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Journal of Chromatography B, 698 (1997) 89–96

JOURNAL OF
CHROMATOGRAPHY B

Dye-incorporated poly(EGDMA–HEMA) microspheres as specific sorbents for aluminum removal

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Received 12 March 1997; received in revised form 12 May 1997; accepted 22 May 1997

Abstract

Aluminum [Al(III)] adsorption onto dye-incorporated poly(ethylene glycol dimethacrylate–hydroxyethyl methacrylate) [poly(EGDMA–HEMA)] microspheres was investigated. Poly(EGDMA–HEMA) microspheres, in the size range of 150–200 μm , were produced by a modified suspension polymerization of EGDMA and HEMA. The reactive dyes (i.e., Congo Red, Cibacron Blue F3GA and Alkali Blue 6B) were covalently incorporated to the microspheres. The maximum dye load was 14.5 μmol Congo Red/g, 16.5 μmol Cibacron Blue F3GA/g and 23.7 μmol Alkali Blue 6B/g polymer. The maximum Al(III) adsorption on the dye microspheres from aqueous solutions containing different amounts of Al(III) ions were 27.9 mg/g, 17.3 mg/g and 12.2 mg/g polymer for the Congo Red, Cibacron Blue F3GA and Alkali Blue 6B, respectively. The maximum Al(III) adsorption was observed at pH 7.0 in all cases. Non-specific Al(III) adsorption was about 0.84 mg/g polymer under the same conditions. High desorption ratios (95%) were achieved in all cases by using 0.1 M HNO_3 . It was possible to reuse these dye-incorporated poly(EGDMA–HEMA) microspheres without significant losses in the Al(III) adsorption capacities. © 1997 Elsevier Science B.V.

Keywords: Aluminum; Poly(ethylene glycol dimethacrylate–hydroxyethyl methylacrylate)

1. Introduction

Aluminum has recently been considered as a causative agent in dialysis encephalopathy, osteodystrophy and microcytic anemia occurring in patients with chronic renal failure who undergo long-term hemodialysis [1,2]. Only a small amount of Al(III) ions in dialysis solutions may cause these disorders. Encephalopathy has also occurred in children consuming aluminum hydroxide as a phosphate

binder for renal disorders [3]. Aluminum has also been implicated in neurotoxicity associated with amyotrophic lateral sclerosis, a form of Parkinsonism and in Alzheimer's disease [4].

Positively charged aqua and hydroxy-monomeric forms have been found to be the most toxic species of aluminum to living organisms in the terrestrial and aquatic environments [5]. Generally, aluminum sulphate is used as a coagulant in the treatment of water to help the removal of suspended matter and highly coloured humic substances [1,4], thus reducing the dose of chlorine later required to ensure satisfactory

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microbiological quality. Hence, potable water often contains high aluminum levels of natural origin and/or from the water purification process [6].

The selective removal of aluminum ions from dialysis solutions and drinking water have been extensively investigated by applying several techniques [7–9]. Among them, the use of specific sorbents has been considered as one of the most promising techniques [10–12]. Specific sorbents consist of a ligand (e.g., ion-exchange function or chelating agents) which specifically interacts with the metal ions, and a carrier matrix which may be an inorganic material (e.g., aluminum oxide, silica, activated carbon or glass) or polymer microspheres (e.g., polystyrene, cellulose, poly(maleic anhydride) or polymethylmethacrylate [13].

In our recent studies, we have developed a series of polymeric microspheres carrying different chelating dyes and metal ions, and evaluated them as affinity sorbents for heavy metal removal and protein adsorption [14–18]. This paper presents the results of a series of experiments in which three reactive dye–ligands, i.e., Congo Red, Cibacron Blue F3GA and Alkali Blue 6B were immobilized onto the poly(EGDMA–HEMA) microspheres, and were used for aluminum removal from aqueous solutions, drinking water and dialysis solution.

