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## Cibacron Blue F3GA-attached polyvinylbutyral microbeads as novel magnetic sorbents for removal of Cu(II), Cd(II) and Pb(II) ions

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### Abstract

Magnetic polyvinylbutyral based microbeads containing 12.4  $\mu\text{mol}$  Cibacron Blue F3GA/g were used in the adsorption–desorption of some selected heavy metal ions, i.e., Cu(II), Cd(II) and Pb(II) from aqueous media containing different amounts of these ions (5–500 ppm) and at different pH values (2.0–8.0). Adsorption rates were high, and adsorption equilibria were reached in about 30 min. The maximum adsorptions of heavy metal ions onto the Cibacron Blue F3GA-attached affinity microbeads from their single solutions were 9.6 mg/g for Cu(II), 38.6 mg/g for Cd(II), 86.2 mg/g for Pb(II). When the heavy metal ions competed (in the case of the adsorption from their mixture) the amounts of adsorption were 6.5 mg/g for Cu(III), 20.3 mg/g for Cd(II) and 41.6 mg/g for Pb(II). Under non-competitive and competitive conditions the affinity order of ions was Pb(II)>Cd(II)>Cu(II). Desorption of heavy metal ions was achieved using 0.1 mol  $\text{HNO}_3$  in 30 min. It was observed that heavy metal ions could be repeatedly adsorbed and desorbed without significant loss in adsorption capacity. © 1998 Elsevier Science B.V.

**Keywords:** Sorbents; Magnetic sorbents; Polyvinylbutyral microbeads; Cibacron Blue microbeads; Adsorption; Heavy metals; Copper; Cadmium; Lead; Metal cations

### 1. Introduction

Heavy metals have become an ecotoxicological hazard of prime interest and increasing significance, owing to their tendency to accumulate in living organisms. The necessity to reduce the amount of heavy metal ions in wastewater streams of hydro-metallurgical and other industries, and subsequent possible re-use of these metal ions, has led to an increasing interest in selective sorbents [1–3]. Recently, there has been increased interest in the use of

magnetic carriers in the removal of heavy metals [4]. Magnetic carriers can be produced using inorganic materials or a number of synthetic and natural polymers [5]. High mechanical resistance, resistance to solvents and excellent shelf life make inorganic materials ideal carriers. The main disadvantage of inorganic supports is their limited functional groups for specific binding. Magnetic carriers can be porous or non-porous. Magnetic carriers are more commonly manufactured from polymers since they have a variety of surface functional groups which can be tailored to use specific applications [6]. Poly(ethylene glycol) [7], polymethylmethacrylate [8], poly(vinyl alcohol) [9] polyacrylamide [10] and

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alginate [11] are typical polymeric carriers which used in heavy metal removal.

In this study, we prepared a new magnetic sorbent based on polyvinylbutyral microbeads. These affinity microbeads were prepared by modified solvent evaporation method. An affinity dye, Cibacron Blue F3GA was then attached covalently to the matrix. In this communication, we present preparation and characterization of magnetic polyvinylbutyral microbeads, and potential for their use in heavy metal adsorption–desorption.

## 2. Experimental

### 2.1. Preparation of magnetic polyvinylbutyral microbeads

The magnetic polyvinylbutyral microbeads were prepared by a modified solvent evaporation method [12]. Polyvinylbutyral was supplied by Hoechst (Germany). The proper amount of polyvinylbutyral was dissolved in chloroform (BDH, UK) and then this solution was transferred immediately into the distilled water as the dispersion medium containing the proper amount of emulsifier (poly(vinyl alcohol), Merck, sodium dodecyl sulphate, Sigma, and Pluronic F6800, BASF). This monomeric mixture was transferred into the glass reactor (volume: 1 l) and stirred with a mechanical stirrer for 16 h at 20°C. The stirring rate was 700 rpm. After allowing the solvent to evaporate, magnetite particles ( $\text{Fe}_3\text{O}_4$ , diameter was less than 5  $\mu\text{m}$ , Aldrich) completely encapsulated in polyvinylbutyral. The polymerization recipe is given in Table 1.

