



Preparation and characterization of immobilized [A336][MTBA] in PVA–alginate gel beads as novel solid–phase extractants for an efficient recovery of Hg (II) from aqueous solutions

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ABSTRACT

The coarse PVA–alginate matrix gel beads entrapping the micro-droplets of the ionic liquid tricaprilylmethylammonium 2-(methylthio) benzoate ([A336][MTBA]) as novel solid-phase extractants were prepared for the removal of mercury (II) from aqueous media. The ionic liquid [A336][MTBA] immobilized PVA–alginate beads (PVA/IL) have been characterized by FTIR, SEM and TGA. The influence of the uptake conditions was investigated including aqueous pH, PVA/IL dosage, the content of [A336][MTBA] and initial Hg (II) concentration; maximum Hg (II) ion adsorption capacity obtained was $49.89 (\pm 0.11) \text{ mg g}^{-1}$ at pH 5.8 with adsorptive removal of approximately 99.98%. The selectivity of the PVA/IL beads towards Hg (II), Pb (II) and Cu (II) ions tested was $\text{Hg} > \text{Pb} > \text{Cu}$. The rate kinetic study was found to follow second-order and the applicability of Langmuir, Freundlich and Tempkin adsorption isotherm model were tested as well. The results of the study showed that PVA/IL beads could be efficiently used as novel extractants for the removal of divalent mercury from aqueous solutions under comparatively easy operation conditions.

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1. Introduction

Mercury and its compounds are one of the most toxic chemicals present in the environment, which can be easily accumulated in humans and animals mainly causing neurological and renal disturbances as well as impairment of pulmonary function [1]. The recommended permissible limit of Hg (II) in potable water is 0.001 mg L^{-1} [2]. Therefore, industry is facing many constraints because of the increasingly drastic regulations concerning

wastewater discharge. Adsorption has been considered as an effective alternative among conventional processes especially for metal ions recovery from dilute solutions. The development of suitable sorbents characterized by a high efficiency and selectivity has been a problem for many years. Recently, the solid-phase adsorbents combining the efficiency of solvent extraction systems (liquid/liquid extraction) and the stability of resins (sorption process) have found the widest application because of easy separation and simplicity of their preparation [3]. Different techniques have been used for manufacturing such solid-phase extractants like impregnation and encapsulation or immobilization of solvents with support materials [4].

The application of ionic liquids (ILs) opens a new route to prepare novel solid-phase adsorbents because of some unique physicochemical properties: a very low (often negligible) vapor pressure, low melting points and good thermal stability [5]. A number of papers have been devoted to the description of synthesis and properties of various ILs, including imidazolium-based ILs and phosphonium-based ILs focusing on their potential for the extraction of organic and inorganic compounds [6]. The

Abbreviations: PVA, poly(vinyl alcohol); IL, ionic liquid; FTIR, Fourier transform infrared spectroscopy; SEM, scanning electron microscopy; ATR, attenuated total reflection; TGA, thermal gravimetric analysis; SDTA, scalable decision tree algorithm; EDAX, energy dispersive X-ray analysis; [A336][MTBA], tricaprilylmethylammonium 2-(methylthio) benzoate; ACS, American chemical society; AAS, atomic absorption spectroscopy; FIMS, flow injection mercury system; CaCl_2 , calcium chloride; DOC, dissolved organic carbon; NPOC, non purgeable organic carbon; TOC, total organic carbon; LOD, limit of determination.

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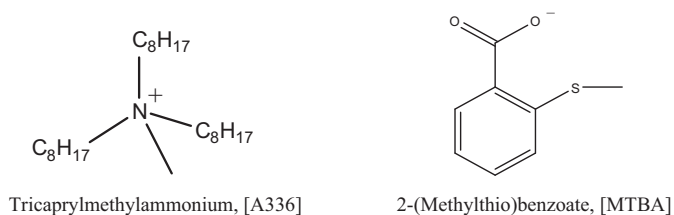


Fig. 1. The structure of the ionic liquid [A336][MTBA].

