fe, Ni, and Co, although essential for plants and animals, can be very harmful to living organisms when present above certain limits. In recent years, increasing concern about the effect of toxic metals in the environment has resulted in stricter environmental regulations for industries that discharge metal-bearing effluents (Kadirvelu *et al.* 2001; Algarra *et al.* 2005). One heavy metal that is toxic to humans and widely studied by many researchers is copper. Copper is considered a micronutrient but is extremely toxic to living organisms at high concentrations.

The main sources of copper pollution are metal cleaning and plating baths, paper board mills, wood pulp production, and the fertilizer industry, as well as brass materials, boiler pipe, cooking utensils, and copper from metalworking, which requires periodic oxide removal by immersing the metal in a strong acid bath. Solution adhering to the cleaned metal surface is rinsed from the metal and contaminates the waste rinse water.

Similarly, plated metal parts are rinsed and produce wastewater (Ho and McKay 2004). Copper may also be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. The World Health Organization (WHO) recommends a maximum acceptable concentration of Cu(II) of 1.5 mg/L in drinking water (Dundar *et al.* 2008). It has been reported that excessive copper intake by humans may lead to hepatic and renal damage, capillary damage, gastrointestinal irritation, and central nervous system irritation (Larous *et al*. 2005).

Copper can be removed from aqueous solutions by a precipitation method as copper hydroxide, but this method is only efficient at high pH values. Conventional methods include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, application of membrane technology, and evaporation recovery. However, these processes have considerable disadvantages including incomplete metal removal, expensive equipment and monitoring systems, large reagent or energy requirements, or generation of toxic sludge or other waste products that require disposal. Adsorption, an alternative technology for conventional wastewater treatment, has received considerable attention for the development of an efficient, clean, and cheap technology. In recent years, this attention has been focused on the removal of copper from aqueous solutions using adsorbents derived from low-cost materials (Kalavathy *et al*. 2005). Many researchers have investigated low-cost materials as viable adsorbents for heavy metal removal, namely rice husk (Wong *et al.* 2003), barks (Reddy *et al.* 1997), teak leaves powder (King *et al*. 2006), tree fern (Ho *et al.* 2002), groundnut shells (Shukla and Pai 2005), macadamia nutshell (Ahmadpour and Do 1997), holly oak (Prasad and Freitas 2000), paper mill sludge (Khalili *et al.* 2000), and *Ipomoea carnea* (Nadeem *et al.* 2006).

Activated carbon has been extensively used as an adsorbent in a variety of industrial and environmental applications. The type of precursor and the method employed for activation are the key factors that determine the quality of the carbon produced. Its adsorption capabilities have been shown to be largely determined by its surface characteristics. Two methods, physical and chemical activation, are used for the preparation of activated carbon. During physical activation, the raw material is carbonized at a high temperature. Then, it is activated by CO_2 or steam under pressure to increase the porosity and surface area of the activated carbon. In chemical activation, both carbonization and activation takes place simultaneously, in which the raw material is first impregnated with activating chemical and then carbonized at the desired temperature, which varies according to activating chemical used (Hayashi *et al*. 2008). The development of a porous structure is better in the case of chemical activation (Karim *et al.* 2006). Chemical activation is held in the presence of dehydrating reagents such as KOH, K_2CO_3, NaOH, $ZnCl_2$, H_2SO_4, and H_3PO_4, which influence pyrolytic decomposition and inhibit tar formation. The carbon yield is higher and the temperature used in chemical activation is lower than that of physical activation. Behaviors of the reagents during chemical activation have different effects on the final product. Zinc chloride is widely used as an activating reagent, since it results in high surface area and high yield. In the use of $ZnCl_2$, the activated carbons have large surface areas and more extensive micropore structure. To prepare activated carbon, a conventional heating method is usually adapted, in which the energy is produced by an electrical furnace. Essentially, vacant interstices in the carbon matrix are formed upon extensive post-heating and washing of the pores. The extent of chemical activation can significantly alter the characteristics of the produced carbons.

Modification of AN was carried out to enhance the adsorption efficiency of adsorbent for Cu(II) ions. The removal efficiency of the adsorbent was investigated and compared using both batch and column adsorption experiments. Various important parameters were studied for the optimization of the copper removal process. Kinetic, thermodynamic, and equilibrium studies were also carried out to gain a better understanding of the removal process.

EXPERIMENTAL

Materials

Collection and preparation of adsorbent

The leaves of *Acacia nilotica* used in this work were collected locally. They were shade-dried and powdered in a grinder. Six grams of dried *Acacia nilotica* were mixed with 30 mL of $ZnCl_2$. The slurry was kept at room temperature for 24 h to ensure the access of the $ZnCl_2$ to the *Acacia nilotica.* Then, the material was washed with 0.5 N HCl, hot water, and cold distilled water until the pH of the washing solution reached 6 to 7. The material was filtered and dried at varying temperatures (50, 100, 150, 200, 250, 300 and 350°C) in a hot air oven for and time (1 to 8 h). The adsorption results were found to be good at 300°C and 6 h, so these conditions were fixed for further experiments, and the adsorbent was labeled as “ZAN”. The prepared material was preserved in an air-tight container for later experimental use. Later, it was characterized by sophisticated techniques such as scanning electron microscopy (SEM).

Preparation of adsorbate

An accurate weight of 1.000 g $CuSO_4.5H_2O$ (Aldrich) was dissolved in 1 L of distilled water to produce the stock solutions of Cu(II). These stock solutions were then diluted to the required concentrations using distilled water when necessary. The stock and standard solutions were prepared freshly for all experiments.

Methods

Batch adsorption experiments

To study the effect of parameters such as adsorbent dose, initial metal ion concentration, and solution pH for the removal of Cu(II) by adsorption onto ZAN, batch experiments were performed. Stock solutions of Cu(II) in single (S) and binary (B) systems were prepared by dissolving Cu(II) (S) and Cu(II)+Co(II),Cu(II)+Cr(VI) (B) in deionized water and further diluting to 50 to 200 mg/L concentrations for the experiments. The pH was adjusted by adding 0.5 N HCl or 0.5N NaOH to the solutions with known initial Cu(II) ion concentrations. Batch adsorption experiments were conducted in 250 mL stoppered flasks containing 0.2 g of ZAN and 50 mL of Cu(II) solutions of differing concentrations (50, 100, 150, and 200 mg/L) at pH 5. The flasks were agitated using a mechanical orbital shaker and maintained at room temperature for 2 h until equilibrium was reached. The suspensions were filtered, and metal concentrations in the supernatant solutions were measured using a UV-Visible spectrophotometer (Shimadzu UV-2450) at 324nm (λ_{max}). All of the experiments were done in duplicates. The objective of the study was to investigate the adsorption of Cu(II) ions onto modified *Acacia nilotica* (ZAN). The uptake of Cu(II) by ZAN at equilibrium (q_e) was calculated by the following mass balance relationship,

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg/L) are the liquid phase concentrations of metal at initial and equilibrium, respectively, V (L) is the volume of the solution, and W (g) is the mass of adsorbent used.

