ADSORPTION OF CADMIUM IONS ON CHITOSAN MEMBRANES: KINETICS AND EQUILIBRIUM STUDIES

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Abstract
The presence of toxic heavy metals in industrial wastewater is a serious pollution problem. The ability of chitosan membranes as an adsorbent for cadmium ions in aqueous solution was studied. Experiments were carried out as function of contact time and concentration of cadmium ions. This study has shown that chitosan is capable of removing cadmium from aqueous solution. The removal efficiency depends on reaction time and concentration of cadmium. The Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. Equilibrium data agreed very well with the Langmuir model. The maximum adsorption capacity of the Langmuir isotherm equation was 94 mg/g and the Langmuir adsorption equilibrium constant was 1.6×10^{-3} *dm*^{3}*/mg at 25 °C.*

Key words: *chitosan, membranes, cadmium, adsorption isotherm.*

1. Introduction

Industrial and mining waste waters are the major source of pollution by heavy metals. Toxic metal ions are difficult to remove from water, but their removal is fundamental to the preservation of the environment. The one of the metals commonly used in a series of industrial processes is cadmium. It is often detected in industrial wastewaters, which originate from metal plating, smelting, battery manufacture, petroleum refining, pesticides, pigment manufactures, photographic industries, etc. Cadmium from these sources is distributed in the water and finds its way into the human system. Various methods exist for the removal of toxic metals from aqueous solution: precipitation, extraction, coagulation, sedimentation, ion-exchange and electrochemical techniques. These conventional methods do not seem to be economically feasible. They are expensive or ineffective, especially when the metal concentrations are very low in the order of 1 to 100 mg/dm^3. These methods are involving high-priced equipment and energy requirements. Adsorption is the most effective and widely used method of all, futhermore it is also considered as an economical method. As adsorbent for the removal of heavy metals from water, biopolymers have been studied. Chitosan is the one of them [1 - 3].

Chitosan is the most abundant natural polymer after cellulose. It is the product of partial deacetylation of chitin. Due to its non-toxic, biocompatible and biodegradable characteristics chitosan has been widely applied in many industries including weastewater treatment. Chitosan has the ability to form complexes with metals. It exhibits higher adsorption capacity for metal ion compared to that of chitin owing to the amino group content. However, the serious drawback of chitosan for metal ion adsorbent from practical utilization is that it is soluble in acidic media [4, 5].

The main purpose of this work was to determine the capacity of the chitosan membranes for adsorption of cadmium.

2. Materials and methods

2.1. Materials

Chitosan was purchased from Aldrich. The chitosan used in this study was 77% deacetylated and its molecular weight is ~ 500 000 g/mol. Acetic acid, sodium hydroxide and cadmium nitrate p.a. were obtained from POCH. All reagents were analytical grade and were used without further purification.

2.2. Preparation of chitosan membranes

The chitosan solution of 1% (w/w) was prepared by dissolving chitosan powder in a 2% (v/v) acetic acid solution. The mixture was stirred 48 hours at room temperature. After that, the solution was filtered. The solution mixture was poured into a Petri dish and dried at 37 ºC. The film was in the NH_3^+ form. It was dipped in 0,1 mol/dm^3 sodium hydroxide solution to reach the uncharged amino form, washed with water to eliminate salts and dried. The thickness of the film was around 200 micrometers.

2.3. Adsorption experiments

Bath equilibrium experiments were performed in 100 cm^3 flasks, containing 75 cm^3 of metal solution with the initial concentration of cadmium ions from 250 to 1760 mg/dm^3. The adsorption bahaviors of Cd(II) ions were investigated at 25 ± 0,5 ºC and pH = 6. All the experiments were conducted with included a control test without metal. Samples were taken from solution after different time to determine optimal contact time. During the adsorption process, the flasks were shaken for 5 min several times. The concentration of cadmium ions in the aqueous phase was analyzed by Varian Spectra AA-20 atomic absorption spectrophotometer. The amount of metal ion q_e (mg/g) was obtained as follows:

$$q_e = (C_o - C_e)V/W$$

where C_o and C_e are the initial and equilibrium liquid-phase concentration, respectively in mg/dm^3, V is the volume of the solution in dm^3 and W is the weight of chitosan film used in g.

