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MASS TRANSFER STUDIES ON THE REMOVAL OF COPPER FROM WASTEWATER USING ACTIVATED CARBON DERIVED FROM COCONUT SHELL

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ABSTRACT

This paper deals with the removal of copper ions from wastewater systems by using activated carbon derived from coconut shell. It was found that the adsorption follows first order kinetics and is slightly endothermic. Standard adsorption isotherm, like Langmuir and Freundlich were used to represent the experimental data. The external mass transfer coefficient has been determined for the process under the influence of a number of variables including initial concentration, temperature, pH and contact time. Enthalpy calculation has been done for the process too. An equilibrium curve has been plotted for the calculation of the amount of carbon required and it was found that there was good agreement between experimental and analytical values.

Keywords: *coconut shell, activated carbon, heavy metal, copper (II), Langmuir isotherm, mass transfer coefficient.*

INTRODUCTION

The increased use of copper in industries such as alloy preparation, wood preservation, plating, tanning, corrosion inhibition has resulted in copper finding its way into natural bodies of water. Over exposure to copper dust and mist causes irritation, lung carcinoma, corrosion of skin and the respiratory tract. High concentrations of Cu(II) in water bodies are lethal to fishes. It has an adverse effect on the performance of biological water treatment processes.

The removal of Cu(II) from water has been studied by several workers [2, 5]. Though activated carbon is an ideal adsorbent, due to its organophilic character, its high costs prohibits its use in wastewater treatment. The high cost of active carbon has prompted a search for cheaper substitutes. Fly ash and china clay [3], saw dust [4], coal fly ash, peat [1], rice husks are some low cost adsorbents. In the present paper the adsorption behavior of Cu(II) on activated carbon derived from coconut shell has been studied. Experiments were set up to estimate the effectiveness of activated carbon derived from coconut shell for the removal of copper at different pH, concentration, temperature and contact time.

The aim of the present study was to assess the parameters which influence the external mass transfer coefficient during the adsorption of copper on activated carbon derived from coconut shell.

EXPERIMENTAL

The coconut shell activated carbon used in this study was prepared by pulverizing the coconut shell into powder, washing and drying in an oven. It was then kept in a furnace at up to 600°C for two hours and then stored. The chemical activation was carried out afterwards. In the chemical activation, the degree of impregnation is an important factor. The known quantity of stored coconut shell powder was mixed with barium chloride in the impregnation ratio of 0.5. The required quantity of water was added to this mixture and kept at boiling until water evaporated, then the slurry type mixture was kept in the oven at 110°C for 24 hours to remove moisture. The activated carbon was washed with

Table 1. Characteristics of the prepared carbon.

Surface area	630.80 m^2g^{-1}
Porosity	0.50 ml g^{-1}
Density	1.28 g dm^{-3}
pH	6
Impregnation ratio	0.5
Moisture Content	6.50

hydrochloric acid followed by hot distilled water for about 6 times to remove the activating agent and hydrochloric acid, respectively. Washed carbon was dried at 110°C, then sieved for the required size of 300 µm and packed in a polyethene bag.

The adsorbents characteristics determined using standard methods [6, 7] are given in Table 1.

Sorption experiments were carried out by adding activated carbon derived from coconut shell to a conical flask in various amounts containing known concentration of Cu(II) solution. The effects of concentration, contact time, and initial concentration were studied. The Langmuir and Freundlich isotherms at different temperatures studied were plotted. Then the mass transfer coefficient, kinetics and enthalpy of adsorption were calculated. An UV-118 Systronic spectrophotometer was used through the experimentation.

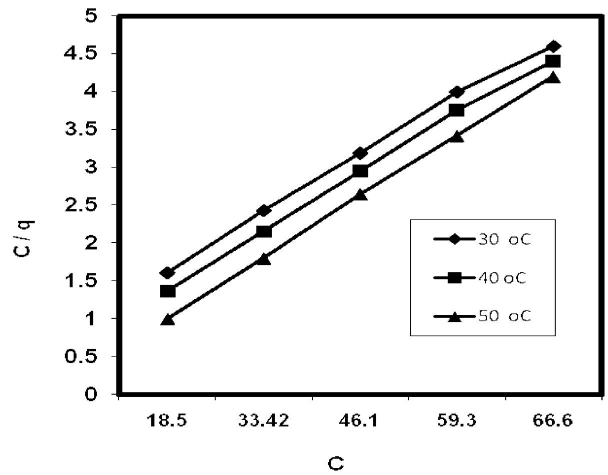

Fig. 1. Langmuir Isotherm.

