

Removal of Cd(II), Hg(II), and Pb(II) Ions from Aqueous Solution Using p(HEMA/Chitosan) Membranes

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ABSTRACT: An interpenetration network (IPN) was synthesized from 2-hydroxyethyl methacrylate (HEMA) and chitosan, p(HEMA/chitosan) via UV-initiated photopolymerization. The selectivity to different heavy metal ions viz Cd(II), Pb(II), and Hg(II) to the IPN membrane has been investigated from aqueous solution using bare pHEMA membrane as a control system. Removal efficiency of metal ions from aqueous solution using the IPN membranes increased with increasing chitosan content and initial metal ions concentrations, and the equilibrium time was reached within 60 min. Adsorption of all the tested heavy metal ions on the IPN membranes was found to be pH dependent and maximum adsorption was obtained at pH 5.0. The maximum adsorption capacities of the IPN membrane for Cd(II), Pb(II), and Hg(II) were 0.063, 0.179, and 0.197 mmol/g membrane, respectively. The adsorption

of the Cd(II), Hg(II), and Pb(II) metal ions on the bare pHEMA membrane was not significant. When the heavy metal ions were in competition, the amounts of adsorbed metal ions were found to be 0.035 mmol/g for Cd(II), 0.074 mmol/g for Hg(II), and 0.153 mmol/g for Pb(II), the IPN membrane is significantly selective for Pb(II) ions. The stability constants of IPN membrane–metal ions complexes were calculated by the method of Ruzic. The results obtained from the kinetics and isotherm studies showed that the experimental data for the removal of heavy metal ions were well described with the second-order kinetic equations and the Langmuir isotherm model. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 169–177, 2007

Key words: pHEMA; chitosan; heavy metal; IPN; adsorption; kinetics; removal; equilibrium

INTRODUCTION

Heavy metal ions such as cadmium(II), lead(II), and mercury(II) are known to be toxic and these are released into the environment in quantities that pose a risk to human health.^{1,2} The toxicity of heavy metals may be caused by mechanisms that include blocking essential functional groups of biomolecules and disrupting the integrity of biomembranes. There are many methods available for the treatment of wastewater such as ion exchange, reverse osmosis, filtration, precipitation with carbonate or hydroxide, coagulation, solvent extraction, adsorption, etc.^{3–6} Among them, adsorption can be considered as an effective technique and several natural and synthetic polymeric materials have been prepared and/or modified for the removal of heavy metal ions from aqueous solutions.^{6–11} Natural materials such as chitosan, zeolites, clay, coal, and some microbial biomass products are classified as low-cost adsorbents because of low cost and local availability.

Chitosan is obtained from the most abundant natural polymer chitin by the alkaline deacetylation. The pendant amino groups of the glucoseamine residues on the chitosan polymer chain are strongly attractive toward metal ions, which is responsible for the removal of metal cations by a chelation mechanism. The chitosan-based adsorbent can be prepared in the various geometric forms such as beads, flakes, fibers, or films.^{10–12} Chitosan-based adsorbents are mechanically weak and/or brittle. For this reason, much attention has been paid to improve the physical properties of chitosan-based material in the aqueous medium. The main effort has been focused on the introduction of a second component such as a hydrophobic or hydrophilic polymer into the chitosan network to obtain durable mechanic strength so-called interpenetration network (IPN).^{13–15} Poly(hydroxyethyl methacrylate) (pHEMA) is a synthetic hydrogel, and it possesses a high mechanical strength and resistance to many chemicals and microbial degradation.^{16–18} An IPN matrix can be prepared by combining the useful properties of the synthetic pHEMA and natural chitosan. In addition, the presence of hydroxyl and amino groups on the prepared IPN offer an easy attachment sites for a variety of metal ions.

Poly(HEMA/chitosan) IPN membrane was prepared by varying HEMA/chitosan ratio in the

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polymerization mixtures. The IPN membrane was utilized as an adsorbent for the removal of Cd(II), Hg(II), and Pb(II) ions from aqueous medium. The metal-adsorption capacities of the membranes were found to depend on the available amine groups of the networks. Changes in the adsorption conditions were evaluated as a function of the contact time, medium pH, metal ions concentration, and another metal ions existence in the adsorption system. The kinetics and the theoretical isotherm models of adsorption of three different metal ions on the membrane were also assessed using experimental adsorption data.

MATERIALS AND METHODS

Materials

Azobisisobutyronitrile (AIBN) and HEMA were obtained from Fluka (Buchs, Switzerland), and the monomer was distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4°C until use. Chitosan was purchased from Sigma (St Louis, USA). All of the other chemicals used were reagent grade from Merck (Darmstadt, Germany).

