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Full Length Research Paper

Isotherms and thermodynamic studies on adsorption of copper on powder of shed pods of *Acacia nilotica*

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This study describes adsorption effectiveness of *Acacia nilotica* pod powder in removing Cu^{2+} ions in order to consider its application in wastewater purification. The batch method has been employed, using metal concentrations in solution and the percentage adsorption was determined for the adsorption system as a function of adsorbate concentration. Effects of the temperature of the Cu^{2+} ion solution, pH, contact time, metal concentration, and adsorbent loading weight on the removal process were also investigated. Langmuir, Freundlich isotherms were applied to experimental data and the goodness of their fit for adsorption was compared. Thermodynamic parameters, like enthalpy (ΔH) and the entropy (ΔS) were also calculated. *A. nilotica* pod powder proves to be a good adsorbent for Cu^{2+} ion removal from wastewater.

Key words: Adsorption, low cost material, adsorbent, copper ions removal.

INTRODUCTION

The effluents of industrial wastewaters often contain substantial amounts of toxic and polluting heavy metals. Small scale industries generate considerable pollution load and in many cases the wastewater is directly discharge into environment without any proper treatment. Cu(II) is one of the hazardous metal ions present in wastewater discharge and effluent from many industries. The existence of Cu(II) imbalance in the body can cause headaches, fatigue, insomnia, depression, skin rashes, detachment, learning disorders, or premenstrual syndrome, and it can even lead to accumulation in the kidneys, brain, skin, pancreas, and heart (Eun-Young et al., 2011). Toxicity of Cu(II) to living organisms is essentially exerted on enzymes, especially enzymes whose activity depends on sulphydryl and amino group, because Cu(II) like other heavy metals has a high affinity for ligands containing nitrogen and sulphur donors (Vedhavalli and Srinivasan, 2005).

There are some separation techniques used for the copper removal from aqueous solution like ion flotation, precipitate flotation and sorptive flotation. The other commonly used treatment involved in reducing the load of the metal is precipitation, coagulation, adsorption, ion exchange and membrane filtration (Onundi et al., 2010).

Furthermore, a number of new approaches has been developed for the removal of the metals like copper from the wastewater by using the natural material, biosorbents and waste materials. Studies on wastewater treatment for removal of heavy metals show that the adsorption is most widely and commonly used (Nasim et al., 2004). Adsorption using activated carbon can remove metals from inorganic effluents. Even though it is an expensive nature, granular, it is the most popular adsorbent and has been used with great success, due to its large surface area, high adsorption capacity and surface reactivity.

The other adsorbents include the agricultural and industrial waste product which are found to retain toxic metal from the aqueous solution and potentially cheaper adsorbents like wood charcoal, limestone, corn cobs, barley waste, coconut fiber (Nami et al., 2008).

In this study, the major focus is on the use of adsorbent for the wastewater treatment, as adsorption has advantages over other methods. Therefore, there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail.

EXPERIMENTAL

Before starting the experiment, *Acacia nilotica* pod powder was

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Table 1. R_L values and type of isotherm.

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

washed several times with hot distilled water to remove all impurities like clay and silt particles. It was then grinded to fine powder and its mesh size was determined. The adsorption experiments were carried out in stirred batch mode. To perform the experiment, working solution of Cu(II) was prepared by dissolving the respective metal nitrate in distilled water to avoid errors in results. *A. nilotica* pod powder was used as adsorbent for adsorption of Cu(II). The residual concentrations of Cu(II) have been measured by using complexometry titration. Samples were withdrawn at appropriate time intervals and filtered, and the absorbance of supernant liquid was determined. The effect of contact time, pH, temperature, etc was studied likewise.

RESULTS AND DISCUSSION

Effect of time

The data obtained from the adsorption of Cu(II) ions on *A. nilotica* pod powder showed that the percentage removal was increased with increase in the time (Table 2) and a contact time of 180 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time.

Effect of initial pH

The amount of metal adsorbed increases with increase in pH (Table 2). At low pH, adsorption of Cu(II) is negligible because the H^+ ion concentration is more than the ions of metal on the surface of the powder which limits the access of metal ions on the surface of grains of the adsorbent. When the pH increases, the effect of competition from H^+ ions decreases, and the positively charged ions take their places on the surface.

At pH values higher than 7, Cu(II) precipitation occurred simultaneously. This could be explained by the fact that at low pH, more protons will be available to protonate amine groups to form groups $–NH^{3+}$, reducing the number of binding sites for the adsorption of Cu(II), while as at higher pH, adsorption of Cu(II) increases because the inhibitory effect of H^+ decreased with the increase in pH (Wan et al., 2004).