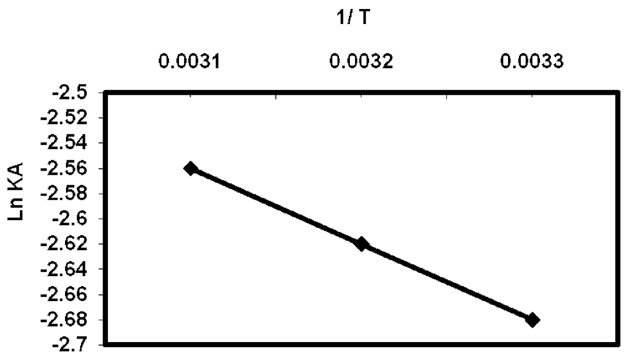

Fig. 2. Enthalpy Calculation.

RESULTS AND DISCUSSION

The equilibrium data for the removal of Cu(II) by adsorption on activated carbon derived from coconut shell at 30°C, 40°C and 50°C were plotted using Langmuir model.

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} \frac{C_e}{Q^0 b} \tag{1}$$

where Q^0 and b are the Langmuir constants indicating adsorptive capacity and energy of adsorption, respectively.

The linear plots of C_e/q_e vs C_e at different temperatures, shown in Fig. 1, indicate the applicability of the Langmuir adsorption isotherm.

The enthalpy change, ΔH, was calculated using the following relationship:

$$ln\, KA = ln\, KA' - \frac{\Delta H}{RT} \tag{2}$$

where KA2 is a constant and the other terms have their usual significance. A plot of ln KA vs 1/T was found to be linear, as shown in Fig. 2. The value of ΔH was determined from the slope of the plot. The positive value of ΔH (4.408 KJ/mol) during the process indicates the endothermic nature of adsorption and suggests weak binding of the adsorbate species with active surface sites of adsorbent.

The specific rate constant K_{ad} for the adsorption of Cu on activated carbon derived from coconut shell was determined using the Bhattacharya and Venkobachar equation [8]:

$$ln(1 - u_t) = -K_{ad}\, t \tag{3}$$

where

$$u_t = \frac{C_0 - C_t}{C_0 - C_e}$$

and Co, Ct, Ce are the concentrations of the adsorbates, initially at time t and at equilibrium, respectively.

The linear plots of ln(1-u_t) vs t shown in Fig. 3 at 30°C prove the validity of the above equation for the present system and follows a first order reaction. The

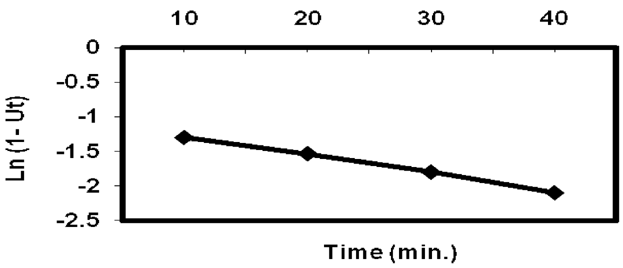

Fig. 3. Kinetics of copper removal (Bhattacharya and Venkobachar Plot).

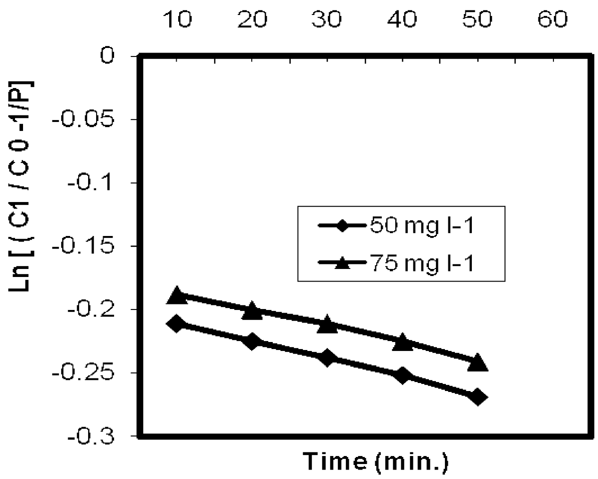

Fig. 4. McKay et al. plot for removal of copper by adsorption.

overall adsorption process is assumed to occur through the following steps:

1.Mass transfer of Cu(II) from the bulk solution to the solid surface.

2. Intraparticle diffusion.

3. Adsorption at an interior site.

The model presented for determining the external mass transfer coefficient B_L is based on the work done by McKay et al. [9].