Synthesis of IPN membranes

The interpenetrating network synthesis was achieved by mixing chitosan solution (between 1.0 and 2.5% chitosan in acetic acid solution (1.0%, 4.0 mL)) with 2-HEMA monomer (2.0 mL) containing 20-mg AIBN. Following the nitrogen flash, the solution was poured into a round glass mold (diameter: 9.0 cm) sealed and exposed to UV radiation for 1 h at ambient temperature. The nitrogen atmosphere was maintained during the UV irradiation. After the polymerization, the resultant product was washed with 1.0% (w/w) NaOH solution and then with distilled water. The IPN membrane was cut into circular pieces (diameter: 0.75 cm) with a perforator and left in the wet state at 4°C.

Characterization of IPN membrane

Scanning electron microscope

The surface morphology of the IPN membranes was obtained using a JEOL (JSM 5600) scanning electron microscope (SEM) after coating with gold under reduced pressure.

Fourier transform infrared spectra

Fourier transform infrared spectra (FTIR) spectra of the membranes were obtained by using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Japan). The dry sample (about 0.01 g) was mixed with KBr

(0.1 g) and pressed into a tablet form. The FTIR spectrum was then recorded.

Swelling of the membrane

Swelling of the membrane was determined in water using a gravimetric method. A weighed amount of dry sample was immersed in a vial containing distilled water at an isothermal water bath with a fixed temperature ($25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$) for 24 h. The IPN membranes were taken out from the distilled water, wiped using a filter paper, and weighed. The water content of the membranes was recorded as a function of time. The water content was defined as the weight ratio of water contained within swollen to dry membrane.

Membranes thickness and density

The thickness of the IPN membrane was estimated using a micrometer thickness gauge. The density of IPN membrane was determined using a pycnometer, and *n*-decane was chosen as the inert liquid that is nonsolvent for the membrane.

Surface area measurements

The surface area of the IPN membrane was determined by N₂ sorption isotherm in a BET apparatus and application of the BET theory.

Determination of amino group

The amount of free amino group contents of the p(HEMA/chitosan) IPN membrane was determined by potentiometric titration. Briefly, the IPN membrane (0.1 g) was allowed to soak into water (10 mL) for 24 h. Then, HCl solution (0.1M, 20 mL) was added to this solution and it was then incubated more in a shaking water-bath at 35°C for 6 h. After this reaction period, the IPN membranes were removed and the final HCl concentration in the solution was determined via potentiometric titration with 0.05M NaOH solution.

Single component heavy metal adsorption studies

Adsorption of heavy metal ions (i.e., Cd(II), Pb(II), and Hg(II)) on IPN membranes from aqueous solutions was investigated batch wise. The effects of chitosan content of the IPN membrane, adsorption equilibrium time, and the pH of the medium on the adsorption capacity were studied. Nitrates of the respective metal ions were used throughout the adsorption studies.

Aqueous solutions (25 mL) containing different amounts of heavy metal ions (25–800 mg/L) were

incubated with IPN membranes at different pH (in the range of 2.0–6.0, which was adjusted with HNO₃ or NaOH at the beginning of experiments and not controlled afterward) at 25°C, and agitated magnetically at 600 rpm. Blank trials without IPN membrane were performed for each tested metal ions concentrations. After the desired adsorption periods (up to 120 min), the aqueous phases were separated from the membranes and the residual concentrations of the metal ions in these phases were measured using a Shimadzu Model AA-6800 Flame Atomic Absorption Spectrophotometer (Japan). For mercury determinations, MVU-1A (Mercury Vapor Unit) 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% (w/v). The working current/wavelength values for cadmium and lead determinations were 8 mA/228.8 nm and 10 mA/283.3 nm, respectively. The instrument response was periodically checked with known heavy metal ions solution standards. For each sample, the mean of 10 measurements was recorded. For each set of data, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples to determine the margin of error. The amount of metal ions adsorbed per unit mass of the membrane was presented as “mg metal ions/g membrane” and was calculated using the experimental data.

Evaluation of equilibrium adsorption isotherms

The adsorption isotherm models were used to characterize the interaction of Hg(II), Cd(II), and Pb(II) with the IPN membranes. The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, and the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir equation is

$$q_e = q_m b C_e / (1 + b C_e) \quad (1)$$

where C_e and q_e show the residual metal concentration (mg/L) and the amount of metal adsorbed on the adsorbent at equilibrium (mg/g), respectively, and b is the energy of adsorption or adsorption equilibrium constant (L/mg) of the system. The maximum adsorption capacity, q_m , is the solid-phase concentration corresponding to a condition in which all available sites are filled.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is used to predict whether an adsorption system is “favorable” or “unfavourable.”^{10,19}

$$R_L = 1 / (1 + b C_o) \quad (2)$$

where C_o is the initial metal concentration. The value of R_L indicates the shape of isotherm to be either unfavorable ($R_L > 1$) or linear ($R_L = 1$) or favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of a metal binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. This empirical equation takes the form:

$$q_e = K_F (C_e)^{1/n} \quad (3)$$

where K_F and n are the Freundlich constants, the characteristics of the system. K_F and n are the indicators of the adsorption capacity and adsorption intensity, respectively.