2. Experimental

2.1. Preparation of dye-incorporated microspheres

Poly(EGDMA–HEMA) microspheres were selected as the base material for the synthesis of chromatographic affinity sorbents, and produced by a modified suspension polymerization of the respective monomers i.e., ethyleneglycol-dimethacrylate (EGDMA, Rohm, Darmstadt, Germany) and 2-hydroxyethyl methacrylate (HEMA, Sigma, St. Louis, MO, USA) in an aqueous medium [14,16]. Benzoyl peroxide (BPO) and poly(vinyl alcohol) (PVAL) (M_n 100 000, 98% hydrolyzed, Aldrich, Rockford IL, USA) were used as the initiator and the stabilizer, respectively. Toluene (Merck, Darmstadt, Germany) was selected as the diluent and used as received. Dispersion medium was distilled water. The EGDMA/HEMA ratio, the amounts of BPO, PVAL, toluene and the

agitation speed were 8 ml/4 ml, 0.06 g, 0.2 g, 12 ml and 600 rpm, respectively. Polymerizations were carried out 65°C for 4 h and 90°C for 2 h. After cooling, the polymeric microspheres were separated from the polymerization medium by filtration, and the residuals (e.g., unconverted monomer, toluene) were removed by a cleaning procedure given in detail elsewhere [19]. Note that, about 90% of the microspheres obtained by the procedure given above were in the size range of 150–200 μm (i.e., the swollen size).

The dyes, i.e. Congo Red, Cibacron Blue F3GA and Alkali Blue 6B were purchased from BDH (UK). A 3 g amount of poly(EGDMA–HEMA) microspheres was magnetically stirred (at 400 rpm) with 100 ml of the dye aqueous solution containing 4.0 g NaOH in a sealed reactor at a constant temperature of 80°C for 4 h. In order to change the amount of dye incorporated in the sorbent, the initial concentration of the dye was varied between 0.1 and 4 mg/ml. After this procedure, the dye microspheres were filtered, and washed with distilled water and methanol several times until all the unbound dye molecules were removed. The dyed microspheres were stored at 4°C with 0.02% sodium azide to prevent microbial growth.

The amounts of dye incorporated in the microspheres were estimated by elemental analysis (Leco, CHNS-932, USA). The amount of dye incorporation on the microspheres was calculated from these data, by considering the nitrogen and sulfur stoichiometries.

The leakage of the dye from the dye microspheres was investigated within the media at the selected pH in the range of 2.0–7.0. These media were the same as those were used in the Al(III) adsorption experiments. The medium with the dye microspheres was stirred for 24 h at room temperature. Then microspheres were separated from the medium, the dye concentrations were measured in the liquid phase by spectrophotometry at 497 nm for Congo Red, 599 nm for Alkali Blue 6B and 630 nm for Cibacron Blue F3GA.

2.2. Adsorption/desorption studies

Adsorption of Al(III) from aqueous solutions was investigated in batch experiments. Effects of the

initial Al(III) concentration and pH of the medium on the adsorption rate and adsorption capacity were studied. A 50 ml volume of aqueous solutions containing different amounts of Al(III) ions (in the range of 1–100 ppm) were treated with the 100 mg of sorbents [i.e., the control and the dye-incorporated poly(EGDMA–HEMA) microspheres] at different pH (in the range of 2.0–7.0) (adjusted with universal buffer solution) at room temperature, in the flasks agitated magnetically at an agitation speed of 600 rpm. The concentrations of the Al(III) ions in the aqueous phases after the desired treatment periods were measured by using an atomic absorption (spectrophotometer, GBC 932 AA, Australia). The extent of adsorption per unit mass of the microspheres were evaluated by using the following expression.

$$Q = [(C_0 - C) \cdot V] / m \quad (1)$$

where Q is the amount of Al(III) ions adsorbed onto unit mass of the microspheres (mg/g); C_0 and C are the concentrations of the Al(III) ions in the initial solution and in the aqueous phase after treatment for certain period of time, respectively (mg/ml); V is the volume of the aqueous phase (ml); and m is the amount of poly(EGDMA–HEMA) microspheres used (g).