The equation used is

$$\frac{C_t}{C_0} = \frac{1}{P} + \frac{mK_L}{P} \exp\left(\frac{P}{mK_L}\right) B_L S_s t \qquad (4)$$

where m - mass of adsorbent per unit volume of particle free adsorbate solution;

P = 1 + mK;

B_L - external mass transfer coefficient;

K - Langmuir constant;

Ss - **o**uter surface of adsorbent per unit volume of particle free slurry;

C_o - **i**nitial adsorbate concentration;

C_t - adsorbate concentration after time t.

The equation can be rewritten as

$$ln\left(\frac{C_t}{C_0} - \frac{1}{P}\right) = ln\left(\frac{mK}{P}\right) - \left(\frac{P}{mK}\right) B_L S_s t \qquad (5)$$

$$- \left(\frac{P}{mK}\right) B_L S_s$$

This is a straight line with slop equal to $-(\frac{p}{mK})B_L S_s$ at different initial concentrations.

Fig. 4 suggests the validity of the equation for the present system. The value of B_L for different initial concentrations was determined from the slope and intercept of the plots. The external mass transfer coefficient ranges from 1.96 x 10^{-9} cm s^{-1} for 50 mg l^{-1} initial Cu(II) and 1.82 x 10^{-9} cm s^{-1} for 75 mg l^{-1} Cu(II) concentration.

It was found that the increasing of the initial concentration results in a decreasing of the external mass transfer coefficient. These results are consistent with previous studies on copper and mercury sorption onto chitosan [10].

The requirement of carbon for the treatment is also an important aspect of wastewater treatment. For this, a plot of the equilibrium curve i.e. the amount adsorbed vs concentration has been plotted in Fig. 5. From the equilibrium curve data have been obtained:

Initial concentration C_o = 75 g l^{-1}

Final concentration C_1 = 59.3 g l^{-1}

$$Actual\ dosage\ taken = \frac{1\ g\ activated\ carbon}{Liter\ of\ Cu\ solution}$$

The operating line equation is as follows:

$$V(C_0 - C_1) = m\left[\left(\frac{X}{m}\right)_1 - \left(\frac{X}{m}\right)_0\right] \qquad (6)$$

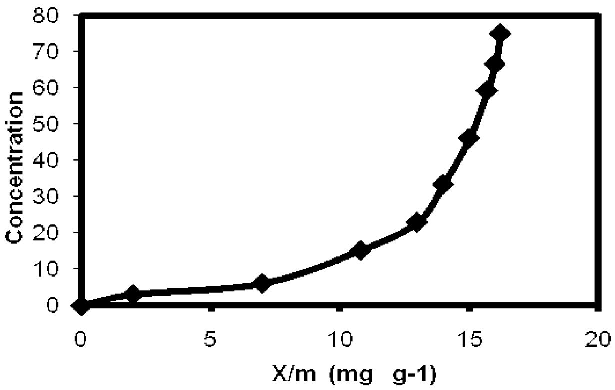

Fig. 5. Equilibrium Curve.

Here the initial concentration of the solute (Cu) in the adsorbent (activated carbon, derived from coconut shell) is assumed to be negligible, i.e. $(X/m)_o = 0$. The slope of the operating line is m/v. From the graph the slope is 0.9691 g l^{-1} and thus

$$\frac{m}{v} = 0.9691 \text{ g } l^{-1}$$

and $v = 50$ ml

so the amount of carbon required is $m = 0.9691 \times 10^{-3} \times 50 = 0.0485$ g.

Now this is the analytical value and the actual carbon taken in the experiment is 0.05 g. Thus, the analytical and experimental data are in good agreement.

CONCLUSIONS

The kinetic model has been developed to explain the external mass transfer of Cu(II) from aqueous solution on to activated carbon, derived from coconut shell. From the results, the adsorption follows both Langmuir and Freundlich isotherms. Moreover, the study includes effects of different temperature ranges used. There is no appreciable change in the nature of the graph and on the adsorption behavior. From the Bhattacharya and Venkobochar plot, a straight line is found, which concludes that the kinetic is of first order. From the McKay et al. plot, straight lines with different slopes corresponding to different initial concentration were found. The mass transfer coefficient B_L is an important design and kinetic parameter. From the enthalpy calculations, it is found that the nature of the adsorption is endothermic and it suggests the possibility of weak binding of adsorbate species with the active surface sites of the adsorbent. From the equilibrium curve and the calculation of the amount of carbon required, it was found that there was a good deal of agreement between experimental and analytical values. The results of this investigation are useful for developing an appropriate technology for designing wastewater treatment plants for the removal of heavy metals, i.e. copper.

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