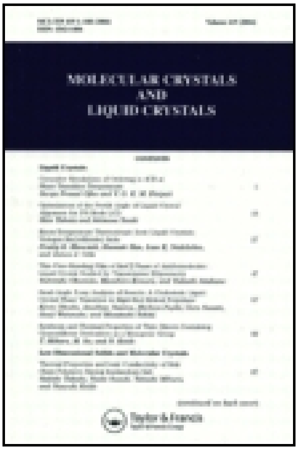

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Azo Direct Dye Immobilized onto Copolymer (Styrene DVB Functionalized with Quaternary Phosphonium Groups) for Removal of Heavy Metal Ions

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AZO DIRECT DYE IMMOBILIZED ONTO COPOLYMER (STYRENE DVB FUNCTIONALIZED WITH QUATERNARY PHOSPHONIUM GROUPS) FOR REMOVAL OF HEAVY METAL IONS

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In this study we investigated a new sorbent system, Azoic Direct Dye-attached poly(S-DVB functionalized) microbeads, for removal of heavy metal ions from aqueous solutions. Quaternary phosphonium salts grafted on a "gel-type" styrene-7% divinylbenzen copolymer were prepared by polymer-analogues direct quaternization reaction, and characterized by IR spectroscopy. A symmetric disazoic direct dye, containing 4, 4′ -diaminobenzanilide as middle component and naphthionic acid as coupling component, was then attached to these microbeads. Microbeads carrying 1.33 mmol Azo Direct Dye/g polymer were used in adsorption/desorption studies. Adsorption rate and capacity of the microbeads for selected metal ions, i.e., Cu(II) and Zn(II), were investigated in aqueous media containing different amounts of these ions (6–200 ppm) at different pH values (2–7). Very high adsorption rates were observed at the beginning, and adsorption equilibria were then gradually achieved in about 5–80 minutes. The maximum adsorptions of metal ions onto the azo direct dye attached microbeads were 2.9 mg/g for Cu(II) ions, and 53.8 mg/g for Zn(II) ions. Desorption of metal ions was studied by using 0.1 M HNO_3 solution (pH 1.0). High desorption ratios (more than 85%) were achieved in all cases. Adsorption/desorption cycles showed the feasibility of repeated use of this novel sorbent system.

Keywords: direct dye; heavy-metal ions removal; styrene-divinylbenzen copolymer

INTRODUCTION

The presence of heavy metal ions in the environment is one of the major concerns due to their toxicity for many life forms. Treatment of aqueous

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wastes containing soluble heavy metals requires concentrating of the metals into a smaller volume followed by recovery or secure disposal [1]. Heavy-metal ions can be removed by adsorption on solid carriers using either non-specific or specific sorbents. Recently, the use of specific sorbents has been considered as one of the most promising techniques [2]. Specific sorbents consist of a carrier matrix, and a ligand (*e.g.*, ion-exchange material or chelating agents) which interacts with the metal ions specifically. The carrier matrix may be an inorganic material (*e.g.*, aluminium oxide, silica or glass) or polymer microbeads (*e.g.*, polystyrene, cellulose, poly(maleic anhydride) or polymethylmethacrylate) [3].

As carrier matrices, polymer microbeads have attracted the most attention because they may easily be produced in a wide variety of compositions, and modified into specific sorbents, by introducing a variety of ligands. Synthetic polymers have almost entirely displaced inorganic carriers, with few exceptions in the separation of heavy-metals ions. One of the most critical points in the use of porous sorbents is their pore structure. Sorbents with highly open pore structures are needed for high adsorption rates. However, high active surface area of the porous sorbents is mainly due to the fine pores in the matrix, which are not available for large molecules. As conclusion, it can be said that the optimization of the pore structures of the carrier matrices is a very important issue to achieve both high adsorption rates and high adsorption capacities.

Polystyrene has been used mostly as support for phase transfer catalysts mainly because of the availability of Merrifield resins [4] and quaternary ammonium ion exchange resins. Thus, quaternary phosphonium salts grafted on copolymer have wide fields of utilization: polar stationary phases for anion chromatography, polymeric reagents for trans-quaternization reactions, phase-transfer catalysts [5], polycationic biocides.

