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Sorption of copper (II) and cobalt (II) ions by using chitin as adsorbent

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ABSTRACT

The present work deals with the adsorption of Cu(II) and Co(II) metal ions on natural bio polymer chitin. Experiments conducted to obtain optimum conditions like effect of pH, initial concentration, particle size. Langmuir isotherm was used to evaluate sorption capacity of chitin. Adsorption process follows first order kinetics. Fixed bed down flow Column studies were also conducted for the removal of Cu(II) and Co(II). The bed depth service times of adsorbent column were also determined at different bed depths. Biopolymer chitin was proved as very good adsorbent for maximum removal of metal ions. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Copper (II);
Cobalt(II) metal ions;
Natural bio polymer chitin.

INTRODUCTION

Pollution of the environment by Heavy metals is normally associated with human activity of one kind or another. Heavy metals are widely distributed in the environment and in water bodies. Excess cobalt concentrations cause gastro intestinal problems. The Copper in kidneys may cause for stone formation.

The main sources of Copper and Cobalt metal ions are electro refineries, biocide production mining and smelting. Ingestion of these metals permisside level causes various types of acute and chronic disorders like hemochromatosis, gastro intestinal problems, and skin dermatitis^[1,2]. Metal removal by activated carbon^[3], flyash^[4], Bituminous coal^[5] are earlier reported. However we used biopolymer^[6] chitin as adsorbent for the removal of metal ions in the present study.

material of skeletons of arthropoda. With few exceptions chitin occurs only in invertebrates. It forms the exoskeleton of Crustaceans, insects etc. Chitin used in the present investigation was supplied by local manufacturing industry. The Cu(II) and Co(II) stock solutions were prepared by taking 1 gram of pure metal.

Batch sorption experiments were carried out by taking 100 ml of metal solution of known concentration in 250 ml conical flask with required dose of adsorbent. The optimum pH of the solutions was maintained by using buffers. The effect of initial concentration of metal ions, particle size and presence of calcium and chloride ions was investigated.

Column studies were conducted using 18 mm diameter adsorbent column with a flow rate of 5 ml/minute. The service time of the column at different bed depths namely 5, 10 and 15 cms were determined.

EXPERIMENTAL

Materials and methods

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RESULTS AND DISCUSSION

Effect of pH: pH is one of the important parameters that may control uptake of metals from aqueous solutions. Batch sorption experiments were conducted at different pH values to investigate the effect of pH on sorption of metals. The percentage adsorption of metals increased with increased in pH. At lower pH values, the H⁺ ions increase which will compete with the metal cations, there by decreasing the efficiency of adsorption.

From the figure 1 it can be observed that percent removal of Cu is not changing with respect of pH over the range of 4.5 to 9.5. All other experiments on copper were conducted at pH 6.0. In the case of cobalt, the percent removal increased rapidly in the pH range of 4.5 to 6.4 and later the increase was marginal. Hence, 6.4 is taken as optimum pH, and maintained in all other experiments on cobalt.

From the figure 1 it can be observed that percent removal of Copper is increased with respect to pH over the range of 5.0 to 9.0. All other experiments on Copper were conducted at pH 8.0. In the case of Cobalt, the percent removal increased rapidly in the pH range of 5.0 to 9.0 and later the increase was marginal. Hence, 9.0 is taken as optimum pH and maintained in all other experiments on Cobalt.

Effect of initial concentration

In the case of Copper and Cobalt the adsorption

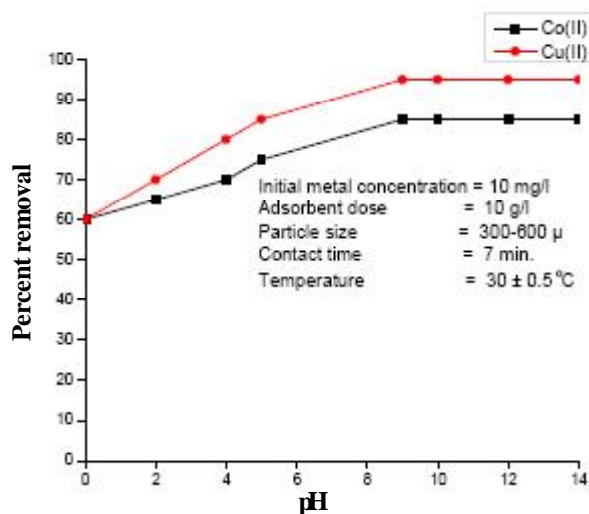


Figure 1: Effect of pH on removal of copper and cobalt

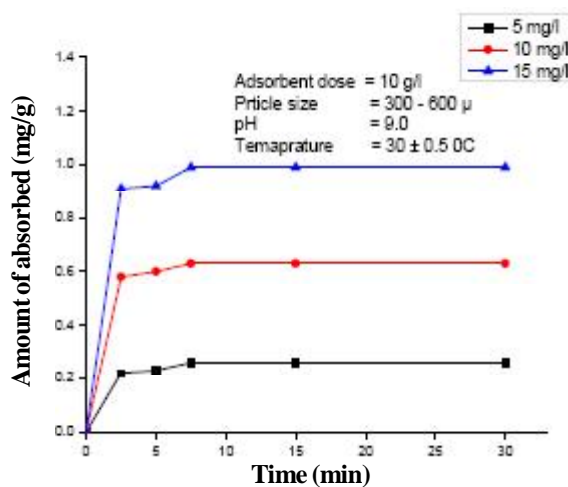


Figure 2: Effect of initial concentration on removal of copper

rates are initially high. The initial rapid uptake was indicated by high initial slope of the curves. This is due to the fact that at the beginning of the sorption process, all the adsorption sites are vacant and hence the extent of metal removal is high. After the rapid initial uptake, there is a transitional phase in which the rate of uptake decreased up to some degree and approached almost a constant value, which indicates equilibrium state. Figures 2 and 3 shows that the time of saturation is independent of initial concentration. The removal of Copper and Cobalt increases as the initial concentration increased from 5 mg/L to 15 mg/L. The equilibrium time is independent of initial concentration and both metals equilibrium time is 15 min.