3. Results and discussion

Figure 1.a shows the effect of the contact time on the adsorption of Cd^{2+} by chitosan membranes. The adsorption of Cd^{2+} increased with contact time. The removal process is not rapid because equilibrium attained at about 48 h. After this equilibrium period, the amount of adsorbed metal ions didn't significantly change with time. The equilibrium isotherm for the adsorption of Cd^{2+} ions by the chitosan membranes is shown in ***Figure 1.b***. It can be seen that the adsorption capacity increases as the concentration of cadmium ions increases. When the concentration of cadmium ions at equilibrium was ~ 1680 mg/dm^3, the adsorption capacity reached ~ 70 mg/g.

The Langmuir and Freundlich adsorption models were used for the mathematical description of the biosorption of cadmium.

Langmuir equation:

$$C_e/q_e = C_e/q_m + 1/q_m K_L$$

where q_m is the maximum capacity of adsorbent, K_L is the Langmuir adsorption equilibrium constant in dm^3/mg.

Freundlich equation:

$$\log q_e = \log K_F + 1/n \log C_e$$

where K_F is Freundlich constant in mg/g and n is the heterogeneity factor.

The received linear plots of C_e/q_e versus C_e and log q_e versus log C_e (***Figure 1.c, 1.d***), prove the opportunity of application of the equations Langmuir and Freundlich for the description of the sorption process of cadmium ions on chitosan membranes.

The values of Langmuir and Freundlich constants were calculated to be of q_m = 94 mg/g, $K_L = 1.6 \times 10^{-3}$ dm^3/mg, K_F = 1.87 mg/g and n = 2.03. From the comparison of correla-

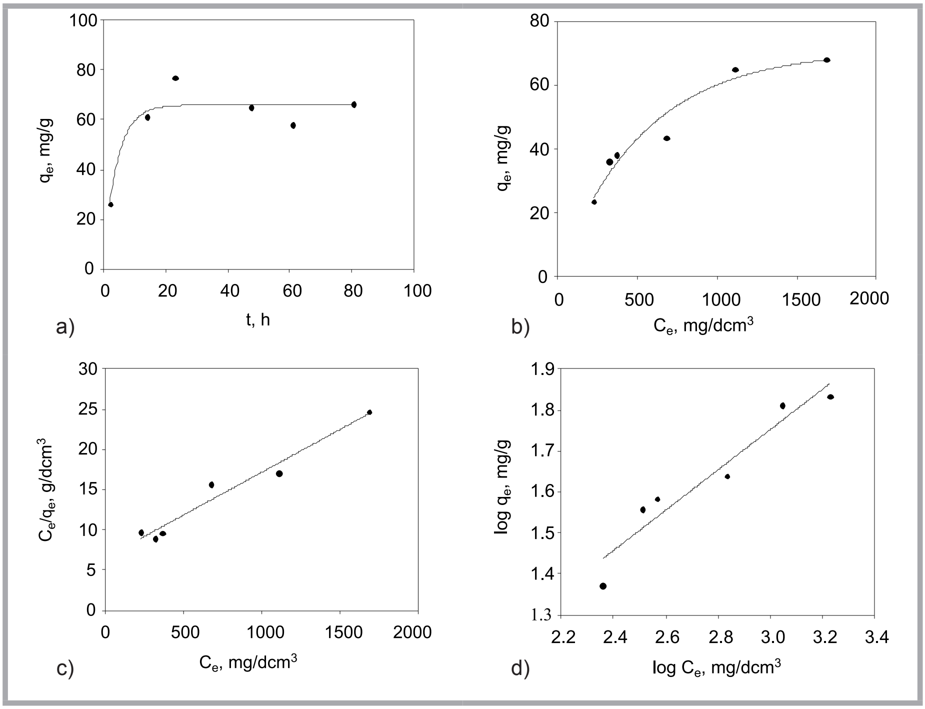

Figure 1. *Sorption of Cd* $^{2+}$ *as a function of time at* C_o*=1150 mg/dm*^{3} *(a), adsorption isotherm of Cd* $^{2+}$ *on the chitosan membranes (b), Langmuir model for the adsorption of Cd* $^{2+}$ *ions on the chitosan membranes (c), Freundlich model for the adsorption of Cd* $^{2+}$ *ions on the chitosan membranes (d).*

tion coefficients for Langmuir ($R^2 = 0.9615$) and Freundlich ($R^2 = 0.9218$) isotherm, it was found the data were fitted better by Langmuir equation than by Freundlich equation.

4. Conclusions

This study has shown that chitosan membranes are capable of removing cadmium from aqueous solution. The removal efficiency depends on contact time and concentration of cadmium. The adsorption behavior followed the Langmuir adsorption isotherm with a maximum adsorption capacity of 94 mg/g and a Langmuir adsorption equilibrium constant of 1.6×10^{-3} dm^3/mg at 25 °C.

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