ability of ILs to be retained on solid surfaces allows one to prepare sorption materials by means of immobilization of ILs on different matrices. Guibal et al. [7] tested adsorption performance of Hg (II) by capsules prepared by immobilization of Cyphos IL-101(trihexyl(tetradecyl)phosphonium chloride) in alginate particles. However, most of those supports reported for the immobilization of ILs focused on alginate, chitosan and mineral materials [6,8]. Poly(vinyl alcohol) (PVA) is a water-soluble material containing large amounts of hydroxide groups that has been developed for biomedical applications since it is biocompatible and exhibits minimal cell adhesion. It has been reported that PVA gel has no degradation by microorganisms and a higher mechanical strength and larger durability in high acid solutions than alginate gel, which has been mostly employed as polymer for microcapsules [9]. So combining PVA gel with ILs would be an interesting and promising solution for developing novel solid-phase sorbents leading to easy possible design for extracting heavy metals industrially.

The present work proposes the coarse PVA–alginate matrix gel beads entrapping the microdroplets of the IL [A336][MTBA], which contains electron donor atoms: S and O. At first, the immobilized [A336][MTBA] PVA–alginate gel beads were prepared and characterized. Then the performance of a Hg (II) extraction process was evaluated in terms of the Hg (II) removal efficiency, the adsorption mechanism, optimization of operation and the effect of coexisting ions. This alternative solid-phase extraction system was expected to be simple, competitive, efficient and environmentally friendly for treating wastewater containing Hg (II) ions.

2. Experimental

2.1. Materials and characterization of the PVA/IL beads

[A336][MTBA] was synthesized in the lab as reported before (shown in Fig. 1) [10]. Polyvinyl alcohol (99% hydrolyzed, average Mw 146,000–186,000) and sodium alginate with a viscosity of 3500 cps (2% solution, 25 °C) were purchased from Sigma–Aldrich, Germany. All the other chemicals in this study were of ACS reagent grade and used as received. Double deionised water (Milli-Q Millipore 18.2 MΩ cm⁻¹ conductivity) was used for all dilutions. A ProLab2000 pH meter was used for the measurement of pH values in the aqueous phase. The concentration of mercury remnant in the solution was determined by a FIMS 400 Mercury Analysis System (PerkinElmer). Lead and copper concentrations were determined using flame-AAS with an AAAnalyst 200 by PerkinElmer. FT-IR spectra of dried PVA beads, ILs, PVA/IL and Hg (II) loaded PVA/IL beads were recorded using a Bruker Vertex 70 FT-IR spectrometer with ATR device (4000–400 cm⁻¹). Thermogravimetric measurements were conducted on a Mettler–Toledo TGA/SDTA 851e analyzer at a scan rate of 10 °C min⁻¹ over a temperature window of 25–700 °C. Nitrogen was used as the purge gas. SEM–X-ray microanalyses: dried beads were split after cooling them in fluid nitrogen and sputtered with carbon prior to the examination in a scanning electron microscope (SEM) XL20 by Philips. Element determination was done by an X-ray microanalysis system (EDAX). DOC was measured

as NPOC with a TOC-VCPH total organic carbon analyser in combination with a total nitrogen measuring unit TMN-1 by Shimadzu, bringing the samples to pH ≈ 2 with HCl (p.a. by Fluka) and sparging them with carrier gas for 5 min prior to combustion. Element concentrations were calculated from the corresponding regression lines (correlation factor >0.9995) using five different dilutions of a potassium hydrogen phthalate solution. LOD was determined as 0.5 mg L⁻¹ C.

