



Procion Green H-4G immobilized poly(hydroxyethylmethacrylate/chitosan) composite membranes for heavy metal removal

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Abstract

The effective removal of toxic heavy metals from environmental samples still remains a major topic of present research. Metal-chelating membranes are very promising materials as adsorbents when compared with conventional beads because they are not compressible, and they eliminate internal diffusion limitations. The purpose of this study was to evaluate the performance of a novel adsorbent, Procion Green H-4G immobilized poly(hydroxyethylmethacrylate (HEMA)/chitosan) composite membranes, for the removal of three toxic heavy metal ions, namely, Cd(II), Pb(II) and Hg(II) from aquatic systems. The Procion Green H-4G immobilized poly(hydroxyethylmethacrylate/chitosan) composite membranes were characterized by elemental analysis, scanning electron microscopy and Fourier transform infrared (FTIR) spectroscopy. The immobilized amount of the Procion Green H-4G was calculated as $0.018 \pm 0.003 \mu\text{mol}/\text{cm}^2$ from the nitrogen and sulphur stoichiometry. The adsorption capacity of Procion Green H-4G immobilized poly(hydroxyethylmethacrylate/chitosan) composite membranes for selected heavy metal ions from aqueous media containing different amounts of these ions (30–400 mg/l) and at different pH values (2.0–6.0) was investigated. The amount of Cd(II), Pb(II) and Hg(II) adsorbed onto the membranes measured at equilibrium, increased with time during the first 45 min and then remained unchanged toward the equilibrium adsorption. The maximum amounts of heavy metal ions adsorbed were 43.60 ± 1.74 , 68.81 ± 2.75 and $48.22 \pm 1.92 \text{ mg/g}$ for Cd(II), Pb(II) and Hg(II), respectively. The heavy metal ion adsorption on the pHEMA/chitosan membranes (carrying no dye) were relatively low, $6.31 \pm 0.13 \text{ mg/g}$ for Cd(II), $18.73 \pm 0.37 \text{ mg/g}$ for Pb(II) and $18.82 \pm 0.38 \text{ mg/g}$ for Hg(II). Competitive adsorption of the metal ions was also studied. When the metal ions competed with each other, the adsorbed amounts were $12.74 \pm 0.38 \text{ mg Cd(II)/g}$, $28.80 \pm 0.86 \text{ mg Pb(II)/g}$ and $18.41 \pm 0.54 \text{ mg Hg(II)/g}$. Procion Green H-4G immobilized poly(hydroxyethylmethacrylate/chitosan) membranes can be regenerated by washing with a solution of nitric acid (0.01 M). The percent desorption

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achieved was as high as 95%. These novel membranes are suitable for repeated use for more than five adsorption/desorption cycles without any considerable loss in adsorption capacity. Adsorption equilibria were well described by Langmuir equation. It can be concluded that Procion Green H-4G immobilized poly(hydroxyethylmethacrylate/chitosan) membranes may effectively be used for the removal of Cd(II), Pb(II) and Hg(II) ions from aqueous solutions.

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1. Introduction

At least 20 metals are classified as toxic and half of these, including cadmium, arsenic, mercury, chromium, copper, lead, nickel, selenium, silver and zinc are emitted into the environment in quantities that pose risks to human health [1,2]. Among them, perhaps the most toxic ones are cadmium, lead and mercury. The toxicities of heavy metals may be caused by mechanisms that include blocking essential functional groups of biomolecules, disrupting the integrity of biomembranes, or binding with bioanions to result in a decreased level of essential bioanions [3,4]. Treatment of aqueous wastes containing soluble heavy metals requires concentrating the solutions into smaller volumes followed by recovery or secure disposal. Heavy metals can be removed by adsorption on solid matrices. Non-specific sorbents, such as activated carbon, metal oxides, and ion-exchange resins have been extensively used [5,6]. Specific sorbents consist of a ligand (e.g. ion-exchange material or chelating agents) which interacts with the metal ions specifically, and a carrier matrix which may be an inorganic material (e.g. aluminum oxide, silica or glass) or polymer microspheres (e.g. polymethylmethacrylate, polystyrene, cellulose). As carrier matrices, polymer microspheres have attracted the most attention because they may easily be produced in a wide variety of composition, and modified into specific sorbents, by introducing a variety of ligands. In conventional applications, non-porous or porous polymer microspheres with average diameters of usually more than 100 μm are used. When the non-porous microspheres are used, only the outer surface is of the microspheres available for the incorporation of the ligands which will give the specificity of these sorbents. A small surface area generally results in a low adsorption capacity. In order to increase the active surface area, porosity may be created within the microspheres. For instance, there are commercially available, polymer-based porous sorbents which exhibit surface areas of 200–500 m^2 or even larger per unit mass of the sorbent. When dealing with highly viscous mediums such as wastewater effluents, however, contact with the adsorbent in the form of spherical beads is not desirable because of viscosity limitations [7]. Adsorptive membrane-mass transfers in a diffusive-transport mode are more efficient where the liquid is made to flow tangentially past the membrane surface while the adsorbate diffuses into the porous membrane to meet the selective metal-complexing ligand immobilized on the membrane. For adsorptive membrane development, it is necessary to use a highly permeable polymer carrier. In addition, conventional chromatography with a packed column of gel beads as a support material is not easy to scale up because the pressure drop in packed columns is significant, leading to compaction of the bed under pressure and low flow-rates [8].

