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Research Paper Chemistry

Adsorption Studies of Cu (II) and Cr (VI) from metal solution using crosslinked chitosan-g-acrylonitrile copolymer

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ABSTRACT

A basic investigation on the removal of Cr (VI) and Cu (II) ions from metal solution using crosslinked chitosan-g-acrylonitrile copolymer was conducted in a batch adsorption system, for finding the effect of various parameters such as initial concentration of the metal solution, contact time, adsorbent dose and pH. The results show the adsorption efficiency of the prepared novel adsorbent for the heavy metal treatment. A pH 5.0 was found to be an optimum pH for both Cr (VI) and Cu (II) adsorption. The adsorption data have been explained in terms of Langmuir and was found to be fit well with the Langmuir isotherm model. The maximum adsorption capacities for Cu (II) and Cr (VI) ions were 230.79 mg/g and 122.83 mg/g, respectively. From the above results it was concluded that under optimum conditions, the chitosan grafted poly AN was found as an effective adsorbent for copper.

Keywords : Heavy metal, Adsorption, Equilibrium model

Introduction

Polymers are playing an important role in all branches of industry today (Guru et al., 2008). Recently the environmental pollution has become one of the most important problems threatening our world. Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems (Toony et al., 2011).

In recent years, the removal of toxic heavy metal ions from sewage, industrial and miningwaste effluents has been widely studied. Their presences are responsible for several types of health problems in animals, plants and human beings (Clement et al., 1995). Most of the commonly used adsorption methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Among the various methods for removing metal ions, adsorption process was found more promising. The adsorbents play the vital role in the process efficiency. Most adsorbents with active functional groups were developed to rely on their interactions with metal ion and hence, the functional groups have important effects on the effectiveness, capacity and reusability of the adsorbents.

Widely available biopolymers are being used for sorption due to their cheap resource (Niu and Volesky, 2003). The deacetylated product, chitosan a biopolymer was used in this present study. Chitosan has an amine functional group, which is strongly reactive with metal ions. To improve chitosan's performance as an efficient adsorbent, crosslinking reagents were used and grafting was done.

The current work is aiming to modify chitosan using grafting phenomenon. The cross linked chitosan-g-acrylonitrile copolymer adsorbent was prepared using ceric ammonium nitrate initiator for the removal of heavy metal ions such as Cr6+ and Cu2+. Batch studies were used to observe the sorption behavior of Cr6+ and Cu2+ on to the prepared grafted copolymer.

Materials and Methods

Materials

The chitosan was kind gift from Indian Sea food, Cochin, Kerala, India. The monomer acrylonitrile and the cross linking agent glutaraldehyde were obtained from Central Drug House Private Ltd, Mumbai. Ceric ammonium nitrate $Ce(NH4)2(NO3)6$ and nitric acid used were of analytical grade reagents from Thomas Bakers Chemical and Company.

Preparation of crosslinked chitosan copolymer

2g of chitosan was dissolved in 2% aq. acetic acid solution with constant. A required amount of glutaraldehyde was added to the chitosan solution, then stirred for 20 minutes using magnetic stirrer. To this crosslinked chitosan solution, 0.1 M ceric ammonium nitrate (CAN) in 10 ml of nitric acid was added followed by a known amount (1 g in 50 ml of water) of acrylonitrile drop by drop with continuous stirring. The temperature of reaction was maintained at 70 °C for 45 minutes. After the completion of addition of monomer the product was precipitated by using sodium hydroxide solution with vigorous stirring. The precipitate was washed with distilled water several times to remove homopolymer formed and it was then filtered.