Desorption of Al(III) ions was studied in buffer solutions containing 0.1 M HNO₃. The microspheres loaded with Al(III) ions were placed in this desorption medium and stirred (at a stirring rate of 600 rpm) for 2 h at room temperature. The final Al(III) concentration in the aqueous phase was determined by atomic absorption. The desorption ratio was calculated from the amount of Al(III) ions adsorbed on the microspheres and the final Al(III) concentration in the desorption medium.

In order to test the reusability of the dye-incorporated poly(EGDMA–HEMA) microspheres, Al(III) adsorption–desorption procedure was repeated six times by using the same batch of polymeric sorbent.

3. Results and discussion

3.1. Dye-incorporated microspheres

Details of the preparation of poly(EGDMA–HEMA) microspheres were given in our previous

papers [14,20]. The microspheres are highly swellable (due to HEMA) in aqueous media (the swelling ratio is 55%), and are in the size range 150–200 μm (i.e., swollen size). They are rigid and very strong because of the highly cross-linked structure (due to EGDMA cross-linker), and therefore, they are suitable for column applications in chromatographic separations.

In this study, we have attempted to prepare specific affinity sorbents with three reactive dyes (i.e., Congo Red, Cibacron Blue F3GA and Alkali Blue 6B) for Al(III) removal from aqueous solutions. Chemical structures of these dyes are given in Fig. 1. Their structures are quite different, and contain several active sites (amino, azo, sulfonyl and triazine groups indicated in Fig. 1) for interaction with aluminum ions.

The dye molecules were covalently incorporated into poly(EGDMA–HEMA) microspheres. Cibacron Blue F3GA is a widely used dye–ligand. It is known that ether linkages are formed between the reactive triazine ring of the dye and the hydroxyl groups of

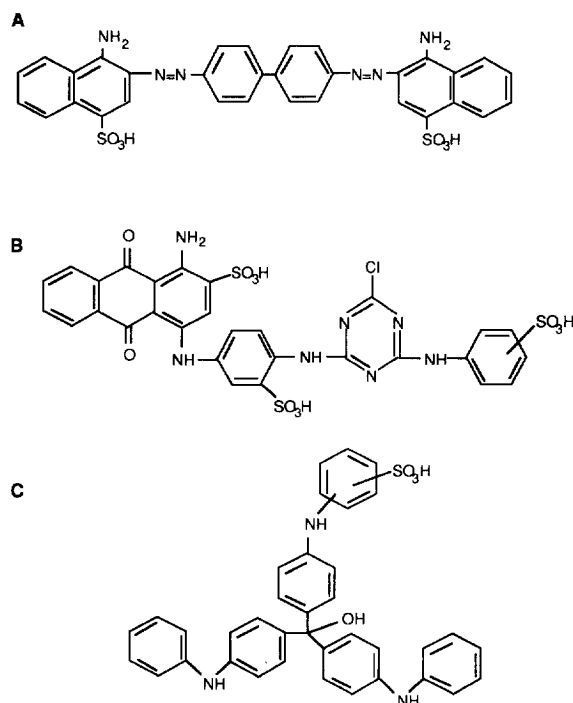


Fig. 1. Structure of: (A) Congo Red; (B) Cibacron Blue F3GA and (C) Alkali Blue 6B.

the sorbent (like HEMA groups in our case) [20]. In the case of Congo Red and Alkali Blue 6B, covalent bonds are formed as a result of the condensation reactions between the aromatic amine groups of the dyes and the hydroxyl groups of the HEMA, [21]. Note that the dye microspheres were extensively washed until there was no leakage from any of the dye microspheres and in any media used at adsorption and/or desorption steps. The visual observations (the colour of the beads), elemental analysis and FTIR spectra all indicated the adsorption of dyes [14,15,20,21].