Surface acidity and basicity

Surface acidity was estimated by mixing 0.2 g of ZAN with 25 mL of 0.5N NaOH in a closed flask. The flask was then agitated for 48 h at room temperature. The suspension was decanted, and the remaining NaOH was titrated with 0.5 N HCl. The surface basicity was measured by titration with 0.5 N NaOH after agitation of 0.2 g of ZAN with 0.5 N HCl. The ZAN had a surface acidity of 1.891 mmol/g and surface basicity of 3.35 mmol/g. Acidity and basicity were confirmed by the Boehm titration method, which quantifies the basic and oxygenated acidic surface groups on activated carbons (Boehm 2002).

Zero surface charges

The zero point charge of ZAN was determined by using the solid addition method (Kumar *et al.* 2008). The experiment was conducted in a series of 250 mL stoppered glass flasks. Each flask was filled with 50 mL of a $NaNO_3$ solution with a different initial pH value and 0.2 g of ZAN. The pH values of the $NaNO_3$ solutions were adjusted between 2 and 9 by adding either 0.1 N HNO_3 or 0.1 N NaOH. The suspensions were then sealed and shaken for 2 h at 160 rpm. The final pH values of the supernatant liquid were noted.

RESULTS AND DISCUSSION

Characterization of Adsorbents

Zero surface charges

The influence of the solution pH on the metal uptake can be explained on the basis of the pH zero point charge of the adsorbent. The pH value necessary to affect a net zero point charge on a solid surface in the absence of specific sorption is called the point of zero point charge (pH_{ZPC}). The difference between the initial pH (pH_0) and final pH (pH_f) values ($pH = pH_0 - pH_f$) was plotted against the values of pH_0. The point of intersection between the resulting curve and the abscissa provides the pH_{ZPC}. The zero point charge was 4.10 for ZAN, which was below the solution pH (pH 5).Therefore, the negative charge density on the surface of ZAN increased, which favors the adsorption of cationic metal ions (Janos *et al.* 2003). This result indicates that the pH_{ZPC} of ZAN depends on the raw material and the activated carbon.

Scanning electron microscopy (SEM) studies

Scanning electron micrographs (Jeol jsm-6390 model at an accelerating voltage of 20KV) with a magnification of ×1000, ×3000, ×1500 of RAN (Raw *Acacia nilotica i.e.,* without any modification with $ZnCl_2$), ZAN, and ZAN with Cu respectively are shown in Figs. 1a, b, and c. It is clear from the SEM images that the external surfaces of three samples were rough and contained abundant porous structures of different sizes and shapes. Additionally, the pore walls of the carbon contained narrow pores, which are responsible for high surface area and high adsorption capacity. The micrographs showed that, during carbonization of the *Acacia nilotica* leaf impregnated with $ZnCl_2$, the volatile matter developed high pressure, which burst the cellular structure of the particle and created cavities on the surfaces of the carbon samples shown by arrows in the Figs. It also caused the evaporation of $ZnCl_2$ during carbonization, leaving open space that was previously occupied by $ZnCl_2$. During impregnation, the molecules of the chemical impregnating agent diffused into the lignocellulosic material. During carbonization at the desired temperature, the chemical impregnating agent evaporated, rendering the remaining carbon porous.

Table 1. Physico-chemical Characteristics of Activated *Acacia nilotica* Leaves

Parameters	Values	Parameters	Values
Moisture content (%)	8.992	Water-soluble matter (%)	13.04
Ash content (%)	9.125	Conductivity (µS cm^{-1})	0.259
pH	7.034	Zero point charge (pH_{ZPC})	4.10
Decolorizing power (mg g^{-1})	1.243	Apparent density (gm L^{-1})	0.389
Specific gravity	1.278		

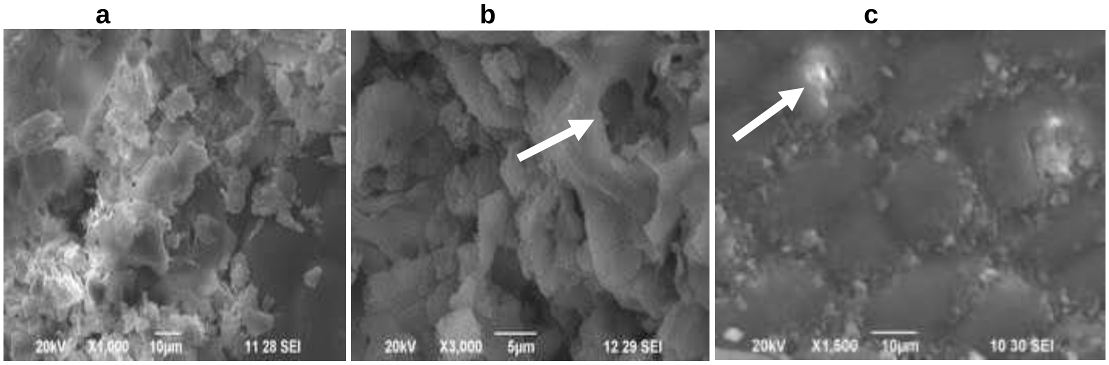


Fig. 1. SEM images of (a) RAN,(b) ZAN without Cu(II), and (c) ZAN with Cu(II)

Effect of pH

The solution pH affected the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. The influence of pH on the adsorption of Cu(II) is presented in Fig. 2. These results indicated that an increase in pH had a positive effect on the metal uptake up to pH 5, since the competition between protons and metal cations for the active sites of the biomass decreased. The maximum adsorption of Cu(II) ions on ZAN was observed at pH 5. Above pH 5, Cu(II) adsorption significantly decreased and Cu(II) was precipitated as its hydroxide complexes (Ho *et al.* 2002). At very low pH values, copper adsorption was very low due to competition between H_3O^+ and Cu(II) ions for adsorption sites. As pH increased, more adsorbent surface was exposed and carried negative charges, which resulted in less repulsion of Cu(II) ions.

