SORPTION OF HEAVY METAL IONS BY POLYELECTROLYTE COMPLEX HYDROGEL MEMBRANES

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Abstract

Ionically crosslinked chitosan/tripolyphosphate membrane (Ch/TPP) was synthesized and used to adsorb heavy metal ions: Cu(II), Zn(II), Cd(II) from aqueous solutions. Batch adsorption experiments were carried out and the effect of pH of solution and an initial metal ion concentration \( C_0 \) were analysed. It was shown that the amount of metal ion adsorption increased with increasing pH and \( C_0 \).

1. INTRODUCTION

Fast industrial development is connected with increasing amount of waste waters that are highly dangerous for our environment. Heavy metal ions are main components among others water contaminations. They are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Adsorption is one of the well known method used for waste water treatment and heavy metal ion sorption [1].

Till now, activated carbon was widely used as a sorbent for industrial effluents treatment. Because of it’s high cost and requirement of complexing agents for improving its removal performance the new adsorbent materials are searched. Such materials like fly ash, silica gel, zeolites, lignin, clay materials etc. have been extensively investigated for the removal of heavy metal ions, like Cd(II), Cr(III), Hg(II), Pb(II) [2]. A special group able to metal ion sorption are natural polymers, including chitosan [1]. In comparison to the other natural polymers obtained from seafood wastes chitosan has highest chelating ability.

To overcome small resistance of pure chitosan membranes in acidic waste water solutions, the crosslinking process has been proposed [1]. In this work ionically crosslinked chitosan membranes were synthesized using sodium tripolyphosphate (TPP) as the crosslinking agent. The sorption
capacity of Cu(II), Zn(II), Cd(II) ions by Ch/TPP hydrogel membranes was studied.

2. EXPERIMENTAL

2.1. MATERIALS

Two different commercially available chitosan samples: high molecular weight chitosan (Ch-HMW) and medium molecular weight chitosan (Ch-MMW), sodium tripolyphosphate (TPP) were purchased from Sigma-Aldrich (Germany). Acetic acid (HAc), zinc nitrate (Zn(NO$_3$)$_2$), copper nitrate (Cu(NO$_3$)$_2$), cadmium nitrate (Cd(NO$_3$)$_2$), sodium acetate (NaAc), sodium hydroxide (NaOH), hydrochloride acid (HCl) and nitric acid (HNO$_3$) were analytical grade and were purchased from Poch (Poland). Chitosan selected for this study varied in their molecular weight (MW), but had similar degree of deacetylation (%DD). Degree of deacetylation of chitosan, determined by potentiometric titration method [3], was equal to 75.7 ± 3.8 (Ch-MMW) and 79.5 ± 1.5 (Ch-HMW). The viscosity average MW, determined by viscosity analysis of chitosan solutions according to Il’ina and Varlamov [4], was equal to 730 kDa (Ch-MMW) and 980 kDa (Ch-HMW).

2.2. POLYELECTROLYTE COMPLEX HYDROGEL MEMBRANES PREPARATION

Pure chitosan membranes were prepared by casting and solvent evaporation technique. Filtered, degassed 1 wt.% chitosan solution in 2 wt.% aqueous HAc solution was cast as film on clean glass plate and evaporated to dryness in an oven at 300 K, then further dried under vacuum at the same temperature.

Chitosan/sodium tripolyphosphate (Ch/TPP) membranes were prepared by dipping pure chitosan membranes in 1.3 wt.% aqueous TPP solution for a proper time period. Conditions of polyelectrolyte complex preparation was as follows: crosslinking time 1h, pH of TPP solution 5.5 (adjusted by adding a small amount of concentrated HCl solution), temperature 277 K. The obtained Ch/TPP membranes were additionally thoroughly washed in deionised water and then dried similarly as chitosan films. Dried polymer films were stored in a desiccator over P$_2$O$_5$ at ambient temperature.

2.3. SORPTION EXPERIMENTS

Aqueous solution of Cu(II), Zn(II), Cd(II) ions was prepared by dissolving metal nitrate salt in deionized water. The total metal concentration varied from 3.2 mM to 16 mM. The initial solution pH was
adjusted in the range 2.2-8.2 by adding a small amount of HNO₃ or NaOH. The solution pH was selected such that no metal hydroxide precipitations were experimentally found in bulk solution.

In adsorption experiments the mixture of dry membrane (0.05g) and metal ion solution (75 cm³) was placed in a 0.1 dm³ glass flask. The flask was shaken and placed for 48 h in thermostatic bath (T = 298.0 ± 0.1 K). After equilibrium the concentrations of metal ions were analyzed using an atomic absorption spectrometry. The amount of metal adsorbed \( q_M \) (mol/kg) was obtained using Eq.(1):

\[
q_M = \frac{(C_0 - C_M)V}{W}
\]

where \( C_0 \) and \( C_M \) are the initial and equilibrium concentrations in aqueous phase (mol/m³), respectively, \( V \) is the volume of the solution (m³) and \( W \) is the weight of dry membrane (kg). Each experiment was triplicate at least under identical conditions.

3. RESULTS AND DISCUSSION

Fig. 1 shows the effect of pH on adsorption of Cu (II) ions \( (q_M) \) onto Ch-MMW/TPP polyelectrolyte membrane.

![Equilibrium adsorption of Cu (II) ions at different initial metal ion concentration on Ch-MMW/TPP membrane](image)

The obtained results indicate that the adsorption capacity both the Cu(II) ions, as well as Zn(II) and Cd(II) ions, depends on the initial metal ion concentration and pH of solution. Value of \( q_M \) increases with increasing pH, up to specified pH value (pH~4.7 for Cu(II) ion adsorption). It is due to
competitive adsorption of protons and metal ions. Amine and hydroxyl groups of chitosan and phosphate groups of TPP may interact with metal ions through different mechanisms (chelation and ion exchange/electrostatic attraction) depending on pH, as was shown in Fig. 2 [5,6].

![Interaction mechanisms of Cu(II) ions with Ch/TPP hydrogel membrane: chelation (a), ion-exchange/electrostatic attraction (b, c)](image)

**4. CONCLUSIONS**

The results obtained in this study show that chitosan/tripolyphosphate membrane can be used as an effective material to remove heavy metal ions from low concentrated salt solutions. The adsorption capacity of Cu(II), Zn(II) and Cd (II) ions is highly dependent on pH and initial metal ion concentration.

**REFERENCES**