Many publications have reported the performance of adsorptive membranes as well as their theoretical description and optimal design [9–11]. The porosity, thickness, metal-complexing ligand density, and pore size can dramatically affect the overall performance of the adsorptive membranes. Ideal adsorptive membranes should have (a) microporous or macroporous structures, (b) available reactive groups for metal ion binding, (c) chemical and physical stability under harsh conditions.

Much attention has been paid to improve the chemical and physical properties of hydrogels in the swollen state. The main effort focused on the introduction of a second component, a hydrophobic or hydrophilic polymer into the hydrogels to form the so-called interpenetrating networks (IPNs). Poly(hydroxyethylmethacrylate) (pHEMA) possesses high mechanical strength, resistance to many chemicals and microbial degradation. The combination of the useful properties of the synthetic pHEMA and natural chitosan as an IPN could introduce a composite matrix in many applications. In addition, the preparation of IPN from these polymers is a simple method and the presence of hydroxyl and amino groups on the IPN offers easy attachment sites for a variety of dye-ligands [10].

In this study, a novel metal-chelating membrane, Procion Green H-4G immobilized pHEMA/chitosan composite membranes (also called interpenetrating network membranes) were synthesized. These membranes were characterized and their efficiency in heavy toxic metal removal was investigated under a wide range of conditions.

2. Experimental

2.1. Materials

The monomer 2-hydroxyethylmethacrylate (HEMA) was obtained from Fluka AG (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4 °C until use. Azobisisobutyronitrile (AIBN) was provided from Fluka AG (Buchs, Switzerland). Chitosan and Procion Green H-4G was purchased from Sigma (St. Louis, USA). The stock solutions for cadmium and lead are prepared in the following way: 1.000 g metal (99.9%) is heated and dissolved with 30 ml nitric acid solution (1 + 1) and is diluted with distilled deionized water to 1000 ml accurately after it has cooled. The stock solution of mercury is prepared from 1.345 g of HgCl₂ dissolved in distilled deionized water and diluted to exactly 1000 ml. These solutions were diluted as required to obtain standard solution containing 30–400 mg/l of metal ions. All the chemicals used were reagent grade from Merck AG (Darmstadt, Germany).

2.2. Synthesis of pHEMA/chitosan interpenetrating networks

The interpenetrating network synthesis was achieved by mixing a chitosan solution (1.0% chitosan in 4.0 ml of 1.0% acetic acid) with 2-HEMA monomer (2.0 ml) containing 20 mg AIBN. Following the nitrogen flushing, the solution was poured into a round glass mold (diameter: 9.0 cm), sealed and exposed to UV radiation for 1.0 h at ambient temperature. The nitrogen atmosphere was maintained during the UV irradiation. After the polymerization

period, the product was washed with 1.0% (w/w) NaOH solution and then with distilled water. The IPNs membrane was cut into circular pieces (diameter: 0.75 cm) with a perforator and left in the moist state at 4 °C.

2.3. Procion Green H-4G immobilization onto IPNs membrane

Procion Green H-4G was covalently immobilized onto the IPNs via the nucleophilic reaction between the chloride of its triazine ring and the amide and hydroxyl groups of the IPNs under alkaline conditions. Procion Green H-4G (300 mg) was dissolved in distilled water (10 ml), and transferred to the same medium (80 ml) in which IPNs membrane disks (15 g) were equilibrated. Ten milliliters of 1.0 M sodium hydroxide was then added to the medium (about pH 13) and heated at 80 °C for 4 h in a sealed reactor. After the reaction period, the solution cooled to room temperature and IPNs membrane disks were washed several times with distilled water, 2.0 M NaCl and 10% methanol. At the last stage, IPNs membrane disks were washed again with distilled water. The Procion Green H-4G immobilized IPNs membrane disks were stored at 4 °C until use.

2.4. Characterization studies

The amount of covalently bound Procion Green H-4G on the membrane was estimated by using an elemental analysis instrument (Leco, CHNS-932, USA), by considering the nitrogen and sulphur stoichiometry.

Fourier transform infrared (FTIR) spectra of the pHEMA/chitosan, and Procion Green H-4G immobilized IPN membranes were obtained by using a FTIR spectrophotometer (Mattson 1000 FTIR, England). The dried membrane (about 0.1 g) was mixed with KBr (0.1 g) and pressed into a tablet form. The FTIR spectrum was then recorded.

The dried IPN membranes were coated with gold under reduced pressure and their scanning electron micrographs were obtained using a JEOL (JSM 5600) scanning electron microscope.

The water content of the IPN membranes was determined at room temperature in saline solution (0.85%) by using a gravimetric method. The water content was defined as the weight ratio of water contained within swollen to dry membrane. The water content of the membranes were calculated by using the following expression:

$$\text{swelling ratio (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_d and W_s are the dry and swollen weights of membranes, respectively.