The effect of pH can be explained in terms of pH at the zero point charge (pH_{ZPC}) and Cu(II) speciation in the solution. The pH at which the charge of the solid surface is zero is referred to as the pH_{ZPC}. Above pH_{ZPC}, the surface charge of the adsorbent is negative, and below it, the surface charge is positive. The amount of adsorption above pH_{ZPC} was maximum because of the interaction of Cu^{2+} and $Cu(OH)^+$ with the positively charged ZAN. At a low pH, particularly below pH_{ZPC}, the positively charged Cu^{2+} and $Cu(OH)^{+}$ species may repel adsorbent surfaces carrying an equal charge and thereby decrease the Cu(II) adsorption. Earlier works have reported a similar pattern for the influence of pH on the adsorption of heavy metals (Krishnan and Anirudhan 2002).

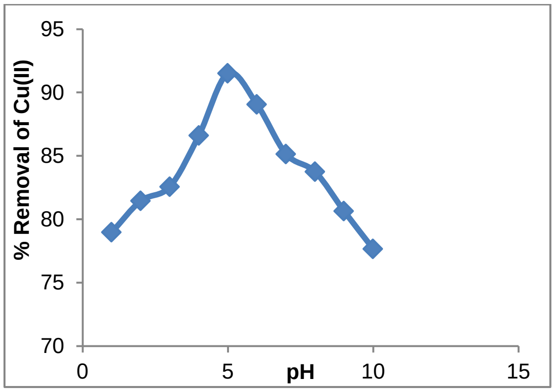


Fig. 2. Effect of pH on ZAN

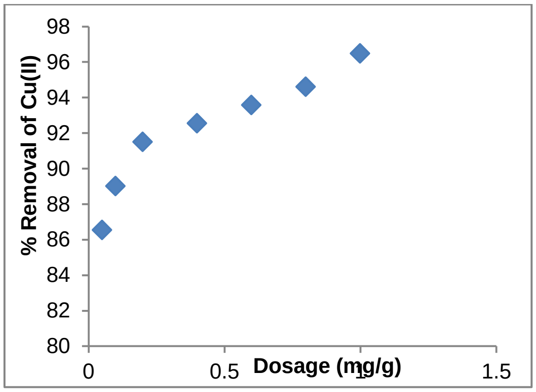


Fig. 3. Effect of dosage on ZAN

Effect of Dosage

Different amounts of both of the adsorbents varying from 0.2 to 1 g/50mL of solution with a copper concentration of 50 mg/L were used to optimize the required amount of adsorbent under the prescribed conditions for maximum uptake. It is shown in Fig. 3 that adsorption capacity increased with an increase in dosage of the adsorbent. This is due to the fact that more adsorbent creates more active sites onto which more copper is adsorbed onto ZAN. The difference in adsorption capacity (q_e (mg/g)) at the same initial metal ion concentration, adsorbent dose, and contact time may also be attributed to the difference in their chemical affinities and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent.

Effect of Initial Concentration and Contact Time

Contact time is an important parameter because this factor determines the adsorption kinetics of an adsorbent at a given initial concentration. The effect of contact time on heavy metal ion adsorption by ZAN was investigated for different times, and the results are shown in Fig. 4. It was observed that the uptake of Cu(II)ions were increased rapidly by increasing the contact time from 5 to 135 min and reached equilibrium after 110 min. The initial rapid phase of adsorption with time indicated that there were a large number of vacant sites and as a result there existed a concentration gradient between adsorbate in the solution and adsorbate in the adsorbent surface. As time proceeded, this concentration gradient was reduced due to the accumulation of Cu(II) ions on the vacant sites, causing a decrease in the adsorption rate after 110 to 135 min.

Different initial concentrations of copper solution varying from 50 to 200 mg/L with 0.2 g of adsorbent were used to optimize the required contact time under the prescribed conditions for maximum uptake. At higher concentrations, more Cu ions were left unabsorbed in the solution due to the saturation of binding sites. This appeared to be due to the increase in the number of ions competing for available binding sites in the adsorbent (Puranik and Paknikar 1999; Khalid *et al.* 2000).

Effect of Temperature on the Uptake of Copper

To investigate the effect of temperature on ZAN, experiments were carried out with five different concentrations of the Cu(II) ion 50, 100, 150, and 200 mg/L at four different temperatures (283, 293, 313, and 323 K). As shown in Fig. 5, the adsorption capacity of the adsorbents increased with increasing temperature, consistent with an endothermic process. The highest capacity was observed on ZAN at 323K (39.21 mg/g). A possible chemical explanation for this finding is that deprotonation reaction occurred readily at high temperatures, which made more positive groups (amino and carboxyl groups) available for metal removal. The increasing temperature likely influenced the internal structure of the adsorbent and simplified the ion distribution in the adsorbent's interspatial structure.

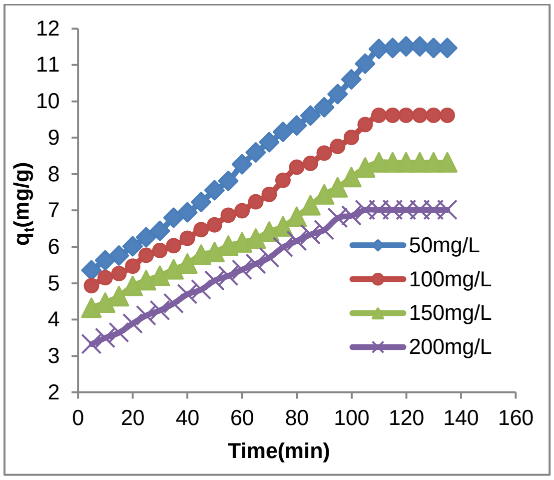


Fig. 4. Effect of contact time and initial concentration on ZAN

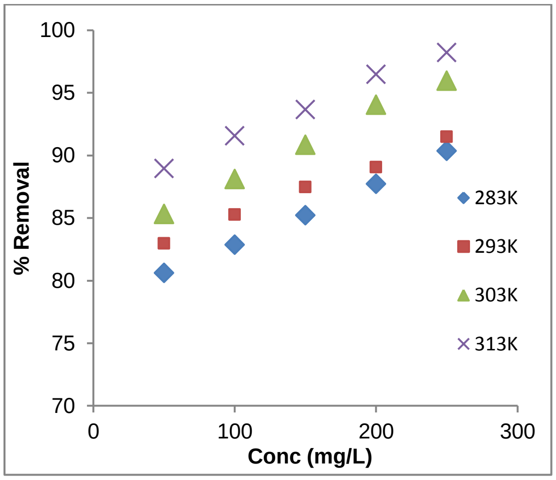


Fig. 5. Effect of temperature on ZAN

Adsorption Isotherm Studies for Cu(II)

The capacity of the adsorption isotherm is fundamental and plays an important role in the determination of the maximum capacity of adsorption. It also indicates how efficiently carbon will adsorb the solute and allows for an estimate of the economic viability of the commercial application of the carbon for the specified solute. For the considered system, an adequate model that can reproduce the experimental results has been created, considering the equations of Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Harkin-Jura, and Frenkel-Halsey-Hill.