In our previous studies we presented synthesis and characterization of some azoic dyes attached on polymers microbeads, [6] and monoazoic dyes capable to complex metals [7]. For heavy metal removal, we proposed a new ligand, i.e., Azoic Direct dye attached to a new carrier matrix - styrene-divinylbenzene functionalized with quaternary phosphonium salts (Co-PPh). We studied adsorption/ desorption of Cu(II), and Zn(II) ions to these specific sorbents in batch experiments.

EXPERIMENTAL

Azoic Direct Dye–Attached Copolymer Microspheres

Details of the preparation and characterization of the direct dye: 4,4′ - diamino-benzanilide ⇔ naphthionic acid (AN) were described in detail in a previous paper [8].

For dye attachment to the styrene-divinylbenzene functionalized with quaternary phosphonium salts (Co-PPh) microspheres, 50 mL aqueous solution containing 60 mg of AN was poured into 50 mL of the functionalized copolymer in distilled water (containing 0.5 g of the microspheres), and then 10 mL Na_2CO_3 solution 2 M was added. The mixture was maintained under continuous stirring for 5 hours. After reaction, the colored microspheres were separated through filtration, washed with distilled water (3 × 20 mL), ethanol (3 × 20 mL) and dried at 50°C for 24 hours.

The amount of Direct dye attached to the poly(Co-PPh) microbeads was evaluated spectrophotometrically, by reading absorption values of the dye after finishing reaction, and determination of their functionalization degree. The UV-VIS spectra was recorded on SPECORD M42 spectrophotometers, in distillate water. The calculation of the functionalization degree as well as the statistical modelling of the structural repetitive unit of the copolymer were reported in a previous paper [9].

Adsorption/Desorption Studies

We investigated adsorption of copper(II), and zinc(II) ions from aqueous solutions using AN-CoPPh as specific sorbent.

AN-CoPPh = direct dye (naphthionic acid ⇔ 4,4′ - diaminobenzanilide) was attached to styrene-divinylbenzene functionalized with quaternary phosphonium salts microspheres.

Aqueous solutions (20 mL) containing various amounts of metal ions (6–200 ppm) were treated with the sorbents at different pH values (3–7) (adjusted with universal buffer solution) at room temperature, in the flasks where the solutions are stirred magnetically. After 3 hours, the coloured microbeads were separated by filtration. The concentrations of the metal ions in the aqueous phases were measured by using an Atomic Absorption Spectrophotometer (PYE UNICAM SP1900). The amount of adsorbed metal ions per unit mass of the microspheres were evaluated by using expression (1).

$$Q = \frac{(C_0 - C)}{m} \times V$$

where: Q = amount of metal ions adsorbed onto a unit mass of the microbeads (mg/g);

C_0, C = concentrations of the metal ions in initial solution and in the aqueous phase after treatment for certain period of time, respectively (mg/mL);

V = volume of the aqueous phase (mL);

m = amount of copolymer microspheres (g).

Desorption of metal ions was studied in 0.1 M HNO_3 solution at pH 1.0. The solutions containing microspheres carrying metal ions were magnetically stirred in Berzelius flasks for 2 h at room temperature. The final metal ion concentration in the aqueous phase was determined by using an Atomic Absorption Spectrophotometer. The desorption ratio was calculated from the amount of metal ions adsorbed on the microspheres and the final metal ions concentration in the desorption medium, by using expression (2).

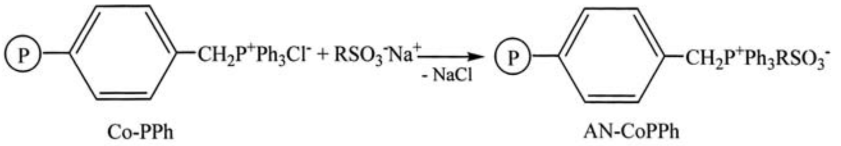
$$\text{Desorption ratio} = \text{amount of metal ions desorbed to the elution medium} / \text{amount of metal ions adsorbed on the microbeads} \times 100$$

Adsorption-desorption cycle was repeated three times by using the same sorbent.

