

SORPTION AND SEPARATION OF HEAVY METALS FROM ETHYLENEAMINE COMPLEXES

Helena PARSCHOVA, Zdenek MATEJKA, Eva MISTOVA

Institute of Chemical Technology, Department of Power Engineering
Czech Republic, Prague 6, 166 28
(helena.parschova@vscht.cz)

The methods of waste water purification used by the chemist are for example filtration, sedimentation, reverse osmosis and ion exchange.

The ion exchange presents one possibility for the purification of waste water polluted by heavy metals. This work is concerned with the study of sorption and separation of heavy metals (copper, zinc and nickel) from ethyleneamine complexes (EDA, DETA, TETA and TEPA).

The selective removal of heavy metal cations requires special resins to be used. The following resins were used in the experimental study:

- a) oligo(ethyleneamine) resins
- b) picolylamine resin
- c) iminodiacetate chelating cation exchanger
- d) carboxylic cation exchanger
- e) sulphonic cation exchanger

During the experiments effects of metal concentration and flow rate were studied. Loading solution contained 1 - 4 mmol/L of ethyleneamine complex and 1 mmol/L of metal. The flow rate of solution was 6 or 18 BV/h. The breakthrough concentration of metal was 1 mg/L. The regeneration consisted of two steps. In the first step 3 BV of 2mol/L HCl was applied and consequently 5BV of 1 mol/L NaOH was applied in the second step. The regeneration flow rate was 3 BV/h. The metals were analyzed by AAS. The values of EDA concentration were analyzed by ion exchange chromatography.

The first part of the study was concerned with the sorption of heavy metals from ethylenediamine complex. Copper, zinc and nickel were chosen for the sorption experiments.

The experimental results show that sulphonic, carboxylic and iminodiacetate cation exchangers are effective for the sorption but oligo(ethyleneamine) resin showed very low efficiency.

The influence of solution flow rate in the range of 6-18 BV/h on the breakthrough capacities was determined. The breakthrough capacities of cation exchangers are in the majority of cases not influenced by the solution flow rate because their sorption rate is high enough. On the other hand the sorption on picolylamine resin is effective only at flow rate 6 BV/h.

The effect of pH value on the sorption capacity in the range of 5 to 8 is following: The breakthrough capacities are increasing with increasing pH value.

The uptake of heavy metals by oligo(ethyleneamine) resins is based on the coordination bond of heavy metal cation to N-atom of functional group in the free base form. The application of oligo(ethyleneamine) resins in the free base form is not efficient for sorption of Cu^{2+} and Ni^{2+} . The breakthrough capacities were very low (0.01 - 0.06 eq/L). The sorption is efficient only for Zn^{2+} . The breakthrough capacities were the highest for resins with tetraethylenepentamine functional group (0.24 - 0.3 eq/L). These resins achieve very low sorption efficiency, but separation of zinc from EDA on oligo(ethyleneamine) resins at solution pH 5 – 6,5 is effective.

The uptake of heavy metals on various cation exchange resins proceeds predominantly through electrostatic attractive forces (between the negatively charged resin's functional group and positively charged metal cation). But on carboxylic cation exchanger and on chelating iminodiacetate cation exchange resin also the coordination of heavy metal cations to N- and/or O- atoms of resin's functional groups contributes to the uptake of metal by ion exchanger. Theoretically, two coordination bonds of heavy metal cation can be consumed by O-atoms of carboxylic cation exchanger, while three coordination sites of heavy metal cation could be consumed by iminodiacetate moiety (2 bonds to O-atoms and 1 bond to N-atom).

Experimental results show that carboxylic cation exchanger achieve very good sorption capacities (0.84 – 3.16 eq/L). The results of effluent analysis showed that separation of metal from EDA is not effective because effluent contained 0.5mmol/L EDA.

The sorption on sulphonic cation exchanger is effective (0.3 - 1.42 eq/L). Strongly acidic cation exchanger takes up metal from EDA ligand in the cation complex $[\text{Me}(\text{EDA})_x]^{2+}$. Thus, separation of metal from EDA is not effective.

Iminodiacetate chelating cation exchanger resin is effective (1,14 - 1,72 eq/L) in the three sorption forms (H^+ , Na/H and Na^+). IDA-resin takes up heavy metals quantitatively, but the separation from EDA is only partial. In the early phase of the sorption run, copper is taken up as Cu-EDA cation complex. As the resin loading by metal continues, the separation degree is improved.

The sorption on picolylamine resin in the protonated form is effective and the breakthrough capacity is 0.11eq/L. The substantial improvement of separation is achieved on picolylamine type resin in the protonated form at solution pH 4. The characteristic feature of this type of functional group is its ability to co-ordinate metals even in the protonated form. The pH value of an effluent is then constantly in the acidic range and copper is sorbed from solution quantitatively as free cation with the total separation from EDA-ligand.

The second part of the study was concerned with the sorption of copper, zinc and nickel from solutions containing these ethyleneamine complexes: EDA = ethyleneamine, DETA = diethylenetriamine, TETA = triethylenetetramine, TEPA = tetraethylenepentamine.

Heavy metals are taken up completely from the solution by cation exchangers. The breakthrough capacity decreases with increasing chelating ability of ethyleneamine complexes in the solution.

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