2.2. Preparation of PVA/IL beads

The PVA–alginate–boric acid immobilization method was used. It was reported that monodiol-type is the cross-linking mechanism between PVA and boric acid [9]. The recommended percentage of PVA in the beads was kept in the range of 8–12.5% (w/v) to get high bead strength as PVA contributed strength and durability to the beads, whereas calcium alginate improved the surface properties, reducing the tendency to agglomerate [11]. In this work, 4 g PVA and 0.675 g sodium alginate were dissolved in 50 mL of Millipore water with boiled water bath for 1 h. The PVA (8%, w/v)–alginate solution and a required amount of [A336][MTBA] were then blended together with stirring at 500 rpm at 30 °C for 6 h to obtain a homogeneous gel blend which was extruded into a gently stirred saturated 3% (w/v) CaCl₂–boric acid solution by a syringe with a diameter of approximately 1 mm and immersed for 24 h to form spherical beads. The PVA/IL beads were washed with Millipore water to remove residual reagents. The wet spherical PVA/IL beads exhibit an elastic property with an average diameter of 1.6 (±0.02) mm and swelling ratio of approximately 56.51 (±0.13)% studied in 100 ml Millipore water using 2 g wet beads. The term wet means the state of the beads immediately after the preparation. After 24 h, the beads were separated from the water. Immediately, the beads were wiped gently with paper and weighed. The swelling ratio was calculated according to the formula: Swelling ratio = (W_s – W_i)/W_i × 100%, where W_s is the weight of the adsorbent in the swollen state and W_i is the initial weight of the adsorbent. Finally, the beads stability was tested as follows: 2 g of plain PVA–alginate beads and wet PVA/IL beads were immersed into 50 mL of Millipore water respectively for 72 h. Then DOC in the solutions was measured for each sample.

2.3. Batch sorption procedure

A 50 mg L⁻¹ solution of Hg (II) was prepared by dissolving 0.0677 g of mercury (II) chloride in 1 L solutions. The solutions (50 mL) including different amounts of the PVA/IL beads (0.01, 0.05, 0.1, 0.47 and 0.94 weight) at initial pH 6.0 were shaken in an electrically thermostatic reciprocating shaker at 120 rpm for 24 h. The batch adsorption experiments were performed to investigate Hg (II) removal as a function of initial metal concentration (10–50 mg L⁻¹), contact time (5 min–24 h), aqueous pH (2–7.0), PVA/IL beads concentration (0.2–20 g L⁻¹), the content of [A336][MTBA] in PVA/IL beads and coexisting ions. The equilibrium time was estimated by drawing samples at regular intervals of time till equilibrium was reached. The adsorption capacity of the PVA/IL beads and the percentage removal of Hg (II) are calculated using the following Eqs. (1) and (2) respectively:

$$\text{Adsorption capacity (mg/g)} = \frac{(C_i - C_f)V/1000}{W} \quad (1)$$

$$\text{Hg(II) ions removal (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where C_i and C_f are the initial and final concentration of Hg (II) in mg L⁻¹, V is the volume of Hg (II) solution in mL and W is the total amount of PVA/IL beads in g.

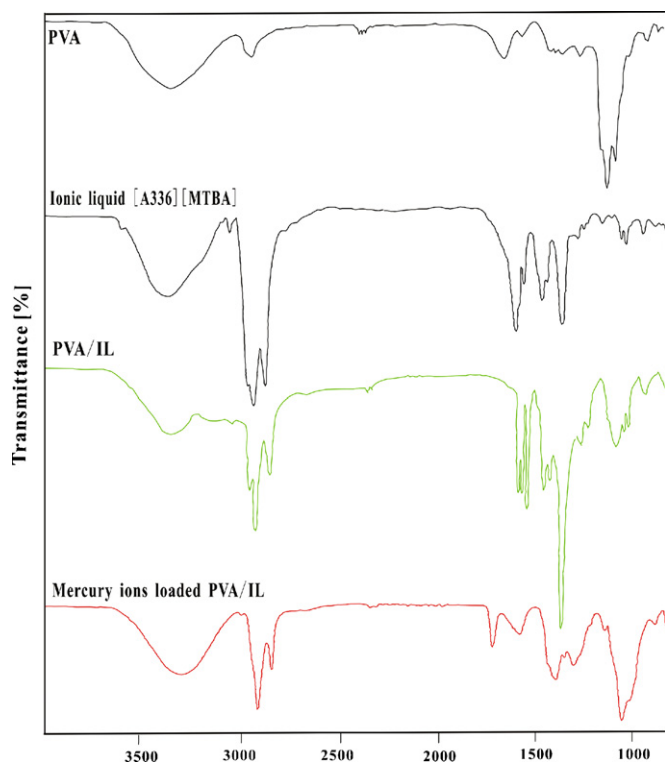


Fig. 2. FTIR spectra of [A336][MTBA], PVA, PVA/IL and Hg (II) loaded PVA/IL.