Experimental

Adsorption experiments were carried out by a batch study varying the concentrations of potassium dichromate and copper sulphate. The extent of removal of the two metals was investigated separately by changing the adsorbent dose, pH of the solution and time of shaking the adsorbent metal solution mixture. A sample of 1 g of chitosan-g-acrylonitrile copolymer was treated with 100 ml of potassium dichromate (200mg of Cr/L) and copper sulphate (200mg/L) solutions separately. It was then agitated at 30°C using orbital shaker at fixed speed of 160 rpm. After attaining the equilibrium adsorbent was separated by filtration using filter paper and aqueous phase concentration of metal was determined with atomic adsorption spectrophotometer (Varian AAA 220FS).

Effect of adsorbent dose

The adsorption of chromium and copper ion by cross linked chitosan-g-acrylonitrile copolymer (adsorbent) was conducted by varying the adsorbent ranging from 1g to 6 g separately, while keeping other parameters (pH, and contact time) constant. The figure 1 indicates that the percentage removal of chromium and copper generally increases with increase in the adsorbent dosage. This is due to the greater availability

of the exchangeable sites or surface area at higher dose of the adsorbent (Jameel Dhabab et al., 2011). The maximum % removal of Cr (VI) was about 84% at the dosage of 6 g, while for Cu (II) it was 86% at the dosage of 6 g.

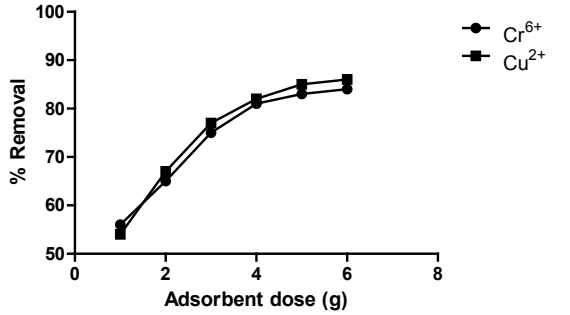


Figure 1: Effect of adsorbent dose on the removal of Cr6+ and Cu2+

Effect of contact time

The plot (figure 2) revealed that the rate of percent copper and chromium removal are higher at the beginning. This was probably due to larger surface area of the graft copolymer being available at beginning for the adsorption of Cu2+ and Cr6+ ions (Ali Shafagat et al., 2012), after some extent further increase in contact time shows a decrease in the uptake which may be due to the decrease of the easily available active sites for adsorption till the equilibrium is reached. The results indicated that for the metal ion Cr (VI), the rate of removal was increased with the increase in the contact time up to 360 min and then remained constant (78.5%). Similarly, Cu (II) removal was increased from 15 to 70% with the contact time variation from 30 to 300 min, respectively. From the results it was concluded that the optimum contact time for both metals are 360 min.

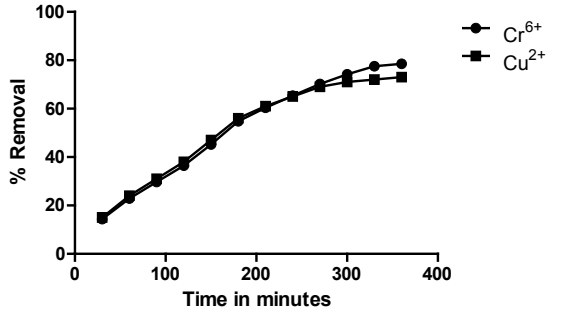


Figure 2: Effect of contact time on the removal of Cr6+ and Cu2+

Effect of pH

The pH value of the solution is an important controlling parameter in the adsorption process. A small variation in pH influences both the adsorbent surface and ionic species of metal ion in water. At different pH values, the protonation and deprotonation behaviors of acidic and basic groups would be influenced (Tooney et al.,2011).The dependence of amount of adsorption of Cr (VI) and Cu (II) ions on pH was shown in Figure 3. The adsorption increases with an increase in pH of the metal ion solution at first and then it shows a decrease. An optimum adsorption was obtained at pH 5 for both Cr (VI) ions and Cu (II) ions. The maximum removal at optimum pH was about 86%.