2.5. Adsorption/desorption studies

The adsorption of Cd(II), Pb(II) and Hg(II) ions by Procion Green H-4G immobilized pHEMA/chitosan membranes from aqueous solutions was studied in batch adsorption-equilibrium experiments. The effects of adsorption contact time and the pH of the medium on the adsorption capacity were investigated. Nitrates of the respective metal ions were used throughout the adsorption experiments. Aqueous solutions (25 ml) containing different

amount of each metal (30–400 mg/l) were incubated with approximately 35 mg of Procion Green H-4G immobilized pHEMA/chitosan membranes at different pH (in the range of 2.0–6.0, which was adjusted with HNO₃ or NaOH at the beginning of experiment and not controlled afterwards) at 20 °C (performed in a temperature-control chamber), in the flasks agitated magnetically at an agitation speed of 600 rpm. After the desired contact periods (up to 60 min), the aqueous phases were separated from the membranes, and the residual concentrations of the metal ions in these phases were measured by using an atomic absorption spectrophotometer. A Shimadzu Model AA-6800 Flame atomic absorption spectrophotometer (Japan) was used. For mercury determinations, mercury vapor unit-1A (MVU-1A) was employed. Deuterium background correction was applied throughout the experiments and the spectral slit width was 0.5 nm. The working current/wavelength values and the optimized experimental conditions for mercury measurements were as follows:

- Working current/wavelength: 6 mA/253.6 nm.
- Concentration of SnCl₂: 1% (w/v).
- Concentration of KMnO₄: 0.5% (w/v).
- Concentration of H₂SO₄: 5% (v/v).

The working current/wavelength values for cadmium and lead determinations were 8 mA/228.8 nm and 10 mA/283.3 nm, respectively. For each sample, the mean of ten measurements were recorded.

The amount of metal ions adsorbed per unit mass of membrane (mg metal ions/g) was obtained by using the following expression:

$$Q = \frac{(C_0 - C)V}{M} \quad (2)$$

where Q is the amount of metal ions adsorbed onto the unit mass of the adsorbent (mg/g), C_0 and C are the concentrations of the metal ions before and after adsorption (mg/l), V the volume of the aqueous phase (l), and M is the amount of the adsorbent (g).

Competitive heavy metal adsorption was from aqueous solutions containing Cd(II), Pb(II) and Hg(II) ions investigated by following a similar procedure described above. These experiments were performed at a constant pH of 5.5 and at 20 °C using solutions containing 1.75×10^{-3} M from each metal ion.

Desorption of heavy metal ions was achieved by using 0.01 M HNO₃ as the desorbing agent. The Procion Green H-4G immobilized pHEMA/chitosan membranes loaded with the heavy metal ions in the following conditions—initial concentration of the metal ions: 200 mg/l, amount of Procion Green H-4G immobilized pHEMA/chitosan membranes: 35 mg; volume of adsorption medium: 25 ml; pH: 5.5; temperature: 20 °C and adsorption time: 60 min. Then, the Procion Green H-4G immobilized pHEMA/chitosan membranes were placed in the desorption medium and stirred at a stirring rate of 600 rpm up to 30 min. The concentrations of the metal ions in the aqueous phase were determined by using atomic absorption spectrophotometer as mentioned above. The extent of desorption percents was calculated from the following expression:

$$\text{desorption (\%)} = \frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}} \times 100 \quad (3)$$

3. Results and discussion

3.1. Properties of dye-immobilized pHEMA/chitosan membrane

Dye immobilization requires a hydrophilic support which possesses chemically modifiable groups. Most frequently used matrices are only the naturally occurring polysaccharide polymers: agarose, dextran, cellulose derivatives and chitosan. Among them only the latter one is resistant to microbial degradation and the others can undergo microbial degradation. However, for some applications, they have insufficient mechanical strength and porosity. In comparison with other supports, the composite pHEMA/chitosan polymeric networks, due to their nature, are very inert toward microbial degradation. Their porosity can be modified by varying the concentration of pore forming agent in the polymerization mixture.

Procion Green H-4G is an aromatic polysulphonated dye, and it contains a ratio of seven acidic sulfonate groups to three basic secondary amino groups. It also has a phthalocyanine moiety (Fig. 1). The hydroxyl and amino groups of the IPNs matrix can react with the chloride of the triazine ring of the Procion Green H-4G under alkaline conditions, thus, giving rise to covalent bonds. Elemental analysis of the untreated and Procion Green H-4G-immobilized pHEMA membrane were performed, and the immobilized dye on the membrane was found to be $0.018 \pm 0.003 \mu\text{mol}/\text{cm}^2$ from the nitrogen and sulphur stoichiometry.

Studies designed to detect leakage of Procion Green H-4G from immobilized IPNs membranes revealed no leakage in any of the adsorption media, and implied that the washing procedure was satisfactory for removing the physically adsorbed dye molecules from the IPNs membranes. The dye leakage was not also observed from the dye-immobilized membrane during a relatively long period of storage (more than 4 months).

The major physical and morphological properties of pHEMA/chitosan IPNs membranes were as follows: the water content of the dye-immobilized IPNs membrane was $50 \pm 2\%$, the thickness in the wet state of the IPNs membrane was 0.06 cm; the density of the IPNs in the dry state was $1.26 \text{ g}/\text{cm}^3$, the untreated surface area of the 1.0 ml wet IPN membrane was 38.5 cm^2 .

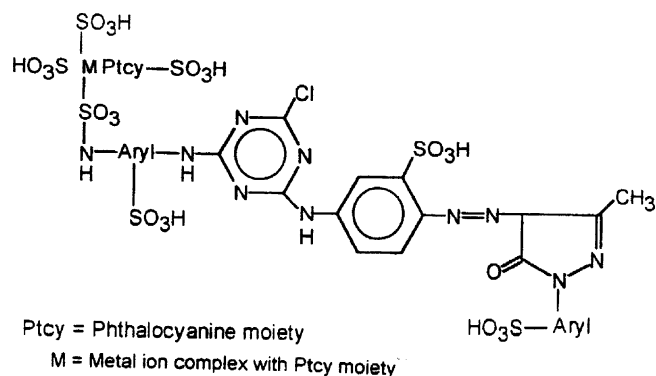


Fig. 1. Structure of Procion Green H-4G.