As the root mean square measures (rms) the difference between experimental and calculated values, it was used to determine how well models represent the experimental data. Chi-square statistic (χ^2) is determined by the following equations:

$$\chi^2 = \sum (q_{\text{exp}} - q_{\text{mod}})^2 / q_{\text{mod}} \quad (4)$$

where, q_{mod} is the modeled amount of metal ion adsorbed (mg/g) and q_{exp} is the experimental amount of metal ion adsorbed (mg/g).

Adsorption kinetic models

The kinetic of Hg(II), Cd(II), and Pb(II) biosorption on IPN membrane was determined with two different kinetic models, i.e., the first- and second-order. The first-order rate equation of Lagergren is one of the most widely used equations for the adsorption of solute from a liquid solution.²⁰ It may be represented as follows:

$$dq_t/dt = k_1 (q_{\text{eq}} - q_t) \quad (5)$$

where k_1 is the rate constant of first-order adsorption (min^{-1}) and q_{eq} and q_t denote the amounts of adsorption at equilibrium at time t (mg/g), respectively. After integration by applying boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ gives

$$\log(q_{\text{eq}}/q_{\text{eq}} - q_t) = (k_1 t) / 2.303 \quad (6)$$

Ritchie proposed a method for the kinetic adsorption of gases on solids.^{21,22} If metal ion adsorption

medium is considered to be a second-order reaction, then Ritchie equation is

$$(1/q_t) = (1/k_2q_{eq}t) + (1/q_{eq}) \quad (7)$$

where k_2 (g/mg/min) is the rate constant of the second-order adsorption.

The intraparticle diffusion rate may be expressed as

$$q_t = k_i t^{0.5} \quad (8)$$

where k_i is intraparticle diffusion rate (mmol/g min^{0.5}).

Determination of binding capacity and the stability constant of IPN membrane by the method of Ružić

Cd(II), Pb(II), and Hg(II) ion-binding properties of the IPN membranes have investigated applying the method of Ružić.²³ According to this data treatment, plotting $[M]_{\text{ionic}}/(M)_T - [M]_{\text{ionic}}$ vs. $[M]_{\text{ionic}}$, a straight line should be obtained, if one type of the complex is predominant (M_T is the total metal concentration and $[M]_{\text{ionic}}$ is the concentration of the labile metal species). From the slope, the metal binding capacity of the ligand (C_L) is determined. From the intercept according to following equation, the apparent concentration stability constant (K') is defined.

$$\{[M]_{\text{ionic}}/(M)_T - [M]_{\text{ionic}}\} = 1/K' C_L \quad (9)$$

Competitive adsorption

Competitive heavy metal adsorption from aqueous solutions containing Cd(II), Pb(II), and Hg(II) ions was investigated by following a similar procedure described earlier. These experiments were performed at a constant pH of 5.0–5.5 and at 25°C using solutions containing 1.5 mM from each metal ion.

Desorption and reuse

Desorption of heavy metal ions was achieved using 0.1M HNO₃ (25 mL) as a desorbing agent. The IPN membrane being loaded with the heavy metal ions was placed in the desorption medium and stirred with a magnetic stirrer at 600 rpm for 60 min at room temperature. The final metal ions concentration in the aqueous phase was determined by AAS as described earlier. The elution ratio was calculated from the amount of metal ions adsorbed on the membrane and the final metal ions concentration in the desorption medium. To determine the reusability of the IPN membrane, consecutive adsorption–desorption cycles were repeated six times using the same adsorbents.

RESULTS AND DISCUSSIONS

Chitosan is a heteropolymer made of D-glucoseamine and a small fraction of N-acetyl-D-glucoseamine residues, and it has several functional groups (amino, hydroxyl, acetyl, glucose). On the other hand, pHEMA polymer contains only —OH groups. Therefore, the adsorption ability of p(HEMA/chitosan) IPN membrane is found to be much higher than that of bare pHEMA. The p(HEMA/chitosan) IPN has sufficient mechanical strength due to the flexible network structures provided by pHEMA. Thus, the IPN membrane can be used for the continuous applications in various reactor configurations.^{24,25}

The p(HEMA/chitosan) hydrogel membrane displayed porous surface structure (Fig. 1). The average pore size and the pore distribution are about 4.45 μm and 4.3 × 10⁷ pores cm⁻², respectively. Hydrogels do not dissolve in aqueous media but do take up water, depending on the degree of crosslinking density and the hydrophilicity of the polymer chains.^{24,25} The IPN membranes prepared in this study have a rather hydrophilic nature. The equilibrium water uptake is reached in about 60 min. When compared with pHEMA (58%), the water-swelling ratio of the IPN membrane increased significantly (69%). The IPN membrane thickness and density were measured to be 600 μm and 1.26 g/cm³, respectively. The plain surface area of the 1.0-mL wet IPN membrane was 38.5 cm². The amino group contents of the IPN membranes were 0.10, 0.16, 0.21, and 0.27 mmol/g membrane for 20, 30, 40, and 50 mg/g chitosan loaded IPN membranes, respectively.