Each determination was replicated two times. For each set of data present, standard statistical methods were used to determine the mean values and stand deviations. Confidence intervals of 95% were calculated for each set of samples to determine the margin of error.

3. Results and discussion

3.1. Characterization of the PVA/IL beads

The FT-IR spectra of PVA, [A336][MTBA], PVA/IL and Hg (II) loaded PVA/IL are shown in Fig. 2. Bands at about 1554 and 1464 cm^{-1} could be assigned to stretching and bending vibrations

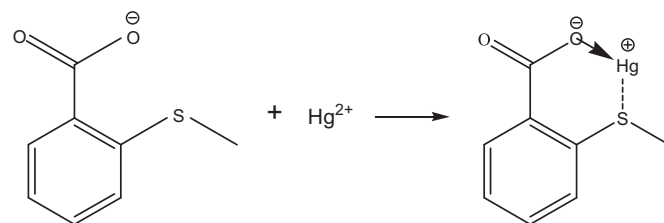


Fig. 3. Proposed main schematic mechanism for Hg (II) adsorption by PVA/IL.

of aromatic C–H groups of [A336][MTBA]. The bands at 2855 and 2925 cm^{-1} correspond to stretching vibrations of CH_3 and CH_2 from [A336][MTBA] as well. COO^- group stretching vibrations were observed at 1598 cm^{-1} for PVA/IL which may contribute to the Hg (II) adsorption (Fig. 3) since it was reported that PVA show little affinity to the heavy metal ions [12]. These observations indicated that [A336][MTBA] was immobilized in PVA/IL beads successfully.

A scanning electron microscope was used for obtaining microscopic images of the immobilized ILs in PVA–alginate gel beads. The shape of the PVA/IL beads and their morphologies of the cross section as well as the porous structure can be seen clearly from Fig. 4(A and B), respectively. From the element analysis by EDAX, it can be clearly seen that the peak of S emerges for PVA/IL beads, which suggests that [A336][MTBA] was wrapped up by porous PVA–alginate matrix after immobilization. And Hg (II) could be found in the PVA/IL beads after adsorption as well (Fig. 4).

Fig. 5 shows the thermal degradation behavior of the IL [A336][MTBA], PVA and PVA/IL beads assessed by TGA. The curve of PVA/IL showed that the degradation process occurred between 155 and 520 $^{\circ}\text{C}$. There were three distinct weight loss stages: 147–248 $^{\circ}\text{C}$; 248–351 $^{\circ}\text{C}$; 351–516 $^{\circ}\text{C}$. The first weight loss stage (about 17%) could be assigned to the decomposition of [A336][MTBA] immobilized onto the PVA–alginate beads; the second and third stages were probably due to the thermal degradation of [A336][MTBA] immobilized into PVA–alginate beads (248–300 $^{\circ}\text{C}$) and PVA. Thus, it was assumed that the required amount of [A336][MTBA] was successfully immobilized in the PVA–alginate beads by the above mentioned encapsulation method. And the results from the stability test showed only 2.2% of the ionic liquid [A336][MTBA] was released from PVA/IL beads prepared with this method after 72 h.

