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REMOVAL OF Cu(II) FROM AQUEOUS SOLUTIONS USING ADSORBENT BASED ON CHITOSAN HYDROGEL BEADS

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Abstract

Mine waters and tailings resulting from mining and mineral processing often have a harmful effect on the local environment. Copper has a strong biocidal activity that greatly affects ecosystems. Therefore, the removal of copper from wastewater is of great importance to the environment. Chitosan, a natural biopolymer, obtained from chitin, the most abundant natural fiber, often has better properties than much more expensive synthetic polymers. This paper investigates the application of chitosan-based sorbents for removing copper from aqueous solutions. A novel adsorbent, chitosan hydrogel beads (CHBs), was synthesized from chitosan flakes (medium molecular weight), via ionic/covalent cross-linking. Batch experiments were carried out to optimize the process conditions for efficient removal of Cu(II) and to determine the adsorption capacity of prepared CHBs. The results showed that the maximum Cu(II) adsorption capacity estimated with Langmuir isotherm modeling was 103.6 mg/g which was three times higher than chitosan flakes (33.7 mg/g).

Keywords: *Copper, chitosan, adsorption.*

1. INTRODUCTION

Wastewaters containing heavy metals as pollutants originate from a large number of metal-related industries and mines [1]. Unfortunately, heavy metals are not biodegradable and tend to accumulate in living organisms, causing several diseases and disorders. Copper is one of the most common heavy metals observed in the aquatic environment [2]. Excess of Cu(II) in human blood system can create reactive oxygen species and damage important compounds such as: proteins, lipids and DNA and can causes various diseases such as Wilson and Alzheimer's disease [3]. Technologies used for metal ion removal from the wastewaters include chemical precipitation, reverse osmosis, membrane separation, flocculation, electrolysis, ion exchange mechanism and adsorption [4].

Various types of adsorbents have been investigated aimed at the adsorption of heavy metal ions. Favorable features of chitosan, such as resource abundance, non-toxicity, biodegradability and existence of sufficiently active sites ($-NH_2$ and $-OH$) for adsorption of various pollutants, make chitosan-based hydrogels the promising adsorbents for the removal of heavy metal ions from aqueous solutions [5].

In the present work, a method for synthesis of citric acid (CA)/ glutaraldehyde (Glu) co-cross-linked chitosan hydrogel beads (CHBs) was developed. The obtained CHBs were used as adsorbents in further batch adsorption experiments designed to investigate their potential application for the removal of Cu(II) ions from aqueous solutions. The effects of the initial solution pH and initial concentration of Cu(II) were evaluated with respect to the removal efficiency of Cu(II) from aqueous solution. For analyzing the equilibrium adsorption data Langmuir and Freundlich isotherms were employed.

2. EXPERIMENTAL

Chitosan flakes (CF) of medium molecular weight, glacial acetic acid (AA), Glu solution, CA and copper(II) nitrate hepta hydrate were purchased from Sigma-Aldrich (USA). All the chemicals were analytical reagent grade and used without further purification.

Preparation of CHBs was carried out by dissolving 1 g of chitosan flakes in 40 cm^3 of (1) 2 wt% of AA, (2) 1 wt% AA and 1 wt% CA and (3) 2 wt% of CA. 5% (v/v) Glu solution was added into the obtained suspension and the mixtures were magnetically stirred for 2 h at room temperature. In order to get the uniform CHBs, obtained solutions, separately, were dropped into 1 mol dm^{-3} NaOH. After 24 hours of aging in the NaOH solution, CHBs were neutralized by rinsing with deionized water.

The experiments were conducted in a batch mode by mixing approximately 0.5 g wet CHBs and 10 cm^3 of the Cu(II) solution of different concentrations. The effect of pH was studied by adjusting pH with either 0.1 M NaOH or 0.1 M HNO$_3$ from 3 to 7.

The mixtures were shaken at a speed of 150 rpm for 24 h. Aliquots above the adsorbent were taken and concentrations of Cu(II) ions were determined by polarography system 797 VA Computrace analyser (Metrohm, Herisau, Switzerland) applying differential pulse anodic stripping voltammetry (DPASV) at a hanging mercury drop electrode. All experiments were performed at room temperature.

The effect of the initial Cu(II) concentration was investigated in the range from 10 to 250 mg dm^{-3}. The obtained results were discussed in terms of removal efficiency, E (%), and adsorption capacity, q_e (mg g^{-1}), at equilibrium defined by the equations:

$$E = \left(\frac{C_i - C_e}{C_i}\right) 100$$

$$q_e = \left(\frac{C_i - C_t}{m}\right) V$$

where C_i and C_e (mg dm^{-3}) are the initial and equilibrium concentrations of Cu(II) ions in the solution, respectively, V (dm^3) is the volume of the solution, and m (g) is the mass of the dried adsorbent.