FTIR spectra of chitosan and IPN membrane showed in Figure 2. The FTIR spectrum of chitosan shows peak of assigned saccharine structure at around 897 and 1155 cm⁻¹. The stronger absorption band at 1656 cm⁻¹ was characteristic of amide absorption. The absorption bands at 1259 and 1084 cm⁻¹ can be attributed from the hydroxyl groups of chitosan. The FTIR spectra of both chitosan and p(HEMA) have the characteristic stretching vibration band of hydrogen-bonded alcohol, O—H, around 3540 cm⁻¹. On the other hand, hydrogen-bonded alcohol O—H stretching band intensity of p(HEMA/chitosan) membrane is higher compared to pure chitosan due to the incorporation of pHEMA into the polymer structure.

Effect of chitosan ratio on adsorption capacity

The effect of chitosan ratio on the metal ions adsorption capacities of the membranes is shown in Figure 3. As observed in this figure, an increase in chitosan ratio led to an increase in adsorption capacity of the IPN membrane to all the tested metal ions (200 mg/L), but this relation leveled off at around 40 mg chito-

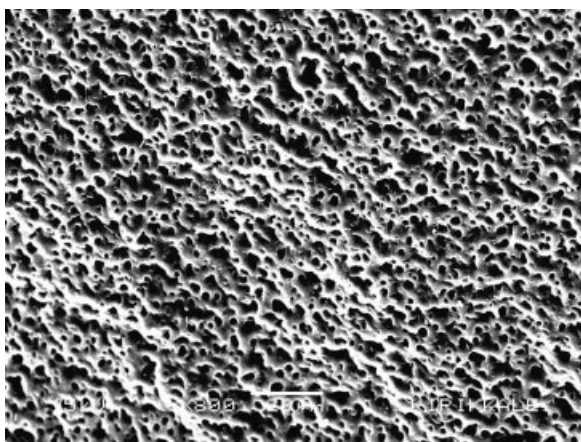


Figure 1 SEM micrograph of the IPN membrane.

san/g membrane structure. At higher chitosan density, however, the increase in metal ions adsorption capacity was not significant. Maximum adsorption values for Cd(II) Pb(II), and Hg(II) ions were found to be 0.062, 0.137, and 0.158 mmol/g, respectively, with the p(HEMA/chitosan). Therefore, the rest of the study was carried out with a chitosan density of 40 mg/g membrane (or 4.0 mL 2% chitosan solution in 6.0-mL polymerization mixture).

Dependence of adsorption properties on medium pH

The pH of medium is one of the most important parameter on removal of metal ions from aqueous solutions. Metal ions adsorption onto nonspecific and specific sorbents is pH-dependent.²⁶ In the absence of complexing agents, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble species. As discussed in detail by Reed and Matsumoto,²⁷ the hydrolysis of metal ions becomes significant at a pH of ~ 7.5 – 8.5 . From this point of view, to establish the effect of pH on the

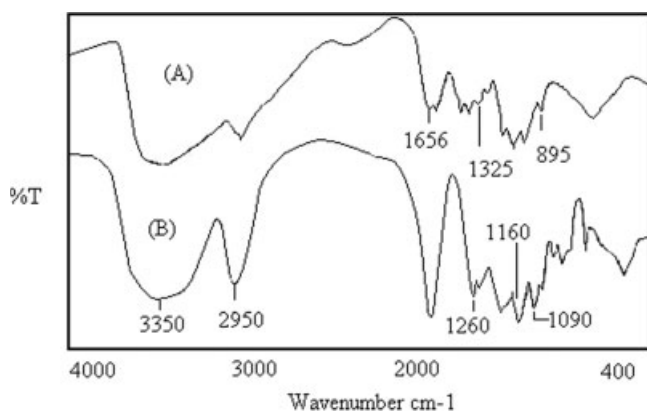


Figure 2 FTIR spectra of chitosan (A) and IPN membrane (B).

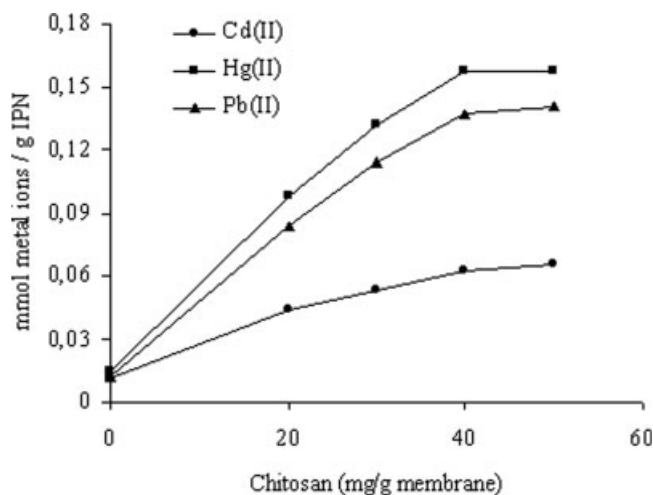


Figure 3 Effect of chitosan ratio on the adsorption of Cd(II), Pb(II) and Hg(II) metal ions by IPN membrane. Adsorption conditions—initial concentration of metal ions: 200 mg/L; volume of the adsorption medium: 25 mL; temperature: 25°C; contact time: 60 min.