Langmuir isotherm

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces (Langmuir 1918) and the Langmuir adsorption isotherm has been successfully applied to many sorption processes. The Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate on the plane of the surface (Dogan *et al.* 2000). Therefore, the Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir nonlinear equation is commonly expressed as:

$$q_{\mathrm{e}} = \frac{(Q_{\mathrm{m}} K_{\mathrm{a}} C_{\mathrm{e}})}{(1+K_{\mathrm{a}} C_{\mathrm{e}})} \tag{2}$$

In Eq. 2, C_e and q_e are defined as in Eq. 1, Q_m is a constant and reflects complete monolayer coverage (mg/g), and K_a is an adsorption equilibrium constant (L/mg) that is related to the apparent energy of sorption. The Langmuir isotherm (Langmuir 1916) assumes monolayer adsorption onto a surface containing a finite number of adsorption sites. The Langmuir isotherm (Eq. 2) can be linearized into the following form (Kinniburgh 1986; Longhinotti *et al.* 1998):

$$\frac{c_e}{q_{\mathrm{e}}} = \frac{1}{K_{\mathrm{a}} Q_{\mathrm{m}}} + \frac{c_{\mathrm{e}}}{Q_{\mathrm{m}}} \tag{3}$$

A plot of $C_\mathrm{e}/q_\mathrm{e}$ *versus* C_e should indicate a straight-line slope of $1/Q_\mathrm{m}$ and an intercept of $1/K_\mathrm{a}Q_\mathrm{m}$. Table 2 shows the values of the coefficient of determination (R^2), sorption capacity (Q_m), and sorption energy (n) calculated from the plot. The obtained value of Q_m was equal to 38.31mg/g. This sorption capacity of adsorbent is high compared to recorded sorbents (Table 5). The correlation coefficient (R^2) was 0.9746, which is slightly less than that of the Freundlich isotherm (0.9955).

Freundlich isotherm

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on a heterogeneous surface or possibly through a multilayer adsorption mechanism, and the adsorption capacity is related to the concentration of metal ions at equilibrium (Freundlich 1906). The Freundlich equation can be given as,

$$q_{\mathrm{e}} = K_{\mathrm{f}} C_{\mathrm{e}}^{\frac{1}{n}} \tag{4}$$

where q_e is the amount of adsorbate at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_f is the Freundlich adsorption constant related to adsorption capacity of the adsorbent, and $1/n$ is the adsorption intensity. A linear form of the Freundlich equation is generally expressed as follows:

$$\log q_{\mathrm{e}} = \log K_{\mathrm{f}} + \frac{1}{n} \log c_{\mathrm{e}} \tag{5}$$

The values of K_f and $1/n$ were calculated from the intercept and slope of the plot of $\ln q_\mathrm{e}$ *versus* $\ln C_\mathrm{e}$. Table 2 shows the calculated Freundlich parameters.

Temkin isotherm

Temkin and Pyzhev considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms, and suggested that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to these interactions (Temkin and Pyzhev 1940). The Temkin isotherm has been used in the following form,

$$q_{\mathrm{e}} = \frac{RT}{b \ln(AC_e)} \tag{6}$$

where A is the equilibrium binding constant (L/g), b is related to the heat of adsorption (J/mol), R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). Equation 6 can be written in the following form:

$$q_\mathrm{e} = \beta \ln \alpha + \beta \ln c_\mathrm{e} \tag{7}$$

$$\beta = \frac{RT}{b} \tag{8}$$

The Temkin isotherm was found to fit quite well with the experimental data, as evident from the values of coefficients of determination. For ion-exchange mechanism, the bonding energy range is reported to be 8 to 16 KJ/mol, and physiosorption processes are reported to have adsorption energy less than −40 KJ/mol. In our study, the value of b showed that the adsorption process involved physiosorption. The Temkin adsorption isotherm parameters were calculated, and the values are summarized in Table 2.

Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich(D-R) equation can be expressed (Acemioglu 2004) as,

$$q_\mathrm{e} = q_\mathrm{m} - \frac{1}{K\varepsilon^2} \tag{9}$$

where ε (the Polanyi potential) is equal to RT ln (1 + 1/C_e), q_e is the amount of the dye adsorbed per unit activated carbon (mol/g), q_m is the theoretical monolayer saturation capacity (mol/g), C_e is the equilibrium concentration of the dye solution (mol/L), K is the constant of the adsorption energy (mol^2/kJ^2), R is the gas constant (8.314 KJ/mol K), and T is the temperature (K). The linear form of the D-R isotherm is:

$$\ln q_\mathrm{e} = \ln q_\mathrm{m} - K\varepsilon^2 \tag{10}$$

The term K is related to the mean adsorption energy E (kJ/mol), as discussed by (Hobson 1969). The apparent energy of adsorption E can be used to judge the adsorption mechanism as physical or chemical ion exchange. A sorption process is generally considered as physical if E<8 KJ/mol and as chemical when the E value lies between 8 and 16 KJ/mol. The apparent energy of adsorption E for Cu(II) ion was 0.3853 J/mol, indicating a physiosorption process. The value of the coefficient of determination was 0.8788, indicating that the Dubinin–Radushkevich isotherm gave a good fit to the sorption process. The mean free energy of sorption (E) was calculated from the following equation:

$$E = \frac{1}{\sqrt{2K}} \tag{11}$$

The calculated D-R adsorption isotherm parameters are summarized in Table 2.

Harkin-Jura adsorption

The Harkin-Jura adsorption isotherm can be expressed as,

$$\frac{1}{{q_e}^2} = \left(\frac{B_2}{A}\right) - \left(\frac{1}{A}\right) \log C_e \tag{12}$$

where B_2 is the isotherm constant and $1/{q_e}^2$ is plotted *versus* log C_e. This isotherm explains the multilayer adsorption by the existence of a heterogeneous pore distribution.