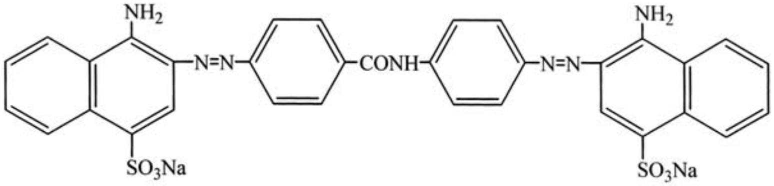
RESULTS AND DISCUSSION

Characterization of Dye-Attached Copolymer Microspheres

Immobilization of direct dyes on the carrier matrix is presented in reaction (1).



where RSO_3Na:



(AN)

The characterization of the dye-attached to copolymer microspheres (AN-CoPPh) was performed by UV-VIS spectroscopy, and results are presented in Table 1.

The fraction of the repetitive unit functionalized with direct dye (AN) was determined based on the phosphorus content in the colored copolymer and the phosphorus content in the copolymer before dye's immobilization, accepting the statistical structure of the repetitive unit of the initial copolymer and final copolymer. The functionalization reaction (dye's

TABLE 1 Characterization of Direct Dye Attached to Copolymer Microspheres (AN-CoPPh)

CoPPh	Dye	Molar ratio	λ_{max} (nm)	C_0 (g/L)	C_f (g/L)	Adsorbed dye (mg dye/0,5g CoPPh)
	AN	1 : 0.25	480	0,923	0,765	15,8

immobilization) does not involve a substitution of an element, it take place only with a chemical transformation of the initial functional group; this process involves a mass variation.

Adsorption Rate

Figure 1 exemplifies adsorption rates of heavy metal ions by direct dye-attached copolymer microspheres as a function of time.

The experiments were performed by using single (not together) solutions of the interested ions. The initial concentration of the ions within the aqueous phase was between 6 and 200 ppm and pH values of medium were 4.1 for Cu(II) ions and 6.8 for Zn(II) ions.

As can be seen from Figure 1, high adsorption rates are observed at the beginning of adsorption, and after approximately 5 minutes the constant values are reached. Adsorption of Zn(II) ions was faster than Cu(II) ions due to much higher affinity of immobilized dye molecules to the first species.

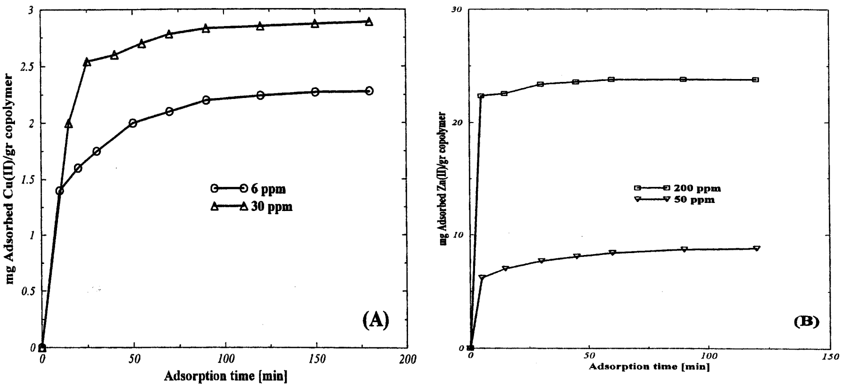


FIGURE 1 Adsorption rates of heavy-metal ions on AN-CoPPh micropheres at 20°C: (A) for Cu(II), (B) for Zn(II).

Several experimental data on the adsorption kinetics of heavy-metal ions by various sorbents have shown a wide range of adsorption rates [10–12]. However, all experimental studies published in the literature have been performed at different conditions, so it is almost impossible to compare the adsorption rates reported.

Adsorption Capacity

Effect of Initial Concentration of Metal Ions

The heavy-metal ions adsorption capacities of the direct dye (AN) – attached to (CoPPh) microspheres are presented as a function of the initial concentration of metal ions in the aqueous phase in Figure 2, using the plateau values shown in Figure 1.