Table 1  
Polymerization recipe

Polyvinylbutyral	20 g
Chloroform	100 ml
Poly(vinyl alcohol)	4 g
Sodiumdodesilsulphate	2 g
Pluronic PE 6800	5 ml (6%, v/v)
Magnetite	0.5 g
Water	400 ml

### 2.2. Cibacron Blue F3GA attachment

Ten ml of the aqueous dye solution containing 300 mg Cibacron Blue F3GA (BDH, UK) was transferred into 90 ml of the mixture of the polyvinylbutyral microbeads pieces in distilled water, and then 4.0 g of NaOH was added. The medium was heated in a sealed reactor for 4 h at a stirring rate of 400 rpm, and at a constant temperature of 80°C. Under these conditions, a chemical reaction took place between the Cl containing group of the Cibacron Blue F3GA and the OH groups of the polyvinylbutyral based microbeads, with the elimination of HCl, resulting in covalent attachment of Cibacron Blue F3GA to the polyvinylbutyral. Later, in order to avoid the future leakage of the Cibacron Blue F3GA during heavy metal adsorption, the microbeads were washed several times with distilled water and methanol until all of the non-specific adsorbed (or diffused/absorbed Cibacron Blue F3GA molecules into the pores of microbead) Cibacron Blue F3GA molecules were removed.

### 2.3. Microbead characterization

#### 2.3.1. Measurement of water content

In order to exhibit swellabilities of the microbeads, swelling ratios were obtained as follows: the apparent volume of the dry microbeads (1 g) was measured in a cylindrical glass tube (10 ml). Water was added into the tube, and the microbeads were allowed to swell at room temperature for 24 h (i.e., the predetermined equilibrium swelling time) with occasional shaking, and then the volume of the swollen microbeads was measured. Swelling ratio was calculated by the following equation.

$$\text{Swelling ratio (\%)} = [(V_{\text{swollen}} - V_{\text{dry}})/V_{\text{dry}}] \times 100 \quad (1)$$

where,  $V_{\text{swollen}}$  is volume of swollen microbeads (ml), and  $V_{\text{dry}}$  is volume of dry microbeads (ml).

#### 2.3.2. Analysis of magnetism

The magnetism degree of the polyvinylbutyral microbeads was measured in a magnetic field by using a vibrating-sample magnetometer (Princeton Applied Research, USA). The presence of magnetite

in the polymeric structure was investigated with ESR spectrophotometer (EL 9, Varian).

### 2.3.3. Scanning electron microscopy

In order to observe the surface topography of the polyvinylbutyral microbeads, scanning electron micrographs of the gold coated samples were taken with a scanning electron microscope (Model: Raster Electronen Microscopy, Leitz-AMR-1000, Germany).

### 2.3.4. Fourier transform (FT) IR studies

FT-IR spectra of the dye (i.e., Cibacron Blue F3GA), the plain and Cibacron Blue F3GA-attached polyvinylbutyral microbeads were obtained by using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Japan). The dry polyvinylbutyral microbeads (about 0.1 g) was thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany), and pressed to form a tablet, and the spectrum was then recorded.

### 2.3.5. Elemental analysis

The amount of Cibacron Blue F3GA attached to the polyvinylbutyral microbeads was determined from the elemental-analysis device (Leco, CHNS-932, USA).

## 2.4. Heavy metal adsorption–desorption

Heavy metal ions adsorption from the single metal aqueous solutions was investigated in batch adsorption–equilibrium experiments. Effects of the initial concentration of metal ions and pH of the medium on the adsorption rate and capacity were studied. 20 ml of aqueous metal ion solutions with different concentrations (in the range of 5–500 ppm) were treated with the plain and Cibacron Blue F3GA-attached polyvinylbutyral microbeads at different pH (in the range of 2.0–8.0, adjusted with universal buffer solution, citric acid–potassium dihydrogenphosphate–boric acid–diethylbarbituric acid) at room temperature, in the flasks agitated magnetically at an agitation speed of 600 rpm. After the pre-determined adsorption time, the microbeads were separated from the adsorption medium, and the concentration of the metal ions in the aqueous phase was measured by using a graphite furnace atomic

absorption spectrophotometer (GBC 932 AA, Australia). The amount of adsorbed heavy metal ions was obtained by using the following expression.

$$Q = [(C_0 - C) \cdot V] / m \quad (2)$$

Here,  $Q$  is the amount of metal ions adsorbed onto unit amount of the polyvinylbutyral microbeads (mg/g);  $C_0$  and  $C$  are the concentrations of the metal ions in the initial solution and in the aqueous phase after adsorption, respectively (mg/ml);  $V$  is the volume of the aqueous phase (ml); and  $m$  is the amount of the polyvinylbutyral microbeads (g).

Competitive adsorption of heavy metal ions from their mixture was also investigated in batch wise form. A solution (20 ml) containing 50 ppm from each metal ions was treated with the Cibacron Blue F3GA-attached polyvinylbutyral microbeads at a pH of 7.0 at room temperature, in the flasks agitated magnetically at 600 rpm. After adsorption, concentration of the metal ions in the supernatant was obtained by an atomic absorption spectrophotometer.

