REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS USING CHELATING RESINS WITH IMINODIACETATE GROUPS

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Abstract

A chelating ion exchange resin bearing iminodiacetate groups derived from an acrylonitrile – divinylbenzene (AN-DVB) copolymer was synthesized in our group and tested as sorbent for some heavy metal ions like: Cu(II), Co(II), Ni(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions by a batch equilibrium technique. The influence of different parameters like: pH, metal ion concentration on the sorption capacity of the resin for the Cu(II), Co(II) and Ni(II) was examined. The overall tendency of the CIE resin toward Pb(II), Cd(II) and Zn(II), under non-competitive conditions, followed the order: Cd(II) > Pb(II) > Zn(II).

1. INTRODUCTION

The contamination of water resources by heavy metals is a serious environmental worldwide problem. The conventional technologies for the removal of heavy metals from wastewater include chemical precipitation, ion exchange, adsorption, membrane processes and evaporation. Adsorption has attracted attention because of new material types available for the removal process according to application. Some of these material types are zeolites, active carbon, fly ash, biosorbents, chelating resins [1].

Organic chelating resins, by their high selectivity in binding metal ions and metal complex ions, have a major implication in concentration control and in inorganic analytical chemistry. Numerous studies and reviews concerning the synthesis and characterization of the selective chelating sorbents, and the wide applicability of these resins in the removal of toxic metals and complex ions from industrial effluents, as well as in selective metal ion recovery processes, have been recently published [2-4]. Therefore, the adsorption properties of a novel chelating ion exchange (CIE) resin bearing iminodiacetate groups derived from an acrylonitrile -
divinylbenzene (AN-DVB) copolymer with 10% of DVB for the removal of heavy metal ions like: Cu(II), Co(II), Ni(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions by a batch equilibrium technique were investigated in this work.

2. EXPERIMENTAL

2.1. MATERIALS

The metal salts used were CuSO₄·5H₂O, CoCl₂·6H₂O, (CH₃CO)₂Ni·4H₂O, (CH₃CO)₂Cd·2H₂O, Zn(NO₃)₂·6H₂O and Pb(NO₃)₂ (all from Aldrich). Hydrochloric acid, potassium chloride, citric acid and dibasic sodium phosphate (Na₂HPO₄·12 H₂O), analytical grade were used for the preparation of HCl-KCl and citrate-phosphate buffer solutions.

2.2. METHODS

The synthesis and the morphological characterization of the AN-DVB copolymer with 10% of DVB and CIE resin were performed as previously shown [5]. The cation exchange capacity was determined according to the method previously presented [6]. The CIE resin was regenerated with HCl 1 M/NaOH 1 M before the metal ion adsorption test. Study of the metal ion retention properties of the CIE resin was carried out using a batch equilibrium procedure. Thus, 0.5 g of dry CIE resin was placed in a flask and contacted with 50 mL of the aqueous solution of each metal ion: Cu(II), Co(II), Ni(II) at the concentration of 0.07 mol/L, each. The influence of pH on Cu(II), Co(II) and Ni(II) metal ions retention was studied for CIE resin and the pH of the metal-ion solution was adjusted before equilibration over a range of 1.2 – 2 with a HCl-KCl buffer solution, and over a range of 2.5 – 6 with a citrate-phosphate buffer solution. The resin was filtered off, and the residual concentration of the metal cation remained in the filtrate was measured by the UV-VIS spectroscopy at 510 nm for Co(II), 720 nm for Ni(II) and 775 nm for Cu(II).