Frenkel-Halsey-Hill isotherm

The Frenkel-Halsey-Hill isotherm can be expressed as,

$$\ln q_e = \frac{1}{n} \ln K - \frac{1}{n} \ln C_e \tag{13}$$

where q_e is plotted *versus* ln C_e. This isotherm describes multilayer adsorption by the existence of a heterogeneous pore distribution in the adsorbent.

Adsorption isotherms describe the interaction of adsorbate with adsorbent materials, and are critical for optimization of the adsorption mechanism pathways (Foo and Hameed 2010). Therefore, the correlation of equilibrium data by empirical equations is essential to the practical design and operation of adsorption systems (Carrasquero-Duran and Flores 2009). The experimental data were modeled using Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Harkin-Jura, and Frenkel-Halsey-Hill isotherm models. Isotherm parameters for the adsorption of Cu(II) onto ZAN are summarized in Table 2. The applicability of Freundlich and Frenkel-Halsey-Hill isotherm models suggests that the adsorption takes place on heterogeneous surfaces.

Table 2. Isotherm Constants for Cu(II) Adsorption onto ZAN

Isotherm Model	Constants and Correlations	Experimental Values
Langmuir	Q_m (mg g^{-1})	38.3142
	b (L mg^{-1})	0.08463
	R^2	0.9746
Freundlich	$1/n$	0.3088
	K_f (mg g^{-1})	1.1542
	R^2	0.9955
Dubinin-Radushkevich	Q_m (mg g^{-1})	185.42
	K (×10^{-5} mol^{2}KJ^{-2})	3.3684
	E (KJ mol^{-1})	0.3853
	R^2	0.8788
Temkin	α (L mg^{-1})	4.9725
	β (mg L^{-1})	0.1573
	b	15856.3
	R^2	0.9624
Harkin-Jura	A	204.1
	B	2.1151
	R^2	0.9418
Frenkel-Halsey-Hill	$1/n$	3.2235
	K	6.4141×10^{-3}
	R^2	0.9955

Adsorption Kinetics

Kinetic models describe the rate of adsorbate uptake on activated carbon. In order to identify the potential rate-controlling steps involved in the process of adsorption, four kinetic models were studied and used to fit the experimental data from the adsorption of

Cu(II)ion onto ZAN. These models are the pseudo-first-order, pseudo-second-order, Elovich, and intra-particle kinetic models.

Pseudo-first-order kinetic model

The pseudo-first-order equation of Lagergren is generally expressed as follows (Crini *et al.* 2007; Ozacar and Sengil 2005):

$$\frac{t}{qt} = \frac{1}{K_2 q_e} + \frac{1}{q_e}(t) \tag{14}$$

After integration and applying boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$; the integrated form of the above equation becomes:

$$q_t = \left(1 - \frac{1}{K_1 t}\right) \tag{15}$$

However, Eq.15 transformed into its linear form for use in kinetic analyses of data can be expressed as,

$$\ln(q_e - q_t) = \ln(q_e) - \frac{K_1}{2.303t} \tag{16}$$

where q_e (mg/g) and q_t (mg/g) are the amount of adsorbed adsorbate at equilibrium and at time t, respectively, and k_1 (1/min) is the rate constant of pseudo-first-order adsorption. Straight-line plots of log ($q_e - q_t$) against t of Eq.16 were created.

The data for the pseudo-first-order kinetic model of Cu(II) onto ZAN are summarized in Table 3. To obtain the rate constants, the values of log ($q_e - q_t$) were linearly correlated with time. The plots of log (q_e-q_t) versus time (t) indicated that the data did not fit well to the first-order rate expression for Cu(II) ion since the coefficient of determination was 0.4608. As presented in Table 3, the experimental value q_e (exp) 11.44 mg/g for Cu(II) was not in agreement with the calculated q_e value of 20.6395 mg/g, indicating that the metal ion adsorption onto the AN cannot be represented by a first-order kinetics.

Pseudo-second-order kinetic model

The rate of sorption was found to be consistent with a second-order model, and the pseudo-second-order chemisorptions kinetic rate equation can be expressed as,

$$\frac{dq_t}{dt} = K_2(q_e - q_t) \tag{17}$$

where q_e and q_t (mg/g) are the sorption capacities at equilibrium and at time t, respectively, and k_2 is the rate constant of pseudo-second-order sorption (g/mg/min). In this equation, h can be regarded as the initial sorption rate as q_t/t tends to zero, hence:

$$h = K_2 {q_e}^2 \tag{18}$$

Equation 18 can be written as:

$$\frac{t}{q_{\mathrm{t}}} = \frac{1}{K_2 q_{\mathrm{e}}} + \frac{1}{q_{\mathrm{e}}}(t) \qquad (19)$$

Equation 18 does not have the problem of assigning an effective q_e. If pseudo-second-order kinetics is applicable, then the plot of t/q_t against t of Eq.19 should give a linear relationship, from which q_e, k, and h can be determined from the slope and intercept of the plot, and there is no need to know any parameter. The q_e and k_2 values were estimated from the slope ($1/q_e$) and intercept ($1/k_2q_e^2$) of the linear plot of t/q_t *versus* t.

The data for the pseudo-second-order kinetic model of Cu(II) onto ZAN are summarized in Table 3. The correlation coefficient for pseudo-second-order kinetic model obtained was 0.9955, which was greater than for pseudo first- order model. In addition, the experimental q_e(exp) 11.44 mg/g values also agreed well with the calculated q_e value of 13.422 mg/g (see Table 4). This indicates that the adsorption system studied belongs to the second-order kinetic model.

Intra-particle diffusion model

The adsorption of Cu(II) onto ZAN may be controlled *via* external film diffusion at earlier stages and later by particle diffusion. The possibility of intra-particle diffusion resistance was identified using the following intra-particle diffusion model (Weber and Morris 1963),

$$q_{\mathrm{t}} = K_{\mathrm{diff}}\sqrt{t} + c \qquad (20)$$

where K_{diff} is the intra-particle diffusion rate constant (mg/g.min$^{1/2}$) and C is the intercept. The values of q_t correlated linearly with the values of $t^{1/2}$ and the rate constant K_{diff} directly calculated from the slope of the regression line. The data for the intra-particle kinetic model of Cu(II) onto ZAN are summarized in Table 3.