In this study, the initial concentration of each dye in the dye-incorporation medium was varied to obtain the extent of dye loading (i.e., the amount of dye per gram of the microspheres). Table 1 gives the extent of dye-incorporations with their respective initial concentrations. In general, dye-incorporations first increased and then reached a saturation value at an initial dye concentration of 2.0 mg/ml (for all dyes). The maximum extent of dye incorporation for Congo Red, Cibacron Blue F3GA and Alkali Blue 6B, was 14.6, 16.5 and 23.7 $\mu\text{mol/g}$ polymer, respectively. The order of dye loading on/in the microspheres is as follows: Alkali Blue 6B > Cibacron Blue F3GA > Congo Red. This may be due to the molecular structures of the respective dyes given in Fig. 1. Most probably, the Congo Red molecules were attached to the matrix through both symmetric amino groups, therefore oriented towards the surface somewhat horizontally and occupied more area than the other two dye molecules. In contrast Alkali Blue 6B and Cibacron Blue F3GA molecules may interact with the surface only through amino and chloride groups therefore placed on the surface somewhat vertically, thus it was possible to

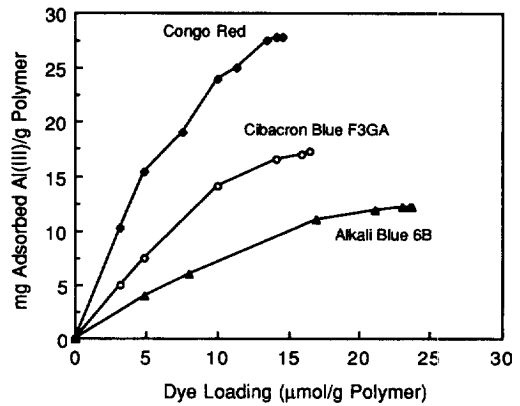


Fig. 2. Effects of dye loading on the Al(III) adsorption onto dye-incorporated poly(EGDMA-HEMA) microspheres. Al(III) concentration: 100 ppm, pH 7.0, T , 20°C.

immobilize more Alkali Blue 6B and Cibacron Blue F3GA molecules on the unit surface of the sorbent.

3.2. Adsorption of Al(III) from aqueous solutions

3.2.1. Effects of dye loading

Fig. 2 shows the effects of dye loading on Al(III) adsorption. When the dye load increased the amount of Al(III) adsorbed onto the dye microspheres first increased and then reached an almost constant values for all dyes. This is expected in view of the number of available active sites on the dye ligands for interaction with Al(III) ions.

It should be mentioned that the highest Al(III) adsorption was obtained with the Congo Red-incorporated microspheres. The maximum Al(III) adsorption for Congo Red, Cibacron Blue F3GA and Alkali Blue 6B, was of 27.9, 17.3 and 12.2 mg/g

Table 1
Dye incorporation onto poly(EGDMA-HEMA) microspheres

Dye concentration (mg/ml)	Congo Red ($\mu\text{mol/g}$)	Cibacron Blue F3GA ($\mu\text{mol/g}$)	Alkali Blue 6B ($\mu\text{mol/g}$)
0.1	3.2	4.8	8.0
0.5	7.5	10.0	17.0
1.0	11.3	14.2	21.1
2.0	13.5	16.0	23.0
3.0	14.5	16.5	23.6
4.0	14.6	16.5	23.7

polymer, respectively. The order of Al(III) adsorption on the microspheres is as follows: Congo Red > Cibacron Blue F3GA > Alkali Blue 6B. It is expected that the ligand molecules should be immobilized on the carrier matrices in such a way that their binding sites in the immobilized state would be available to the molecules with which they interact with. Most probably, Congo Red molecules were immobilized on the microspheres in a more favourable form than the other dye ligands, which led to higher amount of Al(III) adsorption. Although a much higher number of Alkali Blue 6B molecules can be immobilized on the microspheres (Table 1), the extent of Al(III) adsorption cannot be increased further.

3.2.2. Adsorption rate

Adsorption rates of Al(III) ions from aqueous solutions onto the dye-incorporated poly(EGDMA–HEMA) microspheres were also determined. High adsorption rates were observed at the beginning, and then plateau values (i.e., adsorption equilibrium) were gradually reached within 40 min. Adsorption of Al(III) ions was quite fast, especially when the Al(III) ion concentration was high. This may be due to high driving force, which is the difference in Al(III) ion concentration between adsorption medium and the solid-phases, in the case of high Al(III) ion concentration.