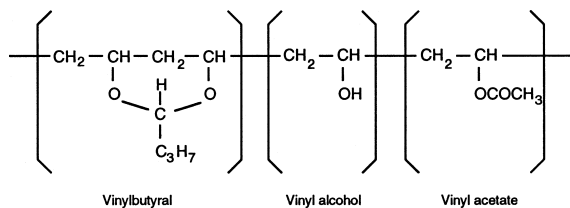
In order to determine the reusability of the Cibacron Blue F3GA-attached polyvinylbutyral microbeads, consecutive adsorption–desorption cycles were repeated five times by using the same affinity microbeads. Desorption of heavy metal ions was achieved by using 0.1 M HNO<sub>3</sub> solution. The polyvinylbutyral microbeads loaded heavy metal ions were placed in this desorption medium and stirred at 600 rpm for 30 min 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 microbeads and the final metal ions concentration in the desorption medium.

## 3. Results and discussion

### 3.1. Properties of polyvinylbutyral microbeads

Polyvinylbutyral based microbeads prepared in this study have a rather hydrophilic structure. The molecular formula of polyvinylbutyral resin is as follows. It consists of vinylbutyral, vinyl alcohol and vinyl acetate comonomers in the approximate ratio

75:22:3, respectively [13]. The polyvinylbutyral microbeads swell rapidly, and the equilibrium is achieved in about 15 min. Note that the equilibrium swelling ratio was about 45% on weight base.



The presence of magnetite in the polymeric structure was confirmed by electron spin resonance (ESR). After the Cibacron Blue F3GA attachment, the intensity of the magnetite peak did not change. A peak of magnetite (i.e.,  $\text{Fe}_3\text{O}_4$  fine particles) was detected in the ESR spectrum as shown in Fig. 1. The behavior of magnetic microbeads in a magnetic field using a vibrating magneto-meter was given in Fig. 2 in terms of emu which is related to the intensity of magnetization of the sample vs. applied magnetic field. In this spectra, 3000 Gauss magnetic field was found sufficient to excite all of the dipole moments of 1.0 g sample which consists of magnetite. After Cibacron Blue F3GA attachment, the intensity of the magnetization of the sample is not affected significantly with the applied magnetic field. This value will be an important design parameter for a magnetically fluidized bed or for magnetic filtration using these microbeads. The value of this magnetic field is a function of the flow velocity, particle size and magnetic susceptibility of solids to be removed. In the literature, this value changes from 8 kG to 20

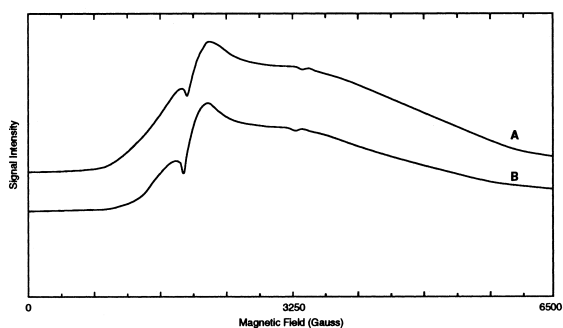


Fig. 1. ESR spectra of polyvinylbutyral microbeads; (A) Cibacron Blue F3GA-attached microbeads; (B) plain microbeads.

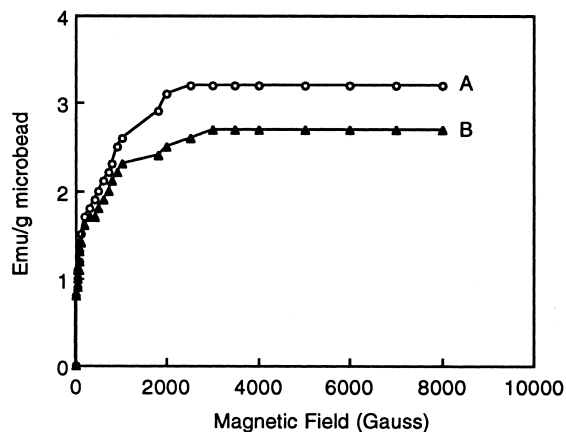


Fig. 2. The magnetic behavior of polyvinylbutyral microbeads; (A) plain microbeads; (B) Cibacron Blue F3GA-attached microbeads.

kG for various applications, thus our magnetic microbeads will need less magnetic intensity in a magnetically fluidized bed or for a magnetic filter.