adsorption of metal ions onto IPN, membrane was studied at different pH values. The adsorption capacities of three different metal ions (i.e., Cd(II), Hg(II), and Pb(II)) on IPN membrane were significantly increased with the increase in pH, but then almost reached a plateau value at around pH 5.0–6.0 (Fig. 4). The reduced adsorption of metal ions at acidic pH values could be attributed to the fact that a lower pH the metal ions that would coordinate with lone pair of nitrogen would have to compete with H_3O^+ for an active site.²⁸ The maximum adsorption values for Cd(II), Pb(II), and Hg(II) ions were 0.062, 0.137, and 0.158 mmol/g membrane, respectively, at pH 5.0,

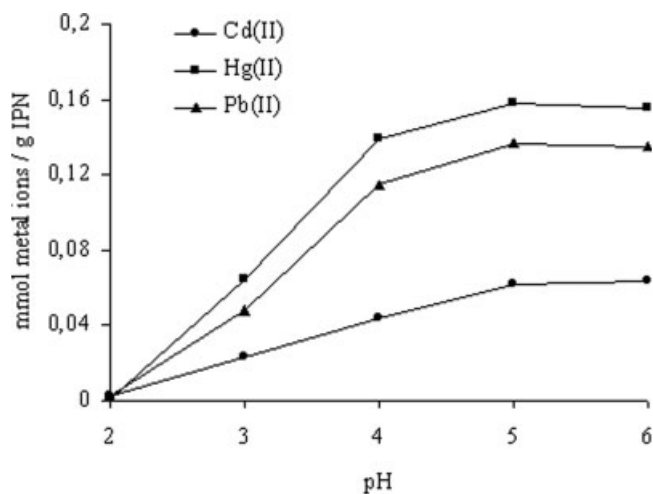


Figure 4 Influence of pH on the adsorption of Cd(II), Pb(II) and Hg(II) metal ions by IPN membrane. Adsorption conditions—initial concentration of metal ions: 200 mg/L; volume of the adsorption medium: 25 mL; temperature: 25°C; contact time: 60 min.

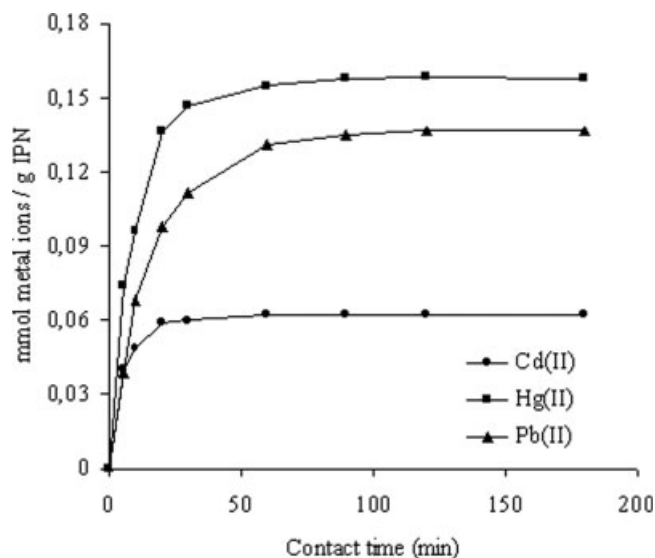


Figure 5 Effect of contact time on the adsorption of Cd(II), Pb(II) and Hg(II) metal ions by IPN membrane. Adsorption conditions—initial concentration of metal ions: 200 mg/L for Pb(II), Cd(II) and Hg(II); volume of the adsorption medium: 25 mL; temperature: 25°C; pH: 5.0; contact time: 60 min.

which correspond to initial metal ion concentrations of 200 mg/L. The influence of pH on adsorption of Pb(II), Cd(II), and Hg(II) metal ions on the IPN membrane can be explained on the basis of ionization of amine groups of chitosan at acidic pH values. It should be noted that the adsorption capacity of the membrane can be determined from the number of available free amine groups rather than the total fraction of amine groups in the IPN network structure. The optimum pH depends on the hydrogels and in general, also on the cation; some of the cations here studied have different optimum pH values in other polymer systems.^{29–32} For example, the optimum pH for the adsorption of Hg(II), Cd(II), and Pb(II) ion on the lignite coal was obtained at pH 6.0.³³ In other reported study, the optimum pH for the adsorption of Cu(II), Cd(II), Hg(II), and Pb(II) on the poly(2-acrylamido-2-methyl-1-propansulfonic acid-co-4-vinyl pyridine) resin was obtained at pH 2.0.³²

The time required to achieve adsorption equilibrium for Cd(II), Hg(II), and Pb(II) metal ions from aqueous solution was determined. The adsorption efficiency measured was plotted as a function of time and showed in Figure 5. As seen in this figure, the initial retention profile of Hg(II) ions to the IPN membranes was very fast and steep compared to other tested metal ions. After this initial retention period, the adsorption equilibrium was gradually established within 60 min for all the tested metal ions. The mechanism of metal ions adsorption process can occur in three following aspects.³³ First, the metal ions are transferred from the solution to the adsorbent surface.