In addition, Al(III) adsorption onto Congo Red-incorporated microspheres was much faster than onto Cibacron Blue F3GA and Alkali Blue 6B incorporated microspheres. The order of adsorption rate is as follows: Congo Red > Cibacron Blue F3GA > Alkali Blue 6B.

3.2.3. Adsorption capacity

Fig. 3 shows the effects of initial concentration of Al(III) ions onto the adsorption capacity of the dye-incorporated poly(EGDMA–HEMA) microspheres. The amount of Al(III) ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) first increased with the initial concentration of Al(III) ions then reached a plateau value at about an initial Al(III) ions concentrations of 50 ppm, which represents saturation of the active sites (available for Al(III) ions) on the microspheres. The maximum adsorption capacities of Al(III) ions for Congo Red,

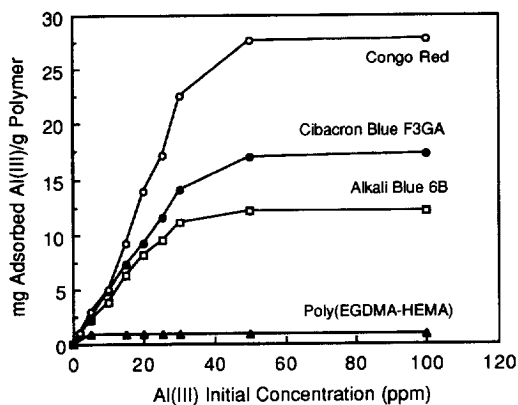


Fig. 3. Effects of Al(III) initial concentration on Al(III) adsorption onto dye-incorporated poly(EGDMA–HEMA) microspheres. Dye loading: 14.5 μmol Congo Red/g; 16.5 μmol Cibacron Blue F3GA/g; 17.0 μmol Alkali Blue 6B/g, pH 7.0 and T , 20°C.

Cibacron Blue F3GA and Alkali Blue 6B, were 27.9, 17.3 and 12.2 mg/g polymer, respectively.

It should be noted that the nonspecific adsorption [adsorption on plain poly(EGDMA–HEMA) microspheres] of Al(III) ions was relatively low 0.84 mg/g. Poly(EGDMA–HEMA) microspheres do not contain ion-exchange or chelating groups. Preferred coordination structure and preferred coordinating ligand atom may be utilized for this adsorption. For example, Al(III) ions may interact with O-atom as the ligand [22]. Diffusion of Al(III) ions into the swollen polymeric structure may also contribute to this nonspecific adsorption.

For comparison of affinities of Al(III) ions for incorporated dye molecules, distribution coefficients (K_d) of Al(III) ions between the polymer phase and the adsorption medium at equilibrium were calculated by using the following expression.

$$K_d = \frac{\text{Adsorbed Al(III) ions (mg) / Amount of polymer (g)}}{\text{Amount of metal ions in solution (mg) / Volume of solution (ml)}}$$

Much higher K_d values were obtained for Congo Red (631.22). This means that the affinity of Al(III) ions is significantly higher for Congo Red molecules than for the other dyes [i.e., Cibacron Blue F3GA (264.52) and Alkali Blue 6B (161.37)].

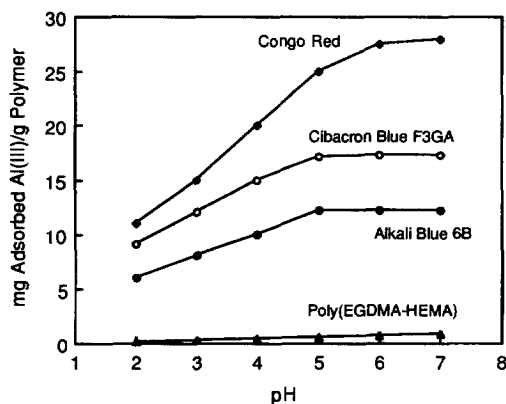


Fig. 4. Effects of pH on Al(III) adsorption upon dye-incorporated poly(EGDMA-HEMA) microspheres. Dye loading: 14.5 μmol Congo Red/g; 16.5 μmol Cibacron Blue F3GA/g; 17.0 μmol Alkali Blue 6B/g, Al(III) initial concentration: 100 ppm and T , 20°C.