The linearity of the plots demonstrated that intra-particle diffusion played a significant role in the uptake of Cu(II) onto ZAN. The coefficient of determination was 0.9593, which indicates the linearity for the adsorption of Cu(II); however, Ho (2003) has shown that if intra-particle diffusion is the sole rate-limiting step, it is essential for the plot of q_t *versus* $t^{1/2}$ to pass through the origin, which was not the case. It may be concluded that surface adsorption and intra-particle diffusion were concurrently operating during the ZAN interactions. Hence, intra-particle diffusion is not a fully operative mechanism in the sorption of Cu(II) onto ZAN.

Elovich kinetics

Elovich kinetics is another rate equation based on the adsorption capacity generally expressed as follows,

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = B_{\mathrm{E}} - \mathrm{e}^{A_{\mathrm{E}} q_{\mathrm{t}}} \qquad (21)$$

where B_E is the initial adsorption rate constant (mg (g/min)) and A_E is the desorption constant (g/mg) during any experiment. The expression can be simplified by assuming $A_EB_E >> t$. By applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = t$ at $t = t$, Eq. 21 becomes:

$$q_{\mathrm{t}} = \frac{1}{A_{\mathrm{E}}}\ln(B_{\mathrm{E}}A_{\mathrm{E}}) + \frac{1}{A_{\mathrm{E}}}\ln(t) \tag{22}$$

If Cu(II) adsorption by ZAN fits the Elovich model, then a plot of q_{t} *versus* ln(t) should yield a linear relationship with a slope of (1/A_{E}) and an intercept of (1/A_{E}) ln ($A_{\mathrm{E}}B_{\mathrm{E}}$). Thus, the constants can be obtained from the slope and intercept of the straight line.

The constants obtained from the slope and intercept are shown in Table 3. The parameter 1/A_{E} is related to the number of sites available for adsorption, while (1/A_{E}) ln ($A_{\mathrm{E}}B_{\mathrm{E}}$) is the adsorption quantity when ln(t) is equal to zero, *i.e.*, the adsorption quantity when t is 1 min. This value is helpful in understanding the adsorption behavior of ZAN (Weber 1963). In the case of using the Elovich equation, the coefficients of determination were lower than those of the pseudo-second-order equation. The Elovich equation does not predict any definite mechanism, but it is useful in describing adsorption on highly heterogeneous adsorbents.

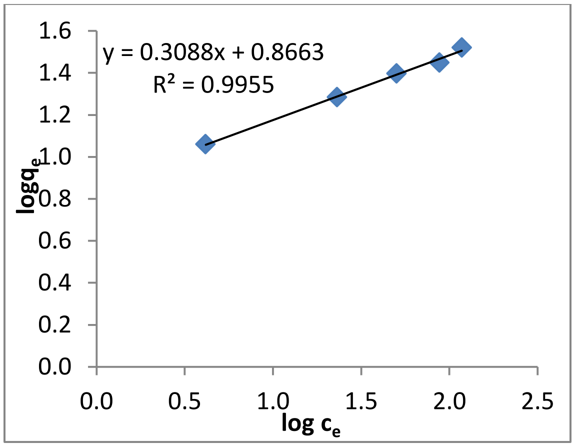


Fig. 6. Freunlich Isotherm of Cu(II) on ZAN

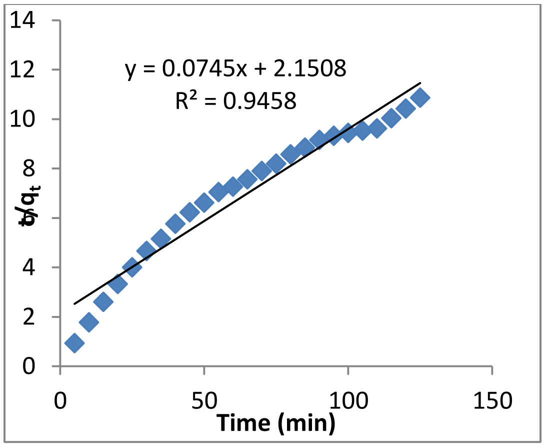


Fig. 7. Pseudo second order kinetic model of Cu(II) onto ZAN

Table 3. Kinetic Parameters for the Adsorption of Cu(II) onto ZAN

Kinetic Models	Constants and Correlations	Experimental Values
Pseudo-first-order	K_1 (min)	0.0193
	q_e (mg g^{-1})	20.6395
	R^2	0.3696
Pseudo-second-order	K_2 (g mg^{-1}min^{-1})	0.012
	q_e (mg g^{-1})	13.422
	R^2	0.9458
Elovich equation	A_E	2.1944
	B_E	8.8125
	R^2	0.8310
Intra-particle diffusion	K_{diff}	1.2121
	C	2.6771
	R^2	0.9554

Thermodynamic Studies

Adsorption studies in the temperature range 283 to 313 K were conducted to determine thermodynamic constants such as Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) for the system and to ascertain the sorption mechanism. For this study, the selected adsorbent dosage was 0.2 g and the Cu(II) concentration was 50 mg/L with pH 5 in a stoppered conical flask. It was allowed to equilibrate for 2 h at different temperatures ranging from 283 to 323 K. The Gibbs free energy change of the process is related to the equilibrium constant by the following equation (Ozcan *et al.* 2006).

$$\Delta G^{\circ} = -RT\ln K_{\mathrm{d}} \tag{23}$$

$$\ln K_{\mathrm{d}} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{24}$$

where K_d is the distribution coefficient for adsorption; $\Delta S°$, $\Delta H°$, and $\Delta G°$ are the changes of entropy, enthalpy, and Gibbs energy, respectively; T (Kelvin) is the temperature; and R (8.314 J/mol/K) is the gas constant. The values of $\Delta H°$ and $\Delta S°$ were determined from the slopes and intercepts of the plots of $\ln K_d$ *versus* $1/T$ (Fig. 6). The negative $\Delta G°$ values, 0.567, 0.645, 0.835, and 1.112 kJ/mol for 293, 303, 313, and 323 K, respectively, increased with increasing temperature, indicating the feasibility and spontaneity of the adsorption process. The positive value of $\Delta H°$ (12.454 kJ/mol) confirmed the endothermic nature of the adsorption process, while the positive value of $\Delta S°$ (41.92 J/mol/K) revealed the increase in randomness at the solid-solution interface during the adsorption process (Zou *et al*. 2006; Gupta *et al.* 2002).