Second, diffusion of ions into pores of adsorbent and the last stage is related to the diffusion of the metal ions on the internal surface of material, binding the pores, and capillary spaces. The first step of adsorption may be affected by metal ion concentration, agitation period, and rate. The last step of the adsorption is considered as a rate-limiting step and as a relatively rapid process. Such a fast adsorption rate could be attributed to the absence of internal diffusion resistance. It is known that the amine groups ($-\text{NH}_2$) on the chitosan chain act as electron donors. The nitrogen electrons present in the amine groups can establish dative bonds with the tested metal ions.³⁴

Influence of metal ion concentration

Figure 6 shows the experimental equilibrium isotherms for adsorption of Cd(II), Hg(II), and Pb(II) metal ions onto IPN membrane. It should be noted that there was no precipitation in these groups of experiments under the concentration and pH condition studied. To reach the plateau values, which represent the saturation of the active sites (available for interaction with metal ions) on the adsorbent, in other terms to obtain maximum adsorption capacities for IPN membranes, the initial concentrations of Cd(II), Hg(II), and Pb(II) metal ions were increased up to 800 mg/L, respectively. The experimental maximum adsorption capacities of Cd(II), Pb(II), and Hg(II) metal ions onto IPN membrane were 0.063, 0.179, and 0.197 mmol/g membrane, respectively. The ratio (in mol) between the IPN repeating unit and metal ions were 3.33, 1.77, and 1.07 for Cd(II), Pb(II), and Hg(II) metal ions, respectively. The results also show that

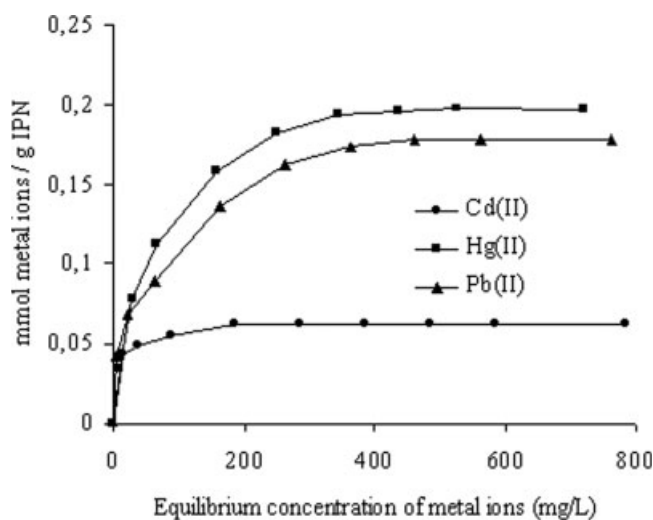


Figure 6 Influence of metal ion concentration on the adsorption of Cd(II), Pb(II) and Hg(II) metal ions by IPN membrane. Adsorption conditions—pH: 5.0; volume of the adsorption medium: 25 mL; temperature: 25°C; contact time: 60 min.

TABLE I
The Langmuir and Freundlich Constants and Correlation Coefficients of Isotherm Models for the Adsorption of Cd(II), Pb(II), and Hg(II) Metal Ions from Aqueous Solution Onto IPN Membrane

Metal ions	Experimental	Langmuir constant			Freundlich constant		
	q_{ex} (mmol/g)	q_m (mmol/g)	$b \times 10^2$ (L/mg)	R^2	K_F	n	R^2
Cd(II)	0.063	0.064	12.73	0.999	0.034	10.10	0.946
Hg(II)	0.197	0.210	0.85	0.989	0.017	2.74	0.992
Pb(II)	0.179	0.182	8.30	0.996	0.052	4.68	0.938

IPN membrane has a great affinity for the mercury ions with respect to other tested metal ions. Similar observations were also reported in the literature.^{32,35} The following order of affinity was formed between p(HEMA/chitosan) IPN membrane and three metal ion studies: Hg(II) > Pb(II) > Cd(II). p(HEMA/chitosan) membrane showed higher binding affinity for third row transition metal ions (i.e., Hg(II) and Pb(II)) than those of the Cd(II) ions. Hg(II) and Pb(II) ions have adsorption capacities that are very close to each other in molar units, and both are higher than that of Cd(II), which is in the second transition row. It should also be noted that Lewis hard acids are hardly polarizable, display a higher affinity toward hard donor atoms such as oxygen and nitrogen, whereas soft acids, being larger and more easily polarizable, have greater affinity toward soft atoms.³² Thus, Cd(II) is a soft acid, and Hg(II) is a hard acid. As expected, a higher adsorption capacity was obtained for mercury ions compared with other tested metal ions.