3.2.4. Effect of pH

Fig. 4 shows the effects of pH on Al(III) adsorption onto the dye microspheres. In all cases studied, adsorption of Al(III) ions increased with

increasing pH and reached almost a plateau value at around pH 5.0. High adsorption capacities at around neutral pH values imply that Al(III) ions interact with dye molecules not only through the nitrogen and oxygen atoms by chelating, but also electrostatically through $-\text{SO}_3\text{H}$ groups, which are ionized at neutral pH.

3.3. Competitive adsorption

Competitive adsorption of the metal ions from drinking water and dialysis water (reverse osmosis) were also investigated. The water containing different amounts of each metal ion was incubated with dye microspheres batchwise. Tables 2 and 3 show the adsorbed amounts for each metal ions. The adsorption capacity of the dye-incorporated poly(EGDMA-HEMA) microspheres for Cu(II) ions was higher than that for other ions. However, it should also be noted that the extent of adsorption of each type of metal ion is strongly dependent upon their relative concentrations within the medium.

Table 2
Aluminum removal from the drinking water

Metal ion	Initial concentration of metal ions (ppb)	Metal ion adsorption ($\mu\text{g}/\text{g}$)		
		Congo Red	Cibacron Blue F3GA	Alkali Blue 6B
Al(III)	65.00	17.63 \pm 0.1	9.91 \pm 0.2	8.35 \pm 0.1
Fe(III)	21.08	7.71 \pm 0.2	7.31 \pm 0.1	5.87 \pm 0.1
Cu(II)	136.50	41.48 \pm 0.5	35.20 \pm 0.3	33.64 \pm 0.6
Cd(II)	0.05	nd	nd	nd
Pb(II)	0.02	nd	nd	nd
Zn(II)	18.06	4.66 \pm 0.1	4.17 \pm 0.1	3.42 \pm 0.1

Adsorption conditions: pH 6.50; T , 20°C.

nd: Not determined. Each experiment was repeated three times.

Table 3
Aluminum removal from dialysis water

Metal ion	Initial concentration of metal ions (ppb)	Metal ion adsorption ($\mu\text{g}/\text{g}$)		
		Congo Red	Cibacron Blue F3GA	Alkali Blue 6B
Al(III)	11.89	4.67 \pm 0.1	3.32 \pm 0.1	3.27 \pm 0.1
Fe(III)	0.03	nd	nd	nd
Cu(II)	0.52	0.12 \pm 0.01	0.11 \pm 0.02	0.10 \pm 0.01
Zn(II)	1.18	0.40 \pm 0.01	0.36 \pm 0.05	0.33 \pm 0.03

Adsorption conditions: pH 6.50; T , 20°C.

nd: Not determined. Each experiment was repeated three times.

The World Health Organization and the European Community guide values for Al(III) ions for drinking water is 200 ppb [23,24]. Al(III) concentrations both in drinking water and dialysis water are below this value. It should be noted that polymer treatment significantly decreases the heavy metal content and these waters can be used safely especially for the preparation of dialysis solutions.

3.4. Desorption and repeated use

Table 4 summarizes the desorption data. Desorption ratios were very high (up to 98.9%) with the eluent system and under conditions used. Therefore, we conclude that HNO_3 is a suitable desorption agent for all dye sorbents, and allows their repeated use.

In order to show the reusability of the dye-incorporated poly(EGDMA–HEMA) microspheres, adsorption–desorption cycle was repeated six times by using the same sample of affinity sorbent. As can be seen from Fig. 5, adsorption capacities for all sorbents did not change noticeably during the adsorption–desorption cycles.