The Competitive Adsorption of Cu(II) in Binary System

The effects of the presence of ZAN on the adsorption of Cu(II) along with a comparison of the adsorbed quantity of Cu(II) onto ZAN in single system(S) at equilibrium between the solutions with Co(II) and Cr(VI) present in the binary system (B) were investigated. In the binary system, a working metal ion (Cu(II)) was used as the main metal, the initial concentration of which remained unaltered while the concentrations of the other two metal ions ($Co^{2+}$and Cr^{6+}) were varied from 10 to 50 mg/L to determine the maximum adsorption. The proposed binary mixtures were in the following combinations: $Cu^{2+}/Co^{2+}$and Cu^{2+}/Cr^{6+}. The adsorption experiment was carried out in a similar fashion as was performed for the single metal ion system (S). It can be seen from Fig. 9 that there was a considerable reduction in the metal sequestering ability of the adsorbents in the binary system compared with the single metal system (*e.g.*, percentage removal of Cu(II) onto S was 92% for ZAN, and the percentage removal of Cu(II) onto for binary (Cu^{2+}/Co^{2+} 23.4%, Cu^{2+}/Cr^{6+}) was 19.2%. It was observed that chromium was preferentially adsorbed over cobalt in B. The results were likely due to the high adsorption affinity of Cr(VI) onto ZAN. Adsorption in multi-component systems is complicated because of the fact that solute-surface interactions are involved. The second metal ion present in the aqueous solution competes with the single metal ion adsorption.

A fixed quantity of Cu(II) onto ZAN(B) could only have access to a finite number of surface binding sites, some of which would be expected to be saturated by the competing metal ion solutions. In the case of the binary metal ion (B) solution, the binding sites were competitively divided among the various metal solutions (Filipovic-Kovacevic *et al*. 2000; Sheng *et al*. 2007).

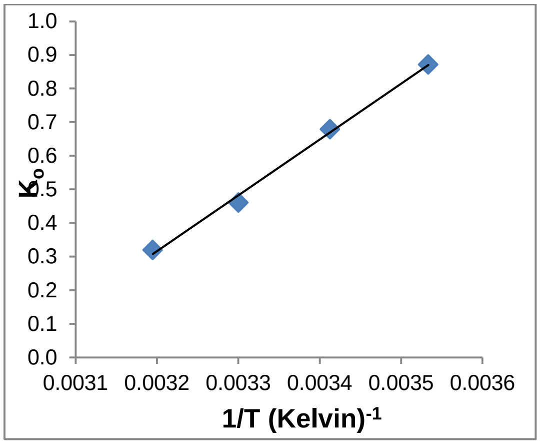


Fig. 8. Effect of temperature of Cu(II) on ZAN

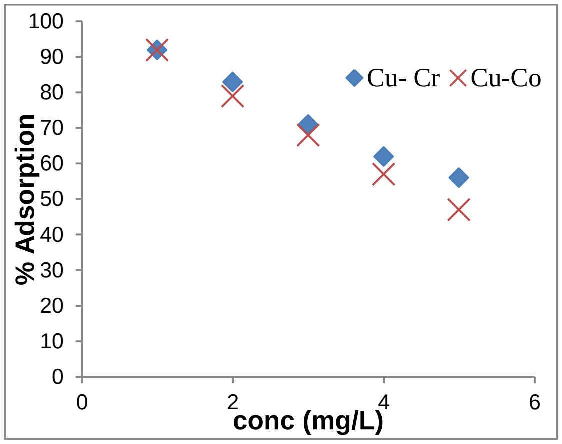


Fig. 9. Adsorption of Cu(II) onto ZAN in binary metal systems

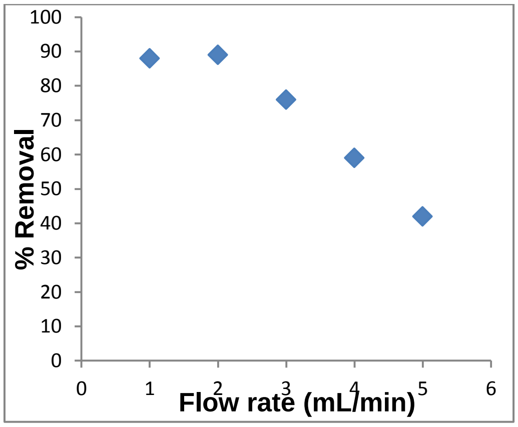
Results of Column Experiment

Effect of flow rate

Experiments were performed where the flow rates were 1 to 5 mL/min and the thickness of the adsorbent was 3 mm. As depicted in Fig. 10, the lower the flow rate, the higher the Cu(II) removal. This is due to the greater contact time when the flow rate is low.

Effect of bed thickness

The removal of Cu(II) by *Acacia nilotica* was in a fixed bed composite of different thickness of ZAN (amount) at a constant flow rate of 1 mL/min. As shown in Fig. 11, increasing the thickness of the fixed bed layer increased the uptake of Cu(II) ions.



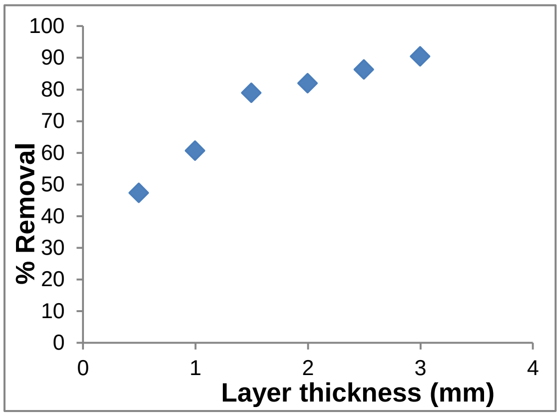


Fig. 10. The effect of flow rate (mL/min) on of Cu(II) adsorbed onto ZAN

Fig. 11. The effect of layer thickness on amount amount of Cu(II) on adsorbed onto ZAN

Increasing the fixed bed layer increased the amount of available interaction sites for adsorption of Cu(II) ions on the composite and provided a thicker layer. The efficiency was increased by allowing sufficient time for the adsorbate to diffuse into the adsorbent. When the thickness of the layer of the composite was increased from 0.5 mm to 3 mm, the percentage removal increased from 36% to 76%. Compared with its efficiency in batch mode, the prepared adsorbent displayed the advantage of separation convenience when a fixed bed column was used. This is because the chromium anions were forced to interact with the active adsorbing sites on the large surface area during penetration.