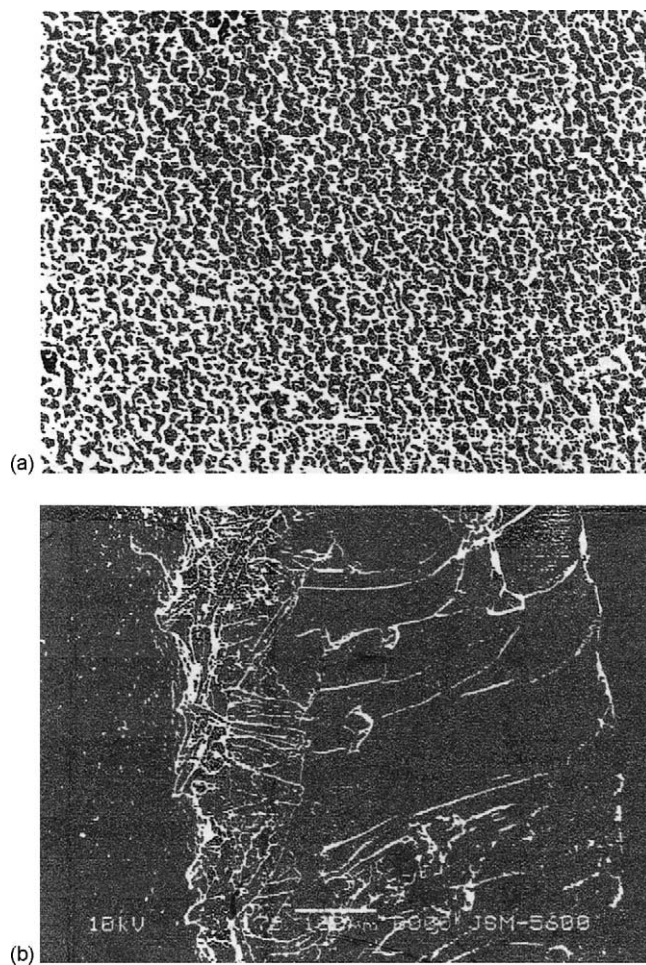


Fig. 2. Representative scanning electron microscope micrograph of Procion Green H-4G immobilized pHEMA/chitosan composite membranes: (a) surface; (b) cross-section.

The microstructure of the interpenetration networks surface was investigated by scanning electron microscopy (Fig. 2). The IPNs membrane displayed a smooth, channel like, and porous structure. The microporous surface structure of the IPNs which may lead to a large internal surface area (suggesting a high ligand immobilization and protein adsorption capacity) with a low diffusional resistance in the matrix (implying a high adsorption rate). Note that, achieving both high adsorption capacities and reaction rates were the main goals in the preparation of the affinity membranes in this work.

To examine the nature of the interaction between the dye (Procion Green H-4G) and the pHEMA/chitosan IPNs, FTIR spectra of the untreated IPNs and dye-immobilized IPNs were obtained. As shown in Fig. 3, FTIR spectra of dye-immobilized pHEMA/chitosan