Fig. 3 shows the SEM micrograph of the polyvinylbutyral microbeads. As clearly seen, the microbeads have a spherical shape and rough surface due to the abrasion of magnetite crystals (diameter  $< 5 \mu\text{m}$ ) during the coating procedure. These surface properties of the magnetic microbeads would enhance adsorption of the heavy metal ions.

As mentioned before, Cibacron Blue F3GA was selected as the affinity ligand, and attached within the polyvinylbutyral microbeads. Fig. 4 gives the chemical structure of this dye. Note that the possible binding sites of heavy metal ions are  $-\text{SO}_3\text{H}$ ,  $-\text{NH}$ ,

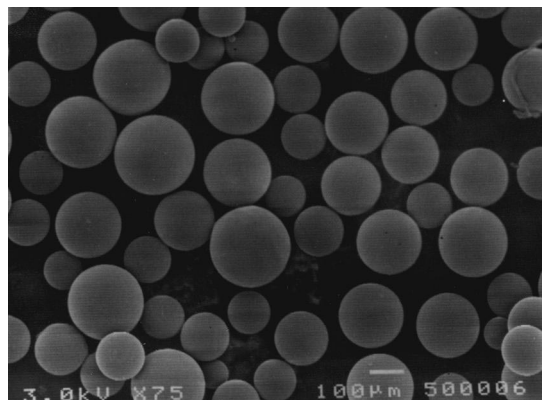


Fig. 3. SEM photograph of polyvinylbutyral microbeads.

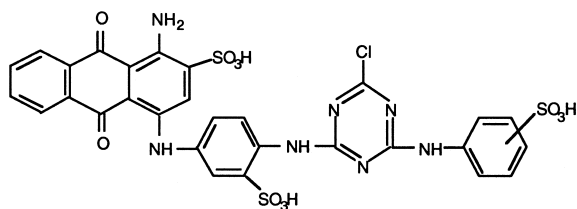


Fig. 4. Chemical structure of Cibacron Blue F3GA.

–NH<sub>2</sub> and triazine groups. Fig. 5 gives the FTIR spectra of the plain and Cibacron Blue F3GA-attached polyvinylbutyral microbeads. The band observed at 1150 cm<sup>-1</sup> was assigned to symmetric stretching of S=O, as also pointed out on the chemical structure of the Cibacron Blue F3GA (Fig. 4). The band observed at 3500 cm<sup>-1</sup> was assigned to the –OH functional group. After Cibacron Blue F3GA attachment, the intensity of the –OH band increases due to NH stretching. The split of the band at 3300–3500 cm<sup>-1</sup> indicates also SO<sub>3</sub>H and NH<sub>2</sub> groups. These bands show the attachment of Cibacron Blue F3GA within the polyvinylbutyral microbeads.

Elemental analysis of the plain and Cibacron Blue F3GA-attached polyvinylbutyral microbeads performed, and the attachment of the Cibacron Blue F3GA was found as 12.4 μmol/g from the stoichiometry. Cibacron Blue F3GA leakage was also studied. There was no Cibacron Blue F3GA leakage

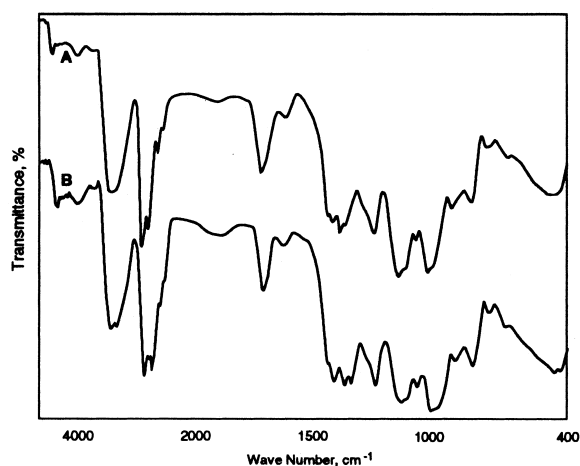


Fig. 5. FTIR spectra of (A) polyvinylbutyral; (B) Cibacron Blue F3GA-attached polyvinylbutyral microbeads.

in any of the heavy metal adsorption and desorption media, which assured that the washing procedure was quite satisfactory for removal of physically adsorbed Cibacron Blue F3GA molecules from the polyvinylbutyral microbeads.