Suitability of ZAN in Industrial Wastewater

Industrial wastewater was collected locally from a metal finishing factory in Vangepalayam (India). Adsorption was carried out in the wastewater with ZAN to remove the toxic metal from water. The effect of pH, adsorption dosage, and desorption were investigated. The initial pH values were adjusted in the range of 1 to 10 before the addition of the adsorbent. Figure 12 shows that the adsorption was highly pH dependent. The maximum uptake was obtained at pH 5 (80%) and decreased gradually. The optimum pH value (5) was adjusted for further experiments.

The effect of changing the adsorbent dosage on the adsorption rate of industrial wastewater was studied by varying the concentration of the sorbent from 0.4 to 1 g, while keeping the other experimental conditions constant. The percentage removal *versus* adsorbent dosage is shown in Fig. 13. An increase in the percentage of adsorption with increasing adsorbent dosage was observed. Desorption studies help to elucidate one mechanism of adsorption as well as recovery of the adsorbate and adsorbent. The maximum desorption of ZAN from industrial wastewater is shown in Fig. 12. The results suggest that the recovery of metal from the adsorbent was possible and that a packed bed system made the process more feasible.

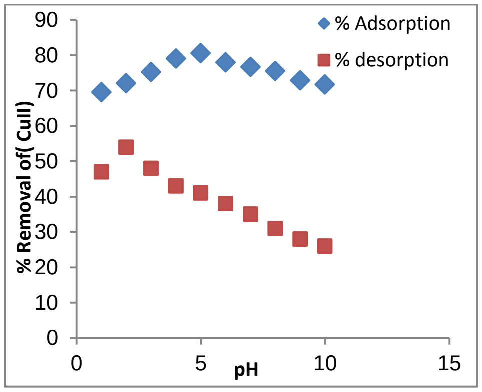


Fig. 12. Percentage of adsorption and desorption

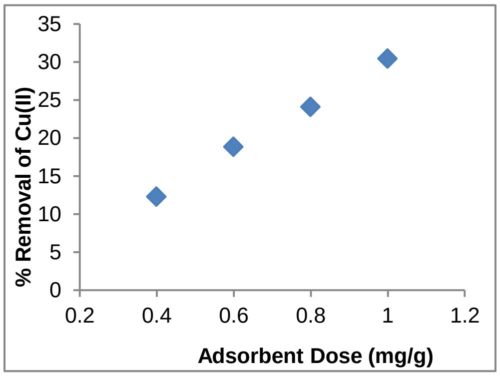


Fig. 13. Effect of sorbent dose on the adsorption of industrial wastewater onto ZAN

Desorption and Regeneration Studies

Sorption of solute on any sorbent can either be by physical bonding, ion exchange, or a combination of both. If the adsorption is by physical bonding, then the loosely bound solute can be easily desorbed with distilled water in most cases. However, if the mode of sorption is by chemical bonding, ion exchange, or a combination of both, then desorption can be affected by stronger desorbents such as acid or alkali solutions. In order to investigate adsorption of Cu(II) ions from metal-loaded ZAN, the metal-loaded adsorbent was treated with HCl. Desorption studies were performed with different hydrochloric acid concentrations. The recovery percentage was obtained from the following equation (Zhao *et al*. 1999; Arica *et al.* 2003; Johnson *et al*. 2008):

$$\text{Recovery (\%)} = \left(\frac{\text{Desorbed}}{\text{Adsorbed}}\right) \times 100 \tag{25}$$

where the "desorbed" is the concentration and/or the mass of metal ions after desorption and the "adsorbed" is equal to (C_o–C_e) and/or (m_o–m_e) for each recovery process; m_o and m_e are the masses of heavy metals in the aqueous solution before and after adsorption, respectively. Maximum desorption of Cu(II) from the spent adsorbent was 73%, which was achieved using 0.2 N HCl. These results indicate that ZAN adsorbent can be used repeatedly in Cu(II) adsorption to keep the process costs down.

Table 4. Desorption Data of Cu(II)

Adsorbent	Initial conc. Cu(II)(mg/L)	Removal efficiency	Desorption[a] with HCl			
			0.05 N[b]	0.1 N[b]	0.2 N[b]	0.3 N[b]
ZAN	50	81	59	65	73	67
	100	79	54	50	67	53
	150	67	43	36	46	42
	200	59	35	31	42	37

[a] All values are percent recovery of copper; [b] Concentration of HCl

Comparison of Different Adsorbents for Cu(II) Adsorption

Table 5 presents a comparison of several adsorbents employed for Cu(II) adsorption. As can be seen, the adsorbent ZAN employed in this work presented very high adsorption capacities for Cu(II) when compared with several other adsorbents. Out of 11 different adsorbents, ZAN presented a higher sorption capacity for Cu(II) than the remaining 10. It should be stressed that Table 5 is not a comprehensive table, in that there is a possibility of a non-listed adsorbent presenting a higher sorption capacity than those reported in this work. On the other hand, the outstanding sorption capacities for Cu(II) places *Acacia nilotica* as one of the best adsorbents for copper ion removal from aqueous solutions.

Table 5. Maximum Capacities of Copper(II) Ions Adsorption by Various Biosorbents*

Adsorbents	q_m (mg/g)	Adsorbents	q_m (mg/g)
Bengal gram husk	25.73	Sugar beet pulp	30.90
Banana peel	4.75	Coconut husk	3.07
Coir pith	10.22	Sago industry waste	12.40
Coco shell	2.87	Cassava tuber bark waste	54.21
Tea wastes(binary system)	6.65	Orange peel	3.65
Raw *Acacia nilotica* leaf	27.2	Treated *Acacia nilotica* (this study)	35.46

*Johnson *et al*. 2008

CONCLUSIONS

1. The present study showed that activated carbon prepared from *Acacia nilotica* leaf can be an effective adsorbent for the removal of Cu(II) from aqueous solutions. The adsorption process is dependent on the initial time, pH, dose, concentration, and temperature.
2. The Freundlich isotherm model gave a better fit than other isotherms for interpreting the adsorption phenomenon of Cu(II). The Cu(II) adsorption system followed a pseudo-second-order kinetic model.
3. The Cu(II) adsorption rate onto ZAN was greater in a single system (S) than in a binary system (B), due to the competitive adsorption of metal ion onto the active sites of the activated carbon.
4. In column studies, the removal efficiency of Cu(II) ions was lower than batch mode studies for ZAN, but the time taken for adsorption was less.
5. Desorption of Cu(II) from the spent adsorbent was achieved with 0.2 N HCl. The use of *Acacia nilotica* as an adsorbent seems to be an economical and worthwhile alternative compared to conventional methods for the removal of Cu(II) from aqueous solutions and industrial wastewater.

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