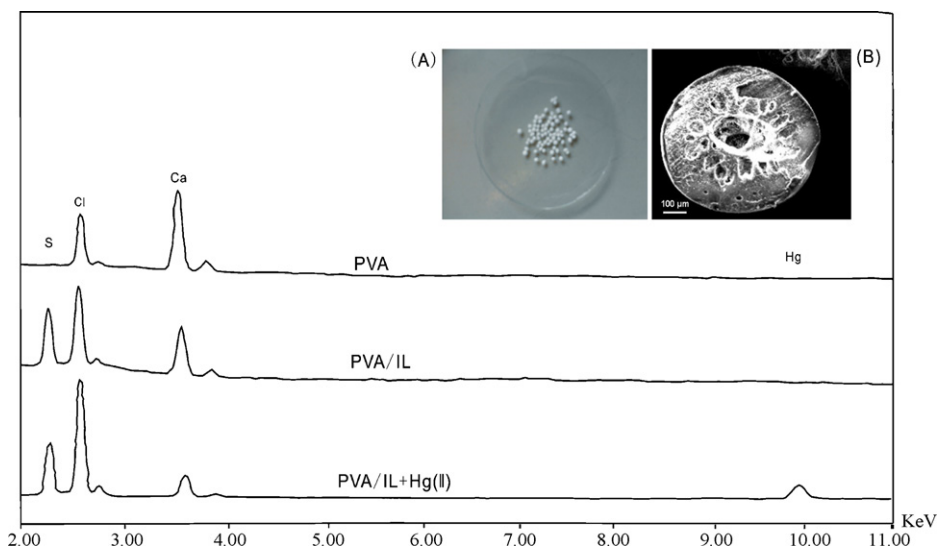


Fig. 4. Element determination of PVA, PVA/IL and Hg (II) loaded PVA/IL by EDAX ((A): digital photo of PVA/IL; (B): SEM picture of the cross section of PVA/IL).

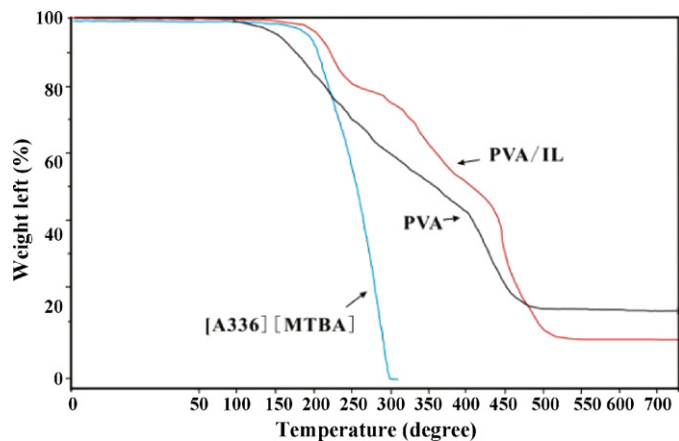


Fig. 5. Thermogram of the IL [A336][MTBA], PVA and PVA/IL.

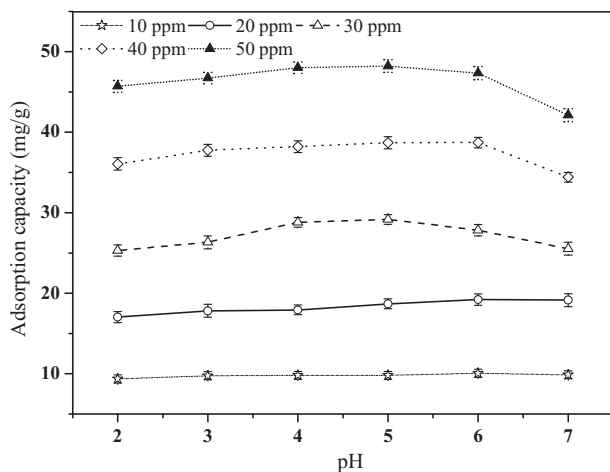


Fig. 6. Hg(II) adsorption onto PVA/IL beads as a function of solution pH (dosage: 2 g wet beads L^{-1} ; room temperature; initial Hg(II) concentration: 50 mg L^{-1} ; solution volume: 50 mL; contact time: 24 h).