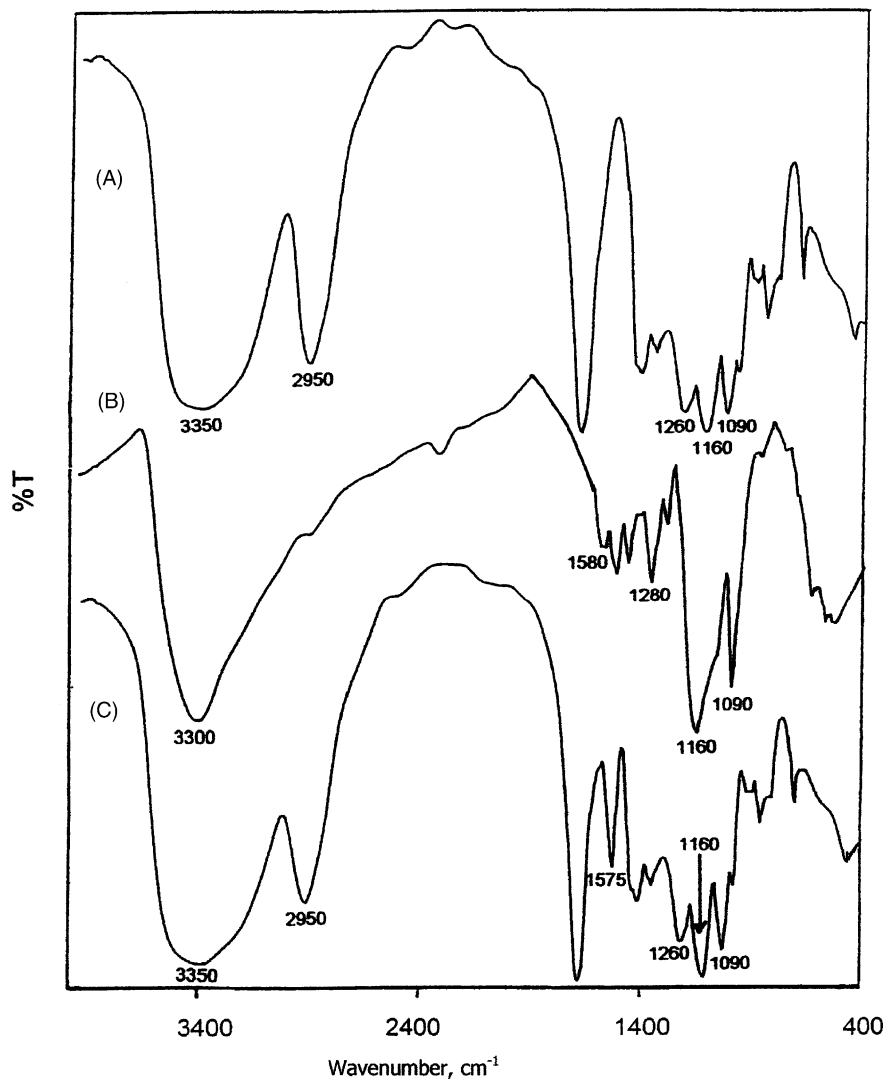


Fig. 3. FTIR spectra of: (a) pHEMA; (b) Procion Green H-4G; (c) Procion Green H-4G immobilized pHEMA/chitosan composite membranes.

IPNs had an absorption band different from that of pHEMA/chitosan at 1575 cm^{-1} . It is the characteristic of aromatic rings stretching vibration band ($\text{C}=\text{C}$) arising from immobilized dye molecules on the IPNs. The bands at 3300 , 1580 , 1090 , 1160 and 1260 cm^{-1} representing N–H stretching, N–H bending (scissoring), symmetric stretching of S=O, asymmetric stretching of S=O and aromatic C–N vibration, respectively, were due to the dye Procion Green H-4G bonded to pHEMA/chitosan. These bands, however, did not appear, because untreated pHEMA/chitosan also had some absorption bands in the same region.

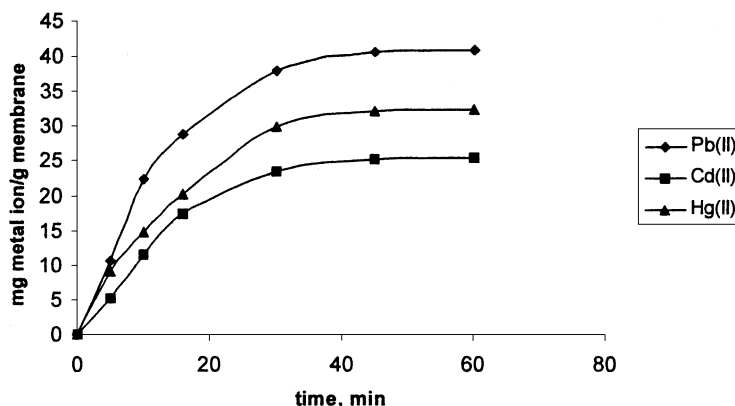


Fig. 4. Adsorption rates of Cd(II), Pb(II) and Hg(II) ions onto Procion Green H-4G immobilized pHEMA/chitosan composite membranes. Adsorption conditions—initial concentration of metal ions: 100 mg/l; pH: 5.5; temperature: 20 °C.

Thus, absorption bands of pHEMA/chitosan overlapped with those of Procion Green H-4G immobilized IPNs at about these wavenumbers.

3.2. Adsorption of heavy metal ions

3.2.1. Adsorption kinetics

Fig. 4 shows adsorption kinetics of Cd, Pb and Hg by Procion Green H-4G immobilized pHEMA/chitosan membranes as a function of time. In other words, it shows the changes in the amounts of metal ions adsorbed, which were calculated by using the expression given in Eq. (2). Adsorption conditions are given in the figure legend. The initial slopes of these curves reflect the adsorption rates. It should be noted that there was no precipitation in these group of experiments. As seen here, relatively rapid adsorption rates were observed at the beginning and then plateau values were gradually obtained within 45 min.

In the literature, different equilibrium adsorption times with different polymeric adsorbents have been reported. Roozmond et al. [12] studied Cu(II) and Cd(II) uptake of 3,5-dimethyl-1-hydroxymethyl pyrazole attached *p*-aminomethyl substituted poly(styrene-co-divinylbenzene) chelating polymer. They reported that adsorption was rather slow and that the equilibrium was reached after 2 days. Latha et al. [13] studied ethylenediamine functionalized polyacrylamide resin for the extraction of several ions including Fe(III), Fe(II), Cu(II) and Ni(II) and they showed that the complexation reaction proceeded very slowly, and that equilibrium was established in 5 h. Ebraheem and Hamdi [14] investigated the adsorption of Cd(II), Ni(II), Cu(II), and Zn(II), on phenol formaldehyde polymer containing poly(salicylaldehyde-3,5-dimethylene) and they reported a 10-h equilibrium adsorption interval. Konishi et al. [15] studied the removal of Zn(II), Cd(II) and La(III) by biopolymer gel beads of alginate and showed that equilibrium was reached in about 2 h. Reed and Matsumoto [16] considered 6 h as a short adsorption time in Cd(II) adsorption on activated carbon. It is worth noting to indicate that in such adsorption processes, there are several

parameters which determine the adsorption rate, such as stirring rate in the aqueous phase or flow-rate in a column system, structural properties of adsorbent used (e.g. surface topography, porosity, swelling ratio), amount of the adsorbent, metal ion properties (e.g. hydrated ionic radius, coordination complex number), initial concentration of metal ions, and the existence of other metal ions which may compete with the metal ion of interest for the same active adsorption sites.