3. RESULTS AND DISCUSSION

Approximately spherically shaped CA/Glu co-cross-linked CHBs had diameters of about 3.0 mm. The three tested CHBs samples (non-cross-linked (CHB), cross-linked with 1% CA (CHB-1% CA) and 2% CA (CHB-2% CA)) contained water in the range of 97.0-97.5%. The surface charge of the adsorbent largely depends on the initial pH of solution influencing the removal efficiency of the adsorbent. pH of initial solutions was studied from 3 to 7 in order to find the value at which adsorption is the highest. In our experiments, the highest removal efficiency (98-99%) of Cu(II) for the three tested adsorbents was achieved in the pH range of 4-6. According to the literature data [6], at low pH (acidic solution), amine groups in the beads became protonated which induced an electrostatic repulsion of Cu(II) ions. On the other hand, solutions with pH values higher than 6 should be avoided due to the possibility of Cu(II) hydroxide formation which will affect the adsorption by the beads. The increase in the adsorption capacity at pH > 4 of CA/Glu co-cross-linked CHBs compared to non-cross-linked CHBs can be explained by the presence of additional carboxylic groups on the surface of the adsorbent. It can be assumed that improved removal of Cu(II) ions by CA/Glu co-cross-linked CHBs comes from deprotonated carboxylic groups which attracts positively charged Cu(II) ions and, hence, improve their adsorption capacity.

There are several isotherm models to investigate the equilibrium of the system and to define the capacity of the adsorbent. Usually, Langmuir or Freundlich model describe accurately the system in the case of two parameters. The Langmuir model assumes monolayer adsorption onto homogenous surface where the binding sites have equal affinity and energy, and there is no transmigration or interaction between the molecules. The Langmuir equation is given by:

$$q_e = \frac{q_m\,K_L\,C_e}{1 + K_L C_e}$$

where q_e is the amount of adsorbed mg per g of adsorbed at equilibrium (mg/g), q_m is the maximum capacity of the system (mg/g), C_e is the adsorbate concentration in solution at equilibrium (mg/dm^3), K_L is the constant of the Langmuir Isotherm model (dm^3/mg).

The Freundlich adsorption isotherm, however, is an empirical model and can be used in the case of a heterogeneous surface energy system.

$$q_e = K_F \cdot C_e^{1/n_F}$$

where C_e is the equilibrium concentration of metal ion (mg/L), q_e is the amount of metal ion adsorbed on adsorbent mass unit (mg/g), K_F is the maximum adsorption capacity of metal ions (mg/g) and n_F is a constant present in non-linear Freundlich isotherm which indicated the adsorption intensity [7].

The Langmuir and Freundlich plots are presented in Figure 1, while the obtained fitting parameters are reported in Table 1.
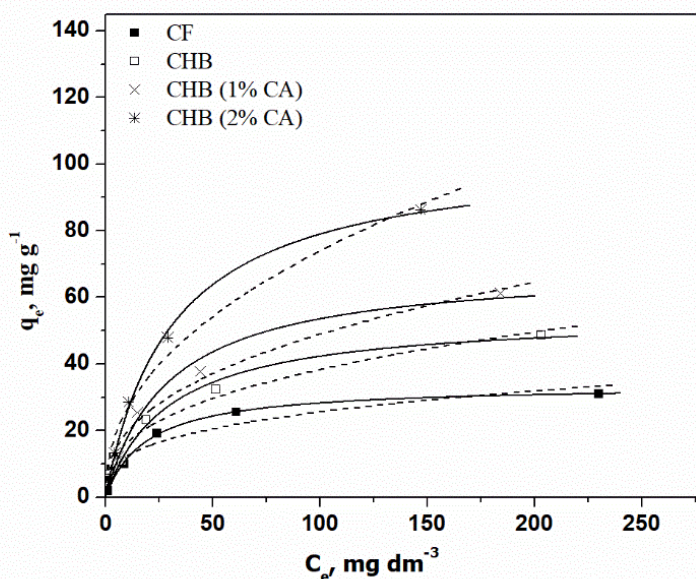

Figure 1 - Fitting of experimentally obtained data for adsorption equilibrium of Cu(II) onto: CF, CHB, CHB (1% CA) and CHB (2% CA). Solid and dash lines represent Langmuir and Freundlich curve, respectively

The equilibrium adsorption data on the effect of the initial concentration of Cu(II) were fitted using the non-linear Langmuir and Freundlich isotherm models in order to determine the surface properties and the affinity of the adsorbent. The corresponding isotherm parameters and the determination coefficients of these two models are reported in Table 1. Based on the values of the R^2, it is evident that adsorption of Cu(II) by CA/Glu co-cross-linked CHBs can be better described by the Langmuir isotherm. CA/Glu co-cross-linked CHBs with the higher content of CA showed

better q_m value compared to other samples, probably due to incorporation of additional carboxylic groups that have positive impact on the features of CHBs.

Table 1 - Langmuir and Freundlich parameters for the adsorption of Cu(II) ions onto CA/Glu co-cross-linked CHBs

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m, mg g^{-1}	*K_L	R^2	n_F	**K_F	R^2
CF	33.7	0.052	0.999	3.15	5.93	0.911
CHB	54.7	0.034	0.993	2.68	6.90	0.988
CHB - 1% CA	69.2	0.034	0.994	2.51	7.78	0.992
CHB - 2% CA	103.6	0.032	0.996	2.23	9.40	0.983

*K_L, dm^3/mg; **K_F, (mg/g)(dm^3/mg)$^{1/n}$

4. CONCLUSION

The adsorption of Cu(II) ions from aqueous solutions onto CA/Glu co-cross-linked CHBs was investigated in the present study. The obtained results showed that the maximum removal efficiency of Cu(II) was achieved in the pH range 4-6. Equilibrium isotherm data were fitted using Langmuir and Freundlich models. The Langmuir model provided the best fit of the experimental data. The maximum adsorption capacity for Cu(II) ions was exhibited by CHB - 2% CA (103.6 mg/g).

It can be concluded that investigated chitosan-based hydrogels could potentially contribute to the environmental friendly method for the treatment of Cu(II) contaminated waters.

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