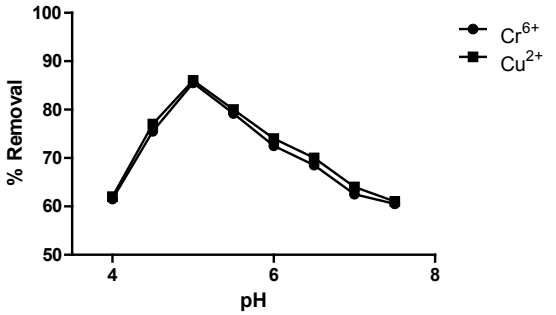


Figure 3: Effect of pH on the removal of Cr6+ and Cu2+

Langmuir isotherm model

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. To get the equilibrium data, initial metal concentration were varied while the adsorbent mass in each sample was kept constant.

The linearised form of the Langmuir isotherm

Ceq/Cads = bCeq/KL + 1/KL --------- (1)

Cmax = KL/b --------- (2)

where

Cads = amount of metal ion adsorbed (mg·g-1)

Ceq = equilibrium concentration of metal ion in solution (mg·dm-3)

KL = Langmuir constant (dm3·g-1)

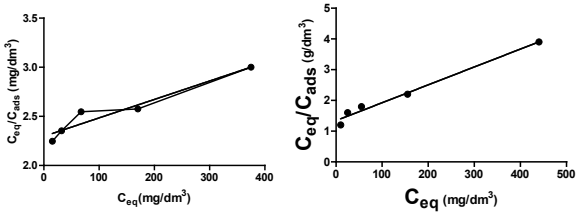
b = Langmuir constant (dm3·mg-1)

Cmax = maximum metal ion adsorbed (mg/g)

The constant “b” in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant KL can be used to determine the enthalpy of adsorption (Schmuchl et al., 2001). The constants “b” and “KL” are the characteristics of the Langmuir equation and can be determined from the linearized form of the Langmuir equation (1). A linearized plot of Ceq/Cads against Ceq gives “KL” and “b.

In a solid liquid system, positive sorption results in the removal of solute from the bulk solution and the concentration at the surface of the solid, until the remaining solute in the solution is in dynamic equilibrium with the solute on the solid surface. At equilibrium there is a defined distribution of the solute between the liquid and the solid phases, which can generally be expressed by one or more isotherms (Findon et al., 1993). Figures 4 show that the isotherm of the sorption of chromium and copper ions by crosslinked chitosang acrylonitrile.

The isotherm is characterized by the initial region, which is represented as being concave to the concentration axis. The isotherm is beginning to reach a plateau, which can typically be described by the Langmuir isotherm (Parfitt and Rochester,1983)



(a) (b)

Figure 4: Langmuir isotherm for (a) Cr6+ and (b) Cu2+

Table 1: Langmuir constants and Cmax value

Metal ions	Langmuir constants		
	KL (dm3/g)	b (dm3/mg)	Cmax (mg/g)
Cr(VI)	2.297	0.0187	122.83
Cu(II)	1.343	0.005819	230.79

It is found that the adsorption of Cr (VI) and Cu(II) onto crosslinked chitosan-g-acrylonitrile copolymer correlates well with the Langmuir equation under the concentration studies. The values of RL was indicates that the adsorption is favourable.

Conclusion

The capacity of crosslinked chitosan-g-acrylonitrile copolymer to adsorb Cr(VI) and Cu (II) ions from aqueous solutions was examined. The observed results showed that the change of adsorbent dose, pH and the contact time had a pronounced effect on the removal of Cr (VI) and Cu (II) ions from metal solution. The functional groups on the biosorbent surface were found to play a role in the entrapment of the target metal ions. Since biosorbent used in this work is freely, abundantly, locally available, and expected to be viable for removal of chromium ion from aqueous solution. The adsorption capacity of the metal ions was found to be as follows Cu(II)>Cr(VI). The adsorption isotherms could be well fitted by the Langmuir equation. This adsorbent is found to be favorable for the metal ions removal from the wastewater.

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