3.2. Hg(II) adsorption

3.2.1. Effect of initial pH value

Generally, the solution pH value has a significant effect on the metal binding capacity. Too high pH values should be avoided as

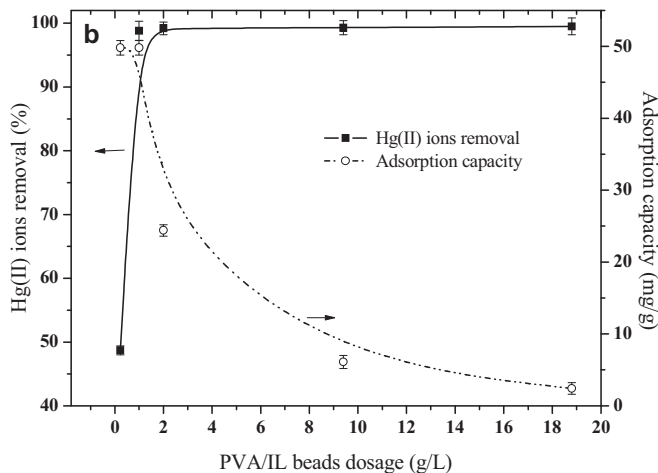
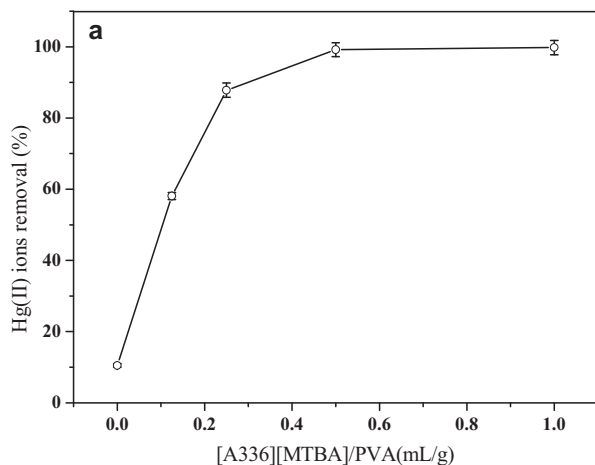


Fig. 7. Effect of [A336][MTBA] content in preparation of PVA/IL beads (a) and the wet beads dosage (b) on Hg(II) adsorption (room temperature; pH: 5.8; initial Hg(II) concentration: 50 mg L^{-1} ; solution volume: 50 mL; contact time: 24 h).

they cause precipitation of metal compounds, which then does not allow one to distinguish between the mechanisms of sorption and/or precipitation. According to the speciation diagram of mercury ($5 \times 10^{-3} \text{ mol L}^{-1}$) [13], HgCl_2 is the main species in solution below a pH of 7.0. In this study the initial mercury ion concentration was in the range of $10\text{--}50 \text{ mg L}^{-1}$ which was much less than the concentration of $5 \times 10^{-3} \text{ mol L}^{-1}$ (1357.5 mg L^{-1}), so a pH range of 2–7.0 was chosen. As shown in Fig. 6, the uptake of Hg(II) onto PVA/IL beads is slightly dependent on the pH value. In aqueous solutions with a mercury ion concentration below 20 mg L^{-1} , the pH hardly affected the adsorption. However, when the Hg(II) initial concentration increased to 30 mg L^{-1} or above, the pH of the solution showed a visible effect on Hg(II) adsorption by PVA/IL beads. This result agrees with that reported previously by Robichaud et al. [14]. This may be mainly owing to the fact that Hg(II) is a ‘soft’ metal, reported to adsorb independently of the pH value [15] and/or a strong affinity of [A336][MTBA] towards mercury ions. It may be concluded that these PVA/IL beads can be used for an efficient removal of mercury ions from solutions of a wide pH range, which might be of great interest for complex wastewater system.