Adsorption isotherms

The adsorbent dosage is another important parameter, which influences the extent of metal uptake from the solution, the adsorption of Cu(II) on adsorbent by varying the adsorbent dose (1 - 5g / 100 ml). The metal uptake was found to increase with increase in amount of adsorbents (Table 2). The Langmuir isotherm is represented by the following equation (Amal, 2004):

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (1)$$

Where Ce is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium time (mg/g), and Q_o and b are Langmuir constants. The values of the Langmuir constants are calculated from the intercept and slope of the plot of C_e/q_e versus C_e.

$$R_L = 1 / (1 + bC_0) \quad (2)$$

Where, C_0 is the initial ion concentration (mg/L) and b is the Langmuir constant (L/mg).

The R_L values indicate the type of isotherm as shown in Table 1 (Raju and Saseetharan, 2007). The Freundlich isotherm may be linearized (Deshpande et al., 1996) as:

$$q = KC_e^n \quad (3)$$

A linear form of this expression is given as:

$$\ln Ye = \ln K + \ln C_e \quad (4)$$

$$\text{Log } q = \text{Log } K + n\log C_e \quad (5)$$

Where K is the Freundlich adsorption constant, and n is the adsorption intensity. The values of the two parameters K and n are calculated from the intercept and slope of the plots Log$q$ versus LogC_e. The value of n is greater than unity (1< n < 10), that means favorable adsorption (Kannan and Sarojini, 2010). The results show that the adsorption of metal follows Langmuir and Freundlich isotherm models (Table 3).

Thermodynamics parameters

The effect of temperature was studied to calculate the percentage removal (Table 3) and the thermodynamic parameters, such as the enthalpy (ΔH) and the entropy (ΔS) for the adsorption of Cu(II) are calculated (Table 3) by using the following equation (Maurya et al., 2007):

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

Where T is the absolute temperature (K), R is the gas constant (J mol^{-1} K^{-1}), and K_d is distribution coefficient

Table 2. Effect of contact time, pH, temperature, dose and concentration on adsorption removal.

Effect contact time		Effect of pH		Effect of temperature		Effect of dose		Effect of concentration	
Time (min)	Percentage removal	pH	Percentage removal	Temp (K)	Percentage removal	Dose (gm)	Percentage removal	Concentration (g/L)	Percentage removal
5	13.27	3	25.12	298	24.78	1	16.37	7.18	25.31
15	17.26	4	28.57	308	23.45	2	24.78	14.36	24.78
30	18.14	5	75.37	318	20.8	3	32.74	21.1	24.68
60	22.12	6	76.85	328	18.58	4	44.25	28.34	23.25
120	24.78	7	79.31	338	17.7	5	49.12	35.9	23.09
180	24.78	8	80.79	-	-	-	-	-	-
-	-	9	81.77	-	-	-	-	-	-

Table 3. Isotherm and thermodynamic parameters value.

Isotherm parameter		Thermodynamic parameters	
Langmuir constant (R_L)	Freundlich constant (n)	$-\Delta H$ (KJ/Mol)	$-\Delta S$ (J/Mol)
0.9026	1.197	9.609	41.328

(cm^3 g^{-1}). The negative value of ΔH shows the exothermic nature of adsorption (Sivkumar and Palanisamy, 2008).

Effect of initial concentration

The removal of Cu(II) was studied at different initial concentration of Cu ions (7.18 to 35.9 g/L) at fixed dose of adsorbent 2 g / 100 ml and contact time (180 min), it was increasing by decreasing the Cu(II) concentration. This is as a result of the increase in the driving force of the concentration gradient, as an increase in the initial Cu (II) ion concentrations. The percentage adsorption at higher concentration levels shows a decreasing trend, whereas the equilibrium uptake of Cu(II) displays an opposite trend. At lower concentrations, all Cu(II) ions present in solution could interact with the binding sites and thus, the percentage adsorption was higher than those at higher initial Cu(II) ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites (Kannan and Srinivasan, 1998; Ahmet et al., 2004).

Conclusions

Removal of Cu(II) from aqueous solution was possible using *A. nilotica* pod powder. It was seen that maximum adsorption takes place after 120 min. The Langmuir and Freundlich isotherms models provided the best fits to predict the adsorption for the copper onto *A. nilotica* pod powder. Thermodynamic study showed that the adsorption process was spontaneous and exothermic because ΔG and ΔH were both negative. The results confirmed that all adsorbents illustrated higher adsorption capacities and can be used for the adsorptive removal of Cu(II) from different aqueous solutions, and its excellent adsorption behaviors for other metal ions can be expected.

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