The amount of metal ions adsorbed per mass unit of copolymer (i.e., adsorption capacity) increased first with the initial concentration of metal ions, and then reached a constant value which represents saturation of the active centre (available for specific metal ions) on the microspheres. The maximum adsorption capacities of the AN-CoPPh microspheres are 2.5 and 40.8 mg/g copolymer for Cu(II) ions and Zn(II) ions respectively.

Effect of pH

It is well known that metal ion adsorption both on non-specific and specific sorbents is pH dependent. Therefore, in our study, in order to establish the effect of pH on the adsorption of metal ions onto the AN-CoPPh microspheres, we repeated the experiments at different pH in the range of

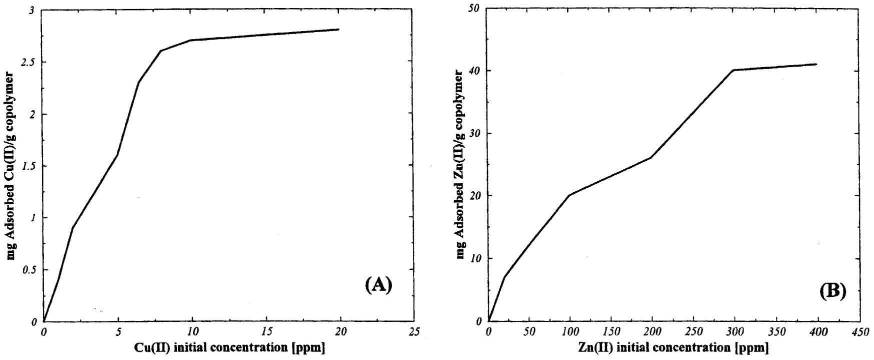


FIGURE 2 Adsorption capacity of AN-CoPPh micropheres for heavy metal ions: (A) for Cu(II), (B) for Zn.

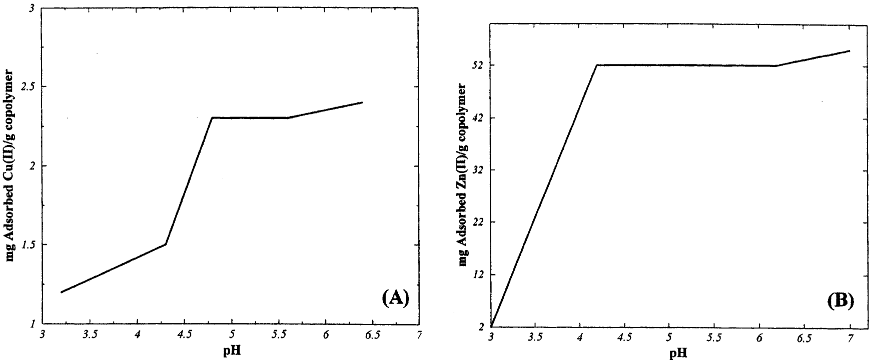


FIGURE 3 Effect of pH on adsorption of heavy metal ions on AN-CoPPh microspheres: (A) for Cu(II), (B) for Zn(II).

2–7. In these experiments, the initial concentration of metal ions was 30 ppm for Cu(II) ions, respectively 200 ppm for Zn(II) ions. Figure 3 presents the specific adsorption of metal ions.

As seen in Figure 3, the adsorption capacity for Cu(II) ions was much lower than the Zn(II). Adsorption of Zn(II)ions first increased linearly with increasing pH and reached almost a constant value at pH ~4.

High adsorption at alkaline pH values implies that metal ions interact with direct dye (AN) not only through the nitrogen atoms by chelating, but also through –SO_3H groups by cation exchanges, which are unprotonated at high pH values.

There was almost insignificant effect of pH on the adsorption of Cu(II) ions.

CONCLUSIONS

From the presented data it can be concluded that the specific sorbent proposed by us, namely (AN-CoPPh) may effectively be used for removal of heavy-metal ions from aqueous solutions.

The characterization method of the sorbent proposed by us – statistical modelling of the structural repetitive unit of the copolymer – is simple, efficient and rapidly.

Heavy-metal ions can be desorbed by using 0.1 M HNO_3 solution at pH 1.0. Therefore, this sorbent can be used in repeated adsorption-desorption cycles.

The amount of metal ions removed is dependent upon their relative concentration zwithin the mixture and pH.

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