3.2.2. Effects of [A336][MTBA] content in preparation of PVA/IL beads and the beads dosage

To study the effect of [A336][MTBA] content on Hg(II) adsorption, a series of PVA/IL beads with different volume of [A336][MTBA] (0, 0.5 mL, 1 mL, 2 mL, 4 mL) were prepared and the result of the adsorption test is shown in Fig. 7(a): the adsorption capacity of Hg(II) increased with the volume increase of [A336][MTBA]. When the ratio of [A336][MTBA] volume (mL) to PVA mass (g) was 0.25, the removal reached 87.8%. Nearly 100% of Hg(II) was removed when [A336][MTBA]/PVA reached 0.5. This suggests that effective adsorption of mercury ions could be mainly attributed to the IL [A336][MTBA] and a ratio in the range of 0.25–0.5 may be the most economical. The optimization of PVA/IL synthesis should thus take into account the rational use of the IL resource. So PVA/IL beads with the ratio of volume of [A336][MTBA] (mL) to the mass of PVA (g) 0.5 were used in all following experiments.

Another important parameter for an economical design is the dosage of PVA/IL beads. Therefore, the adsorption efficiency and capacity for Hg(II) ions as a function of PVA/IL beads dosage was investigated (Fig. 7(b)). The percentage of adsorption removal steeply increased with the PVA/IL loading up to 1 g L^{-1} . This may be due to the increase in active sites on the adsorbent and thus allowing an easier penetration of the metal ions into the sorption sites.

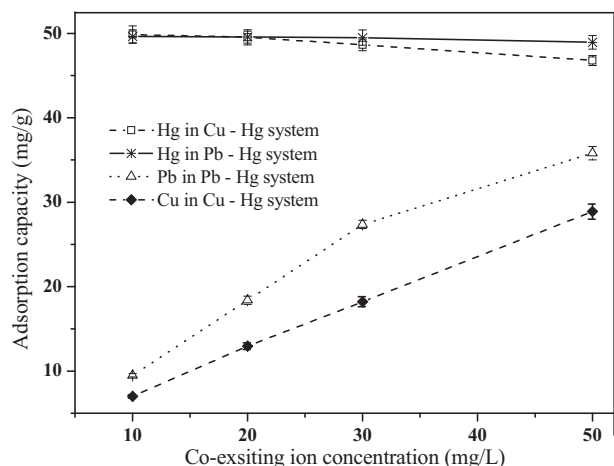


Fig. 8. Selective adsorption of Hg (II) onto the PVA/IL beads in binary system (Pb^{2+} - Hg^{2+} , Cu^{2+} - Hg^{2+}) (initial concentration of metals: $\text{Pb(II)}=10$ – 50 ppm, $\text{Cu(II)}=10$ – 50 ppm, $\text{Hg(II)}=50$ ppm; $\text{pH}=5.78$; PVA/IL dosage = 1 g L^{-1} ; temperature = 298 K , contact time = 24 h).

The maximum adsorptive removal was found to be 99.3% as PVA/IL concentration was 2 g L^{-1} . The percent removal was almost the same at higher dosages of 9.4 and 18.8 g L^{-1} . A further increase in PVA/IL dosage over 1 g L^{-1} did not lead to a significant improvement in adsorptive removal due to the saturation of Hg (II) with active sites of PVA/IL beads. Therefore, the optimal wet PVA/IL dosage was selected as 1 g L^{-1} for further experiments.

3.2.3. Effect of coexisting ions

Adsorption of coexisting metal ions onto the PVA/IL beads was examined in both binary and ternary system. As shown in Fig. 8, generally, the Hg (II) adsorption amount decreased slightly with the increases in the concentration of Pb (II) and Cu (II) varying from 10 to 50 mg L^{-1} . However, absorbed Hg (II) content in the binary system Pb (II)-Hg (II) was higher than that in the system of Hg (II)-Cu (II). Moreover, the adsorption capacity of PVA/IL beads for Pb (II) was higher than that for Cu (II). The same trend can be seen from the ternary system Pb (II)-Hg (II)-Cu (II). The highest adsorption of Hg (II) may be due to [A336][MTBA], which can combine Hg (II) strongly, while higher adsorption of Pb (II) onto PVA/IL beads could be owing to PVA-alginate matrix, which shows a better affinity to Pb (II) than Cu (II) [16]. It may be concluded that the adsorption affinity of metals onto the PVA/IL beads is in the following order: $\text{Hg(II)} > \text{Pb(II)} > \text{Cu(II)}$. As shown in Fig. 9, Hg (II