### 3.2. Adsorption/desorption studies

#### 3.2.1. Adsorption rates

The adsorption rates of heavy metal ions [i.e., Cu(II), Cd(II) and Pb(II)] on the Cibacron Blue F3GA-attached polyvinylbutyral microbeads were given in Fig. 6 as a function of time. The initial concentrations of the ions within the aqueous phase changed between 5–500 ppm. As seen from Fig. 6, very high adsorption rates are observed at the beginning of adsorption, and then plateau values (i.e., show the adsorption equilibria) are gradually achieved in 30 min for all metal ions. Adsorption of metal ions was very fast, especially when the metal ion concentration was high. This may be due to high driving force, which is the metal ion concentration difference between the liquid (i.e., adsorption medium) and the solid (i.e., the microbead) phases, in the case of high metal ion concentration. Notice that Pb(II) was adsorbed much faster than Cd(II) and Cu(II) due to much higher affinity of the ligand (i.e., Cibacron Blue F3GA) molecules. The order of adsorption rate is as follows: Pb(II) > Cd(II) > Cu(II).

Experimental data on the adsorption kinetics of heavy metal ions by various sorbent systems in microbead form have shown a wide range of adsorption rates. For example, Reed and Matsumoto [14,15] have considered 6 h as a short equilibrium time in their cadmium adsorption kinetic studies, in which they have used activated carbon as sorbent. Sarkar et al. [16] have investigated the effect of shaking time on the adsorption of heavy metals on silica and reported that equilibrium adsorption time is 2 h. Shreedhara-Murthy and Ryan [17] have investigated mercury, copper, cadmium, lead and uranium adsorption on cellulose–dithiocarbamate resins and reported that the adsorption rates were very slow. Egawa et al. [18] have studied uranium adsorption on polyacrylonitrile fibers containing amidoxime groups and reported a 7 h equilibrium adsorption time. Denizli et al. [19] have used Alkali

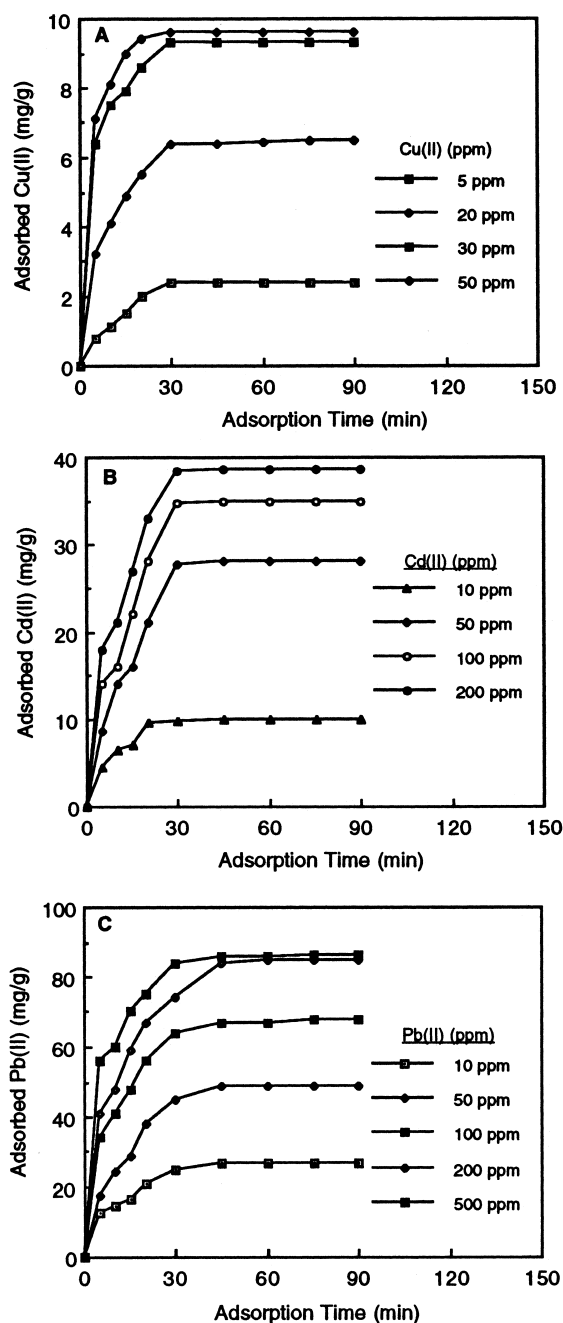


Fig. 6. Adsorption rates of heavy metal ions on the Cibacron Blue F3GA-attached polyvinylbutyral microbeads: (A) for Cu(II); (B) for Cd(II) and (C) for Pb(II). Temperature: 20°C; pH 7.0.