Effect of dose of adsorbent: To determine the ef-

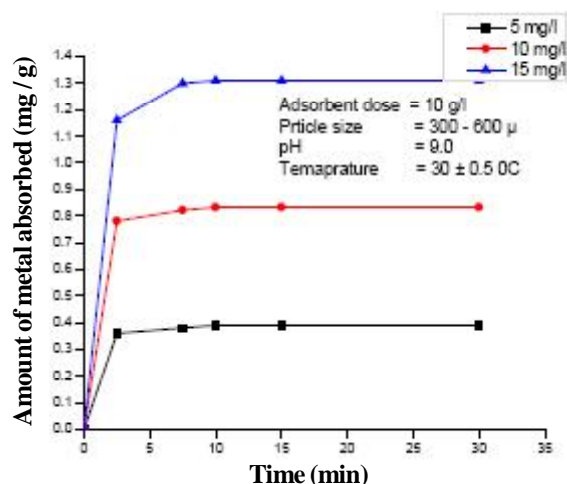


Figure 3: Effect of initial concentration on removal of cobalt

TABLE 1: Kinetic rate constants for copper and cobalt

Metal	Rate Const $K_1 \text{ min}^{-1}$
Copper	0.0389
Cobalt	0.0364

TABLE 2: The Langumair constants for copper and cobalt

Metal	Q° (mg/g)	$b(1/\text{mg})$
Copper	3.142	0.7680
Cobalt	1.284	1.9990

TABLE 3: Column studies for copper and cobalt

Metal	Breakthrough capacity, mg/gm	Total column capacity, mg/gm
Copper	1.520	1.600
Cobalt	0.750	0.800

fect of adsorbent (chitin) dose on metal removal batch sorption experiments were conducted. Initial concentration of metals 10 mg/lit and doses of adsorbent namely 4,6,8,10,12 mg/lit. From the results it can be observed that, as the dose of adsorbent increased from 4mg/lit- 12mg/lit. The percent removal of copper increased from 65.5 to 92.0% and for cobalt the percent removal increased from 55.7 to 90.5%.

Effect of Particle size: In the case of adsorption process, the extent of adsorption increases with increase in specific surface area. The specific surface area available for adsorption will be greater for smaller particles and hence, the percent removal of metal increases as the particle size decreases. The effect of particle size on uptake of metals was studied with different particle sizes namely 75-150 μ , 150 to 300 μ and 350-600 μ . From the results, it was observed, that the percent removal of copper increased from 85.5% to 98.8%

and in the case of cobalt, percent removal increased from 78.8 to 95.5% as the particle size decreased from 300-600 μ to 75-150 μ .

Kinetic rate constants

Adsorption is normally considered to be a forward reaction of first order. Kinetic rate constants provide an insight into the nature of sorbent metal reaction. The rate constants can be determined using the following equation.

$$\log(C/C_0) = (K/2.303)t,$$

$$\log(C/C_0) = K_1 t$$

where, C = Initial Conc.(mg/L) of metal, C_t = Conc. remaining in solution at any time 't'. t = time (min), K_1 = Proportionality constant (or) kinetic rate constant.

The rate constants for Copper and Cobalt are presented in following TABLE 1.

Adsorption isotherms

The equilibrium data for the adsorption of Copper and Cobalt on chitin were fitted in langmuir isotherms. The Langumair constants are presented in following TABLE 2.

$$1/(x/m) = 1/Q^\circ + 1/(bQ^\circ C_e)$$

Where Q° = amount of adsorbent to form a complete monolayer on the surface (mg/g); b = Constant which increases with increasing molecular size; C_e = Equilibrium concentration (mg/L); x = amount of metal adsorbed (mg/L); m = weight of adsorbent (gm/L).

Column studies

Down flow column studies were conducted using 18 mm diameter adsorbent column with bed depth of 15cm. A constant flow rate of 1.179 $\text{m}^3/\text{hr}/\text{m}^2$ (5 ml/min) was maintained during the studies. The breakthrough capacities and total column capacities were given below.

CONCLUSION

Chitin is found to be a good adsorbent for removal of Copper and Cobalt from aqueous solutions. The equilibrium time for these metals by using chitin is less when compared to that of other adsorbents. As the initial concentration of metal increased the amount of metal adsorbed per gram of adsorbent increased. The equilibrium time is independent of initial concentration. As the dose of adsorbent increased, the percent removal

of metal is increased. As the particle size of adsorbent decreased from 300μ - 75μ , the percent removal of metals increased. The reaction rate kinetics of adsorption of heavy metals on to chitin follow a simple first order equation. The kinetic rate constant of Cu(II) was higher than that of Co(II). The heavy metal adsorption on to chitin can be well described by Langumuir isotherm. From the fixed bed column studies, it was found that column capacity and service time of Copper were more.

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