3.2.2. Adsorption capacity

3.2.2.1. Effect of initial metal ion concentration. The heavy metal adsorption capacities of Procion Green H-4G immobilized pHEMA/chitosan membranes are presented in Fig. 5 as a function of the initial concentration of Cd(II), Pb(II) and Hg(II) ions within the aqueous adsorption medium in Fig. 5. These batch experiments were performed by using the single solutions of the interested metal ions. Adsorption conditions are given in the figure legend.

As expected, the amount of metals adsorbed per unit mass of the membranes increased with the increase in the initial concentration of metal ions. In order to measure the maximum adsorption capacities which represent saturation of the active sites (available for specific interaction with metal ions) on the sorbent, the initial concentrations of Cd(II), Pb(II) and Hg(II) ions were increased to 400 mg/l. The maximum adsorption capacities of Procion Green H-4G immobilized pHEMA/chitosan membranes were 43.60 ± 1.74 mg/g for Cd(II), 68.81 ± 2.75 mg/g for Pb(II) and 48.22 ± 1.92 mg/g for Hg(II). The Procion Green H-4G immobilized pHEMA/chitosan membranes showed the following metal ion affinity order, based on a weight uptake: Pb(II) > Hg(II) > Cd(II). When considered on molar bases, however, these values were 0.39 mmol Cd(II)/g, 0.33 mmol Pb(II)/g, 0.24 mmol Hg(II)/g; and the order of affinity was: Cd(II) > Pb(II) > Hg(II). The heavy metal ion adsorption on the pHEMA/chitosan membranes (carrying no dye) were relatively low; 6.31 ± 0.13 mg/g for Cd(II), 18.73 ± 0.37 mg/g for Pb(II) and 18.82 ± 0.38 mg/g for Hg(II).

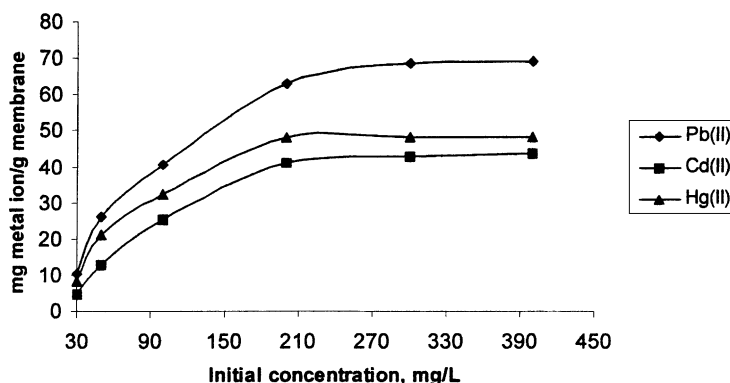


Fig. 5. Adsorption capacities of Procion Green H-4G immobilized pHEMA/chitosan composite membranes for Cd(II), Pb(II) and Hg(II) ions. Adsorption conditions—amount of membrane: 35 mg; volume of the adsorption medium: 25 ml; pH: 5.5; temperature: 20 °C; contact time: 45 min.

Various adsorbents with a wide range of adsorption capacities for heavy metal removal or recovery have been reported in the literature. Liu et al. [17] studied Cd(II) adsorption onto *N*-(hydroxymethyl) thioamide anchored macroreticular acrylonitrile-divinylbenzene copolymer and they found an adsorption capacity of 22.4 mg/g. Jyo et al. [18] used phosphoric acid functionalized poly(glycidyl methacrylate-co-divinylbenzene) beads and they reported 4.5 mequiv. Cd(II)/g polymer. Shreedhara-Murthy and Ryan [19] found 3.9–14.4 mg Cd(II)/g recovery by cellulose-dithiocarbamate resins. Denizli et al. [20] investigated Cd(II) removal by using Procion Blue MX-3B attached pHEMA based microspheres and reported an adsorption capacity of 4.2 mg/g. Büyüktuncel et al. [21] used poly(vinylalcohol) coated/Cibacron Blue F3GA-attached polypropylene hollow fiber membranes for removal of Cd(II) ions from aquatic systems, and they found 46 mg/g adsorption capacity. Shah and Devi [22] used dithizone-anchored poly(vinyl pyridine) support and found 144.4 mg Hg(II)/g. Cestari and Airoidi [23] found 186.5 mg Hg(II)/g with 3-trimethoxysilyl-1-propanethiol immobilized on silica. Jyo et al. [18] reported 40 mg Hg(II)/g with phosphoric acid-treated poly(glycidylmethacrylate-co-divinyl benzene) beads. Say et al. [24] used dithiocarbamate-incorporated monosize polystyrene microspheres for adsorption of organomercury species and they reported adsorption capacities of 122.36 mg/g for CH₃HgCl, 114.34 mg/g for C₂H₅HgCl and 20.06 mg/g for C₆H₅HgCl. Denizli et al. [25] reached an adsorption capacity of 125 mg Pb(II)/g by Alkali Blue 6B-attached poly(EGDMA–HEMA) microspheres. Dev and Rao [26] used polystyrene-vinylbenzene macroreticular resin functionalized with bis-(*N,N'*-salicylidene) 1,3-propanediamine and reported 80.8 mg Pb(II)/g adsorption capacity. The adsorption capacities obtained in this study with Procion Green H-4G immobilized pHEMA/chitosan composite membranes were 43.60 ± 1.74 mg/g for Cd(II), 68.81 ± 2.75 mg/g for Pb(II) and 48.22 ± 1.92 mg/g for Hg(II). When compared with the values reported in the literature, the novel Procion Green H-4G immobilized pHEMA/chitosan composite membranes presented in this communication are promising for the removal of heavy metal ions from aquatic systems.