Evaluation of adsorption isotherm models and parameters

Equilibrium data, commonly known as adsorption isotherms, are the basic requirements for the design of adsorption systems. Obtaining equilibrium data for a specific adsorbate/adsorbent system can be performed experimentally, with a time-consuming procedure that is incompatible with the growing need for adsorption systems design. Analysis of equilibrium data is important for developing an equation that can be used to compare different adsorbents under different operational conditions and to design and optimize an operating procedure.³⁶⁻⁴¹ Various adsorption isotherm models, such as the Langmuir and Freundlich models, have commonly been used to predict the adsorption efficiency and potential of an adsorbent. Therefore, semireciprocal (C/q versus C) of the experiment data for the adsorption of Cd(II), Hg(II), and Pb(II) ions is plotted for the IPN membrane. The ability of the Freundlich model to fit the experimental data was also examined. For this case, the plot of $\log C$ vs. $\log q$ was employed to generate the intercept value of K_F and the slope of n .

The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms with the

correlation coefficients are presented in Table I. The maximum theoretical adsorption capacity of Cd(II), Pb(II), and Hg(II) calculated from Langmuir equation was 0.064, 0.181, and 0.210 mmol/g IPN, respectively. The correlation coefficients show that the adsorption process could be described by the Langmuir equation. This was also supported by the root mean square values. The magnitudes of K_F and n (Freundlich constants) show easy separation of Cd(II), Pb(II), and Hg(II) ions from aqueous medium and indicate favorable adsorption. The intercept K_F value is an indication of the adsorption capacity of the adsorbent; the slope $1/n$ indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. As seen from Table I, n values were found high enough for the separation of heavy metal ions from aqueous medium. The conformity of the adsorption data to the Langmuir isotherm (correlation coefficient > 0.95) could be interpreted as indicating a homogeneity adsorption process, leading to monolayer binding. On the basis of the effect of separation factor, R_L values are in the range of $0 < R_L < 1$, which indicates that the IPN membrane are favorable adsorbents for Cd(II), Pb(II), and Hg(II) removal from aqueous solution (Table II).

Determination of kinetic properties of adsorption systems

For the Lagergren first-order kinetic model, a plot of $\log(q_{eq} - q_t)$ against t according to the eq. (7) should give a straight line to confirm the applicability of the

TABLE II
 R_L Values Based on Langmuir Equation

Concentration of metal ions (mg/L)	R_L values		
	Cd(II)	Hg(II)	Pb(II)
25	0.239	0.825	0.321
50	0.136	0.702	0.191
100	0.073	0.541	0.106
200	0.038	0.371	0.056
300	0.026	0.282	0.038
400	0.019	0.228	0.029
500	0.016	0.191	0.023
600	0.013	0.164	0.019
800	0.097	0.129	0.015

TABLE III
Kinetic Parameters for the Adsorption of Cd(II), Pb(II), and Hg(II) Metal Ions Onto IPN Membrane

Metal ions	Experimental	Intraparticle diffusion		First-order kinetic			Second-order kinetic		
	q_{exp} (mmol/g)	$k_i \times 10^2$ (mmol/g min ^{0.5})	R^2	k_1 (min ⁻¹)	q_{eq} (mmol/g)	R^2	k_2 (g/mmol/min)	q_{eq} (mg/g)	R^2
Cd(II)	0.063	0.57	0.966	0.083	0.037	0.940	0.321	0.065	0.989
Hg(II)	0.197	3.06	0.999	0.175	0.717	0.968	0.122	0.210	0.996
Pb(II)	0.179	2.40	0.991	0.044	0.142	0.976	0.102	0.182	0.997

kinetic model. In a true first-order process $\log q_{\text{eq}}$ should be equal to the intercept of a plot of $\log (q_{\text{eq}} - q_t)$ against t . On the other hand, a plot of $1/q_t$ vs. $1/t$ [eq. (8)] should give a linear relationship for the applicability of the second-order kinetic. The rate constant (k_2) and adsorption at equilibrium (q_{eq}) can be obtained from the intercept and slope, respectively, and there is no need to know any parameter beforehand. The comparison of experimental adsorption capacities and the theoretical values estimated from the first- and second-order equation are presented in Table III. The Lagargren model was not enough or satisfactory to explain the experimental kinetic data. Whereas, the theoretical q_{eq} values for the adsorption of heavy metal ions on the IPN membrane were very close to the experimental q_{eq} values in the case of second-order kinetic. This suggests that the rate-limiting step may be the chemical adsorption not the mass transport limitation.¹⁰ Increasing metal ion concentration in the aqueous solutions seems to reduce the external diffusion of the adsorbate and enhances intraparticle diffusion.⁷ The intraparticle diffusion rate equation fits well to the initial stages of the adsorption process for all the tested metal ions with the IPN membranes.