Blue 6B-attached poly(EGDMA-HEMA) microbeads for removal of Cu(II), Cd(II), Zn(II) and Pb(II) ions and they reported that adsorption equilibria was achieved in 30–90 min. Note that in such an adsorption process, there are several parameters which determine the adsorption rate, such as sorbent structural properties (e.g., size, porosity, surface area), amount of sorbent, metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, chelate-formation rate, and of course existence of other ions which may compete with the ions of interest for the active adsorption sites. All individual experimental studies published in the literature have been performed under different experimental conditions. Hence, it can be concluded that it is difficult to compare the adsorption rates reported. However, the magnetic polyvinylbutyral microbeads produced by us seem to be very suitable.

### 3.2.2. Adsorption capacities

#### 3.2.2.1. Effects of initial concentration of metal ions

The heavy metal ion adsorption capacities of the Cibacron Blue F3GA-attached polyvinylbutyral microbeads are given as a function of the initial concentration of metal ions within the aqueous phase in Fig. 7. The amount of metal ions adsorbed per gram of the polymer (i.e., the adsorption capacity) increased first with the initial concentration of metal ions then reached a plateau value which represents

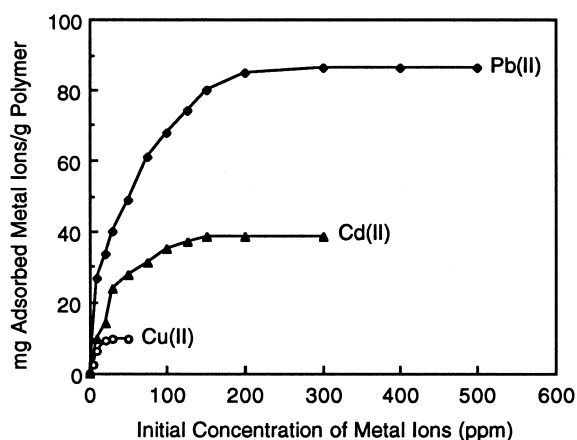


Fig. 7. Heavy metal ions adsorption capacity of the Cibacron Blue F3GA-attached polyvinylbutyral microbeads. Temperature: 20°C; pH 7.0.

saturation of the active points (which are available for specific metal ions) on the microbeads. These plateau values are 20 ppm, 125 ppm and 200 ppm for Cu(II), Cd(II) and Pb(II), respectively. The maximum adsorption capacities of the Cibacron Blue F3GA-attached polyvinylbutyral microbeads are 9.6 mg/g, 38.6 mg/g and 86.2 mg/g for Cu(II), Cd(II) and Pb(II), respectively, at pH 7.0. These values clearly show that Cibacron Blue F3GA-attached magnetic polyvinylbutyral microbeads exhibits the following metal ion affinity: Pb(II) > Cd(II) > Cu(II).

It should be also noted the non-specific adsorption values (adsorptions on the underivatized polyvinylbutyral microbeads) of heavy metal ions are relatively low, about 0.34 mg/g, 0.75 mg/g and 1.6 mg/g for Cu(II), Cd(II) and Pb(II), respectively. Note that these microbeads are highly swellable and also porous, which therefore may absorb (or entrap) heavy metal ions within the matrix of the microbead. In addition, the butyral, acetate and underivatized hydroxyl groups may interact with heavy metal ions (similar to solvation with water), which may cause these nonspecific-adsorption capacities.

For comparison of adsorption capacities of the Cibacron Blue F3GA-attached microbeads, we calculated distribution coefficients ( $K_d$ ) of metal ions between the sorbent phase and the adsorption medium at equilibrium, by using the following expression.

$$K_d = \frac{\text{Adsorbed metal ion (mg)/Amount of polymer (g)}}{\text{Amount of metal ion in solution (mg)/Volume of solution (ml)}} \quad (3)$$

Note that the distribution coefficient defined as the ratio of the amount of metal ion adsorbed by 1 g of the polymeric sorbent to the amount of metal ion retained in 1 ml of the solution. Table 2 gives the  $K_d$  values. As seen here, higher  $K_d$  values (indicating preferential adsorption) were obtained for Pb(II) ions than for Cd(II) and Cu(II) ions.