The performance of CIE resin for removal of Cd(II), Pb(II) and Zn(II) metal ions was measured by contacting the known amount of swollen polymer with solution containing metal ions; an amount of resin containing 10-fold molar excess of ligand relative to the metal cations in solution was shaken with 25 mL of the solution for 24 h and then metal concentration was determined using atomic absorption spectroscopy (AAS) with wavelengths set at 228.8 nm for Cd(II), 213.9 nm for Zn(II) and 283.3 nm for Pb(II).
3. RESULTS AND DISCUSSION

CIE resin was prepared according to the method previously presented [5]. The main physical and chemical features of this resin in the Na\(^+\)-form are as follows: surface area: 5.67 m\(^2\)/g; mean pore radius: 7.058 nm; cation exchange capacity per dry resin: 4.885 meq/g; water regain: 1.385 g/g.

3.1. ADSORPTION PROPERTIES OF CIE RESIN FOR Cu(II), Co(II), Ni(II)

The preliminary studies [5] prompted us to investigate in detail the sorption properties of heavy metal cations by CIE resin. Fig.1a shows sorption isotherms determined for Cu(II), Co(II) and Ni(II) at 25\(^\circ\)C.

![Fig.1. a) M(II) retention as a function of the equilibrium metal concentration for the CIE resin; b) Metal ion retention as a function of pH, at an initial concentration of 0.07 mol/L, \(T = 25^\circ\)C](image)

The maximum uptakes of Cu(II), Ni(II) and Co(II) was calculated using Langmuir equation and were equal to: 3.257, 2.809 and 2.512 mmol per gram of dry resin, respectively.

From Fig.1b, it can be observed that M(II) could hardly be adsorbed by CIE resin when pH < 3. With the increasing pH value, the M(II) retention increased gradually, the optimum adsorption pH of M(II) being located at 5. At pH > 5 the M(II) retention decreased probably because small amount of M(II) started to deposit as M(OH)\(_2\). The CIE resin showed a good retention ability for the metal ions in the following order: Cu(II) > Ni(II) > Co(II), at pH = 5 and at the concentration of 0.07 mol/L of metal ions, each.

3.2. ADSORPTION PROPERTIES OF CIE RESIN FOR Pb(II), Cd(II), Zn(II)

Pb(II), Cd(II) and Zn(II) were tested for their affinity to the iminodiacetate ligand anchored to an AN-DVB matrix. Batch-mode
sorption studies were performed separately for each cation at 10-fold excess of the ligand relative to the amount of metal cations present in solution. The distribution coefficients of the CIE resin for the cations studied under non-competitive conditions are presented in Tab. 1.

Table 1. Distribution coefficients of the CIE resin for Pb(II), Cd(II), Zn(II)

<table>
<thead>
<tr>
<th>Resin</th>
<th>Cation</th>
<th>Distribution coefficient ((k))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIE</td>
<td>Cd(II)</td>
<td>2240</td>
</tr>
<tr>
<td></td>
<td>Pb(II)</td>
<td>727</td>
</tr>
<tr>
<td></td>
<td>Zn(II)</td>
<td>292</td>
</tr>
</tbody>
</table>

The distribution coefficients \((k)\) were calculated as the ratio of the amount of metal adsorbed by 1 g of resin and the amount of metal remaining in 1 mL of solution after sorption. It can be seen that the overall tendency of CIE resin toward Pb(II), Cd(II) and Zn(II) under non-competitive conditions follows the order: Cd(II) > Pb(II) > Zn(II). The retention capacity of CIE resin for Cd(II) and Pb(II) ions increased with the increase of the equilibrium metal concentration according to a type I isotherm and the maximum adsorption capacity calculated with Langmuir equation were equal to: 0.812 mmol/g, 0.514 mmol/g and 0.224 mmol/g for Cd(II), Pb(II), and Zn(II), respectively.

3. CONCLUSIONS

The adsorption of Cu(II), Co(II), Ni(II), Cd(II), Pb(II) and Zn(II) on a novel CIE resin bearing iminodiacetate groups was reported in this work. The retention capacity for the metal ions on CIE resin, under non-competitive conditions, showed the following order: Cu(II) > Ni(II) > Co(II) > Cd(II) > Pb(II) > Zn(II).

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