In general, serum aluminum levels of chronic hemodialysis patients are high. Abnormal aluminum accumulation can cause encephalopathy, osteomalacia and renal anemia. Recently, desferrioxamine (DFO) has been used clinically for the removal of aluminum. Hosokawa et al. [25] applied DFO therapy to hemodialysis patients for 3 months to decrease aluminum levels. The results showed that

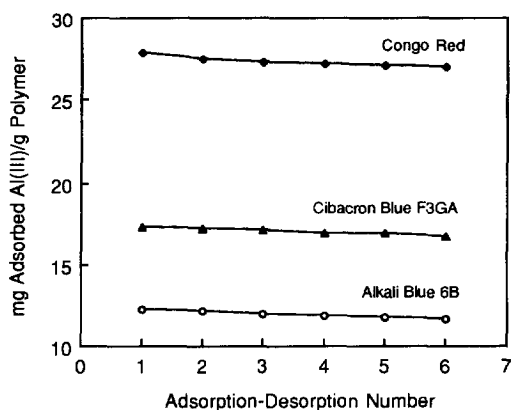


Fig. 5. Repeated use of dye-incorporated poly(EGDMA–HEMA) microspheres. Dye loading: 14.5 μmol Congo Red/g; 16.5 μmol Cibacron Blue F3GA/g; 17.0 μmol Alkali Blue 6B/g. Al(III) initial concentration: 100 ppm; pH 7.0 and T , 20°C.

serum aluminum levels significantly decreased. Botella et al. [26] reported that serum aluminum levels significantly decreased with DFO treatment lasting 6 months. But, hemoperfusion (i.e., adsorption onto specific sorbents) is more effective than hemodialysis in removing metal ions [27]. Chang and Barre [7] used desferrioxamine adsorbed colloid coated activated charcoal and reported that adsorbent hemoperfusion is more efficient than hemodialysis in removing aluminum after desferrioxamine infusion. Previously, many researchers reported that in order to decrease serum aluminum levels in chronic hemodialysis patients it was necessary to use low aluminum dialysate [28,29].

Table 4

Desorption of Al(III) ions from dye microspheres

Al(III) concentration (ppm)	Desorption ratio (%)		
	Congo Red	Cibacron Blue F3GA	Alkali Blue 6B
2.0	92.9±1.4	94.7±2.2	91.5±1.7
5.0	96.9±1.8	96.7±1.7	91.5±2.6
10.0	96.8±1.9	97.3±1.2	95.9±2.5
15.0	98.0±2.3	98.1±2.1	95.4±1.8
20.0	98.6±2.1	97.4±1.3	96.3±1.4
25.0	98.0±2.6	97.6±1.4	96.8±2.1
30.0	98.9±1.1	98.0±1.5	96.1±2.5
50.0	98.7±1.4	98.1±2.0	95.9±2.1
100.0	98.2±1.0	97.9±1.6	95.0±1.7

Al(III) adsorption medium: Al(III) concentration: 100 ppm; pH 7.0; T , 20°C.

Each experiment was repeated three times.

4. Conclusions

Poly(EGDMA–HEMA) microspheres, in the size range of 150–200 μm , were produced by a modified suspension copolymerization of EGDMA and HEMA. These novel microspheres were then successfully charged with reactive dyes, namely Congo Red, Cibacron Blue F3GA and Alkali Blue 6B. The highest dye loading was achieved with Alkali Blue 6B. However, the maximum Al(III) adsorption was observed in the case of the Congo Red-incorporated microspheres, which may be attributed to the most favorable molecular orientation of this dye molecules in the immobilized state. The maximum Al(III) adsorption was observed at pH 7.0 in all cases, which may be due to the preferential interaction between Al(III) ions and dye molecules at this pH. Successful desorption ratios (more than 95% of the adsorbed Al(III) ions) were achieved by using 0.1 M HNO_3 . It was possible to reuse these novel sorbents without significant losses in their adsorption capacities.

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