3.2.2.2. Effect of pH. Metal ion adsorption onto non-specific and specific sorbents is pH dependent [27,28]. In the absence of complexing agents, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble species. The solubility of metal ions is governed by hydroxide or carbonate concentration. Reed and Matsumoto [16] reported that hydrolysis of metal ions such as Cu(II), Cd(II) and Pb(II) becomes significant at approximately pH 7.5–8.5. For this reason, in this study, in order to study the effect of pH on the adsorption of metal ions onto the Procion Green H-4G immobilized pHEMA/chitosan membranes the batch experiments were repeated at different pH values in the range of 2.0–6.0. Fig. 6 shows the effect of pH on adsorption. The adsorption of Pb(II), Cd(II) and Hg(II) ions by the adsorbent first increased with pH, and then almost reached a plateau value at about 5.5.

3.3. Competitive adsorption

Adsorption capacities of Procion Green H-4G immobilized pHEMA/chitosan membranes for Pb(II), Cd(II) and Hg(II) ions under competitive conditions (adsorption from ternary-solute solutions) were also studied. The adsorption capacities under competitive

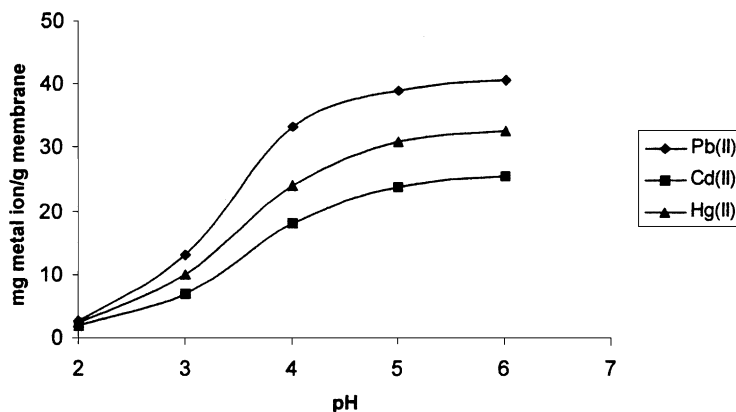


Fig. 6. Effect of pH on the adsorption capacity of Procion Green H-4G immobilized pHEMA/chitosan composite membranes for Cd(II), Pb(II) and Hg(II) ions. Adsorption conditions—initial concentration of metal ions: 100 mg/l; amount of membranes: 35 mg; volume of the adsorption medium: 25 ml; temperature: 20 °C; contact time: 45 min.

conditions were 12.74 ± 0.38 mg Cd(II)/g, 28.80 ± 0.86 mg Pb(II)/g and 18.41 ± 0.54 mg Hg(II)/g (Table 1). The Procion Green H-4G immobilized pHEMA/chitosan membranes show the following metal ion affinity order, on molar bases, under competitive adsorption conditions: Pb(II) > Cd(II) > Hg(II).

As seen from Table 1, the adsorption capacity of Procion Green H-4G immobilized pHEMA/chitosan composite membranes decreased considerably in competitive adsorption experiments using solutions containing 1.75×10^{-3} M from each metal ion. This decrease is, of course, due to the competition of metal ions with each other (in ternary solutions) for the active sites of the membranes.

3.4. Desorption and regeneration

To be useful in metal ion recycling processes, adsorbed metal ions should be easily desorbed under suitable conditions. Desorption experiments were performed by using 0.01 M HNO₃ solution as the desorption agent. Desorption ratios for Cd(II), Pb(II) and Hg(II) ions from the membranes loaded with 200 mg/l of respective metal ions (loaded from their single-solute solutions) were calculated by using Eq. (3) and given in Fig. 7. More than 95% of the adsorbed metals were desorbed with HNO₃ solution. Adsorption/desorption

Table 1
Comparison of adsorption capacities of the Procion Green H-4G immobilized pHEMA/chitosan membranes for Pb(II), Cd(II) and Hg(II) ions

Ions	Non-competitive adsorption (mg/g)	Competitive adsorption (mg/g)	Non-competitive adsorption (mmol/g)	Competitive adsorption (mmol/g)
Cd(II)	43.60 ± 1.74	12.74 ± 0.38	0.39	0.11
Pb(II)	68.81 ± 2.75	28.80 ± 0.86	0.33	0.14
Hg(II)	48.22 ± 1.92	18.41 ± 0.54	0.24	0.09