Competitive adsorption

The competitive adsorption of Cd(II), Pb(II), and Hg(II) from a mixture was also investigated. These experiments were performed at a constant pH of 5.0 and at 25°C using solution containing 1.5 mM from each metal ion. The adsorbed amounts of Pb(II) ions are higher than those obtained for Hg(II) and Cd(II) not only in weight basis but also in molar basis. The adsorption capacities for Cd(II), Hg(II), and Pb(II) ions were 0.035, 0.074, and 0.153 mmol/g membranes, respectively. Under competitive condition, the order of affinity of the IPN membrane is Pb(II) > Hg(II) > Cd(II), which correspond to the order of the Irving–Williams series.³⁹ In general, the Irving–Williams series for affinity to most organic ligands is followed: Pb(II) > Hg(II) > Pa(II) > Cu(II) > Cd(II).^{40,41} It should be noted that under competitive conditions, the ion selectivity observed for Pb(II) being higher than those of Hg(II) and Cd(II) might be attributed to the physical aspects of the adsorption process. The

ionic radius of Pb(II) ions, 1.21 Å, is larger than those of Hg(II) (1.10 Å), and Cd(II) (0.90 Å), and thus a stronger physical affinity for Pb(II) is expected for binding sites on the IPN membrane.

Stability constants of metal ions

It was of great importance to know the formation constants of the metal ion complexes to gain an understanding of the affinities of heavy metal ions to the amine groups of IPN membrane. The formation constants of metal ion-sorbent complex have been investigated applying of Ruzic method.²³ According to this treatment, plotting $[M]_{\text{ionic}}/(M_T - [M]_{\text{ionic}})$ vs. $[M]_{\text{ionic}}$, a straight line should be obtained if one type of complex is predominant (M_T is the total metal concentration and $[M]_{\text{ionic}}$ is the concentration of the labile metal species). From the slope, the metal-binding capacity of the IPN membrane is determined. From the intercept according to the eq. (9), the apparent stability constant ($K_{\text{stability}}$) is defined. $[M]_{\text{ionic}}/(M_T - [M]_{\text{ionic}})$ vs. $[M]_{\text{ionic}}$ are plotted for the metals studied. The straight-line relationship indicates that the interaction of metal ions with IPN membrane occurs via one type of functional groups. The obtained $K_{\text{stability}}$ values were 1.24×10^4 L/mol for Pb(II), 1.24×10^4 L/mol for Hg(II), and 4.28×10^2 L/mol for Cd(II); a much higher $K_{\text{stability}}$ value was obtained for Hg(II) and Pb(II) compared to Cd(II) ions. The order of p(HEMA/chitosan) stability constant for the metal tested at pH 5.0 is Pb(II) = Hg(II) > Cd(II). As explained earlier, Hg(II) and Pb(II) ions, the third row transition metals, have the same stability constant value, and is higher than that of the Cd(II), which is second row transition metal. These results suggest that Cd(II) ions do not significantly compete with Hg(II) and Pb(II) ions in aqueous solution. However, Hg(II) and Pb(II) ions compete with each other for binding p(HEMA/chitosan) complexation sites, when they are present in the aqueous solution at the same concentration.

Desorption and reusability of IPN membrane

Desorption experiments were performed with 0.1M HNO₃ as the desorption agent. The metal ions adsorbed IPN membrane transferred into the desorp-

tion medium. The amount of metal ions desorbed more than 95% after six cycles of consecutive adsorption/desorption. Therefore, IPN membrane can be used repeatedly without significantly losing their adsorption capacities for adsorption system.

CONCLUSIONS

The suitable materials for the removal of heavy metal ions in the water treatment applications include chitosan but it shows insufficient mechanical strength and porosity. To improve the mechanical properties of chitosan, a novel IPN hydrogels were prepared by combining the useful properties of the synthetic pHEMA and natural chitosan. The p(HEMA/chitosan) network films were synthesized at low temperature via UV-initiated photo-polymerization. The IPN membrane was quite efficient adsorbent for the fast adsorption of Cd(II), Pb(II), and Hg(II) metal ions from aqueous solution at pH 5.0. The contact time required to achieve the adsorption equilibrium was 60 min. The equilibrium adsorption behavior of Cd(II), Pb(II), and Hg(II) onto IPN membrane followed the Langmuir adsorption isotherm with a maximum theoretical adsorption capacity of 0.064, 0.181, and 0.210 mmol/g, respectively. The adsorption process could be best described by second-order equation. Finally, it should be stated that the Pb(II) removal from the metal ions mixture by IPN membrane is highly selective compared to Cd(II) and Hg(II) ions.

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