Table 2  
Distribution coefficients

Metal ions	$K_d$
Cu(II)	320
Cd(II)	386
Pb(II)	431

A wide variety of sorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Shreedhara-Murthy and Ryan [17] found 3.9–14.4 mg Cd(II)/g and 4.8–27 mg Cu(II)/g removal by cellulose–dithiocarbamate resins. Roozmond [20] showed 40 mg Cd(II)/g and 31.9 mg Cu(II)/g with pyrazole-containing poly(styrene–divinylbenzene) sorbents. Konishi et al. [21] reported 4.8–96.3 mg Cd(II)/g with alginic acid gels. Liu et al. [22] achieved 93 mg Pb(II)/g and 16.5 mg Cu(II)/g adsorption capacities with N-hydroxymethyl thioamide resin. Maeda et al. [23] obtained 88.7 mg Cu(II)/g with aminomethyl phosphonic acid containing methylmethacrylate–divinylbenzene copolymer beads [23]. Hudson and Matejka [24] investigated the length of pendants groups on Cu(II) ion-adsorption onto poly(styrene–divinyl benzene) copolymer beads and concluded that the type of pendent groups is important in the adsorption of heavy metal ions. They reported adsorption capacities between 0.15–46.4 mg/g. Sağ and Kutsal [25] have used *Zoogloea ramigera* microorganisms for heavy metal adsorption. The maximum amounts of adsorption capacities achieved were 35 mg Cu(II) and 85 mg Pb(II)/g dry weight of microorganisms. Shambhu et al. [26] immobilized polyamines (i.e., ethylene diamine, diethylene triamine and triethylene tetramine) onto polystyrene and reached an adsorption value of 33 mg Cu(II)/g polymer. Janus et al. [27] used poly(vinyl amine) sorbent for copper adsorption and reported an adsorption capacity of 0.5 mg Cu(II)/g. Khalfaoui et al. [28] achieved an adsorption capacity of 0.04 mg Cu(II)/g on raw charcoal. Denizli et al. [19] used Alkali Blue 6B-attached P(EGDMA–HEMA) sorbents, in which the maximum adsorption capacities were 2.3 mg Cu(II)/g, 5.5 mg Cd(II)/g and 125 mg Pb(II)/g. Marzal et al. [29] immobilized ethylene diamine and hexamethylene diamine by glow-discharge method and obtained 5.3 mg Cu(II)/g for EDA and 6.8 mg Cu(II)/g for HMDA–plasma treatment. Biçak et al. [30] reported 155 mg Cu(II)/g by using sorbents based on *p*-dichloromethylbenzene. Dev and Rao [31] reported 29.2 mg Cu(II)/g 51.7 mg Cd(II)/g and 80.8 mg Pb(II)/g adsorption capacity for polystyrene–vinylbenzene macroreticular resin functionalized with bis-(N,N'-salicylidene)1,3-propanediamine. Denizli et al. [32] reported 5.3–6.8 mg

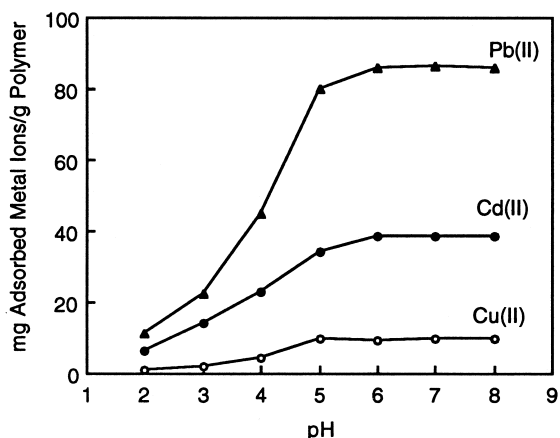


Fig. 8. Effect of pH on adsorption of heavy metal ions on the Cibacron Blue F3GA-attached polyvinylbutyral microbeads. Temperature: 20°C. Initial concentrations of metal ions: 50 ppm for Cu(II), 200 ppm for Cd(II) and 500 ppm for Pb(II).

Cu(II)/g and 136.2–174.2 mg Pb(II)/g for diamine glow-discharge treated polyhydroxyethyl-methacrylate microbeads. From the data that we obtained in this study, we may conclude that the Cibacron Blue F3GA-attached polyvinylbutyral microbeads presented in this paper is promising for the removal of metal ions from aqueous media.

### 3.2.2.2. Effects of pH

The heavy metal ions adsorption capacities of the Cibacron Blue F3GA-attached polyvinylbutyral microbeads were determined under non-competitive conditions (i.e., adsorption from single metal ions-solutions) at different pH values of buffered solutions. The adsorption results are given in Fig. 8. In all of the cases the adsorption increases with increasing pH, reaching a saturation value at around pH 7.0. The behaviour of Cibacron Blue F3GA-attached polyvinylbutyral microbeads shows that the adsorption of Pb(II) increases rapidly with increasing pH

up to 86.2 mg/g at pH 7.0. All the studied pH values, the sorbent shows substantially higher adsorption capacity for Pb(II) ions than for the other heavy metal ions [i.e., Cd(II) and Cu(II)]. At low pH values, i.e., pH < 4, the adsorption capacities are lower for all heavy metal ions. The maximum adsorption capacities were 9.6 mg/g for Cd(II), 38.6 mg/g for Cd(II) and 86.2 mg/g for Pb(II). The difference in adsorption behaviour of Pb(II) compared to Cd(II) and Cu(II) can be explained by the different affinity of the heavy metal ions for the donor atoms in the ligand Cibacron Blue F3GA. A difference in coordination behaviour is most probably also case for the attached Cibacron Blue F3GA ligand resulting in a relatively high adsorption of Pb(II) ions at high pH under non-competitive conditions.

### 3.2.3. Competitive adsorption

The heavy metal ion adsorption capacities of Cibacron Blue F3GA-attached polyvinylbutyral microbeads under competitive conditions (adsorption from solutions containing all heavy metal ions) for Cu(II), Cd(II) and Pb(II) were given in Table 3. This Table shows the amount of adsorption for each metal ion both in mass and molar basis, which were 6.5 mg (102.4  $\mu\text{mol}$ ) for Cu(II), 20.3 mg (181.1  $\mu\text{mol}$ ) for Cd(II) and 41.6 mg (200.9  $\mu\text{mol}$ ) for Pb(II). It should be mentioned that the adsorption capacity of the Cibacron Blue F3GA-attached magnetic polyvinylbutyral microbeads for all metal ions studied (in the case of adsorption from single metal ions solutions) was higher than competitive adsorption capacity. When they exist in the same concentrations, a competition will start for the same attachment sites. It can be concluded that Cibacron Blue F3GA-attached magnetic polyvinylbutyral microbeads exhibits the following metal ion affinity sequence under

Table 3

Competitive adsorption of Cu(II), Cd(II) and Pb(II) ions on the Cibacron Blue F3GA-attached polyvinylbutyral microbeads

Ions	mg Adsorbed ion/g polymer	$\mu\text{mol}$ Adsorbed ion/g polymer
Cu(II)	6.5	102.4
Cd(II)	20.3	181.1
Pb(II)	41.6	200.9

Initial concentration of metal ions: 50 ppm; temperature: 20°C.



Table 4  
Adsorption–desorption cycles for heavy metal ions

Cycle No.	Cu(II)		Cd(II)		Pb(II)	
	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)
1	9.60	95.3	38.60	92.2	86.20	94.4
2	9.45	96.7	38.41	96.8	86.01	93.8
3	9.31	94.8	38.23	97.1	85.94	96.9
4	9.19	98.1	38.21	96.9	85.81	91.5
5	9.15	95.9	37.84	93.2	85.62	90.6

both non-competitive and competitive adsorption conditions: Pb(II)>Cd(II)>Cu(II).

#### 3.2.4. Desorption and repeated use

Desorption experiments were performed with 0.1 mol HNO<sub>3</sub> as the desorption agent. The polyvinylbutyral microbeads loaded with the maximum amounts of the respective metal ions were placed in the desorption medium and the amount of metal ions desorbed in 60 min was measured. Table 4 gives the adsorption of heavy metal ions by Cibacron Blue F3GA-attached magnetic microbeads after several cycles of consecutive adsorption and desorption. This Table clearly shows that the magnetic microbeads can be used repeatedly without losing significantly their adsorption capacities for all metal ions studied here.

## 4. Conclusions

Cibacron Blue F3GA-attached magnetic polyvinylbutyral microbeads have shown great promise in removal of heavy metal ions [i.e., Cu(III), Cd(II) and Pb(II)] from aqueous media. Some results are given briefly: the heavy metal adsorption is rapid, and adsorption equilibria were reached in about 30 min. Adsorption capacities of these affinity microbeads from their single metal ions solutions were 9.6 mg/g for Cu(II), 38.6 mg/g for Cd(II) and 86.2 mg/g for Pb(II). However, when the heavy metal ions competed (in the case of the adsorption from their mixture) the amounts of adsorption were 6.5 mg/g for Cu(III), 20.3 mg/g for Cd(II) and 41.6 mg/g for Pb(II). Cibacron Blue F3GA-attached polyvinylbutyral microbeads exhibit the following metal ion affinity sequence under non-competitive

and competitive conditions: Pb(II)>Cd(II)>Cu(II). In addition, the affinity of microbeads under competitive conditions did not change. Adsorbed metal ions were easily desorbed by using 0.1 M HNO<sub>3</sub>. Consecutive adsorption and desorption showed the feasibility of these novel affinity magnetic microbeads for heavy metal adsorption.

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