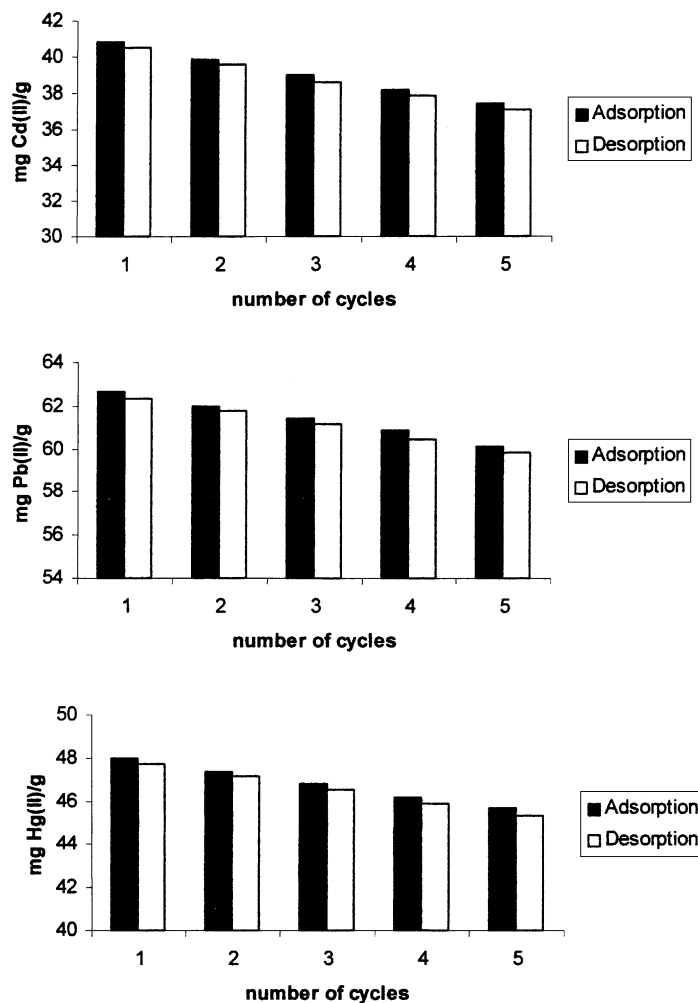


Fig. 7. Adsorption/desorption cycles.

cycles were repeated 5 times. When HNO_3 solution is used as the desorption agent, the coordination spheres of chelated metal ions were disrupted, and subsequently metal ions were released from the solid surface into the desorption medium. Therefore, Procion Green H-4G immobilized pHEMA/chitosan membranes can be used repeatedly without significantly losing their adsorption capacities for the metal ions studied.

3.5. Equilibrium studies

In order to optimize the design of an adsorption system to remove metal ions, it is important to establish the most appropriate correlations for the equilibrium isotherms. Two isotherm equations were applied in the present study, namely Langmuir and Freundlich.

One of the most widely used isotherm equations for modelling adsorption data is the Langmuir equation, which for dilute solutions may be represented as

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (4)$$

where q_e is the amount of metal ions adsorbed onto the unit mass of the adsorbent, K_L the Langmuir equilibrium constant, C_e the solution phase metal ion concentration, and a_L is the Langmuir constant. The constants K_L and a_L are the characteristics of the Langmuir equation and can be determined from a linearized form of Eq. (4), represented by Eq. (5).

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (5)$$

Therefore, a plot of C_e/q_e versus C_e yields a straight line with a slope of a_L/K_L and intercept $1/K_L$. The constant K_L is the Langmuir equilibrium constant and the ratio a_L/K_L gives the theoretical monolayer saturation capacity. The Langmuir equation is applicable to homogeneous adsorption where each metal ion-adsorbent adsorption process has an equal adsorption activation energy. The Langmuir equation obeys Henry's Law at low concentrations.

The Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface. The Freundlich equation is commonly presented as

$$q_e = a C_e^b \quad (6)$$

where a and b are the Freundlich constants. The equation may be linearized by taking logarithms:

$$\ln q_e = b \ln C_e + \ln a \quad (7)$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ enables the constant a and exponent b to be determined. The isotherm model constants and correlation regression coefficients have been determined for each metal ion and are given in Table 2.

The Freundlich correlation regression coefficients were generally lower than the Langmuir coefficients. Consequently it would appear that the Langmuir equation gives a better representation of the experimental isotherm data.

Table 2

Isotherm model constants and correlation coefficients for adsorption of Cd(II), Pb(II) and Hg(II) ions from aqueous solution

Metal ion	Langmuir			Freundlich		
	a_L/K_L (mg/g)	K_L ($\times 10^4$) (mol/l)	R^2	a	b	R^2
Cd(II)	50.25	10	0.996	6.88	0.336	0.915
Pb(II)	71.43	50	0.998	12.67	0.317	0.929
Hg(II)	56.49	24	0.997	11.58	0.261	0.932

Temperature: 20 °C and pH: 5.5.

4. Conclusions

When compared with the adsorption capacity values obtained by various materials in the literature, Procion Green H-4G immobilized pHEMA/chitosan membranes showed great promise in the removal of heavy metal ions from aqueous media. The immobilization of Procion Green H-4G on pHEMA/chitosan membranes increased the adsorption capacity values 6.9 times for Cd, 3.7 times for Pb, and 2.6 times for Hg. The adsorption capacity values found under competitive conditions (adsorption from their ternary solutions) showed that the membranes used in this study had no selective affinity for any of the metal ions investigated. The adsorption capacities of the membranes did not significantly changed during the five repeated adsorption/desorption cycles. The overall performance of Procion Green H-4G immobilized pHEMA/chitosan membranes indicated the feasibility of continuous use of these novel membranes in adsorption columns for removal of heavy metal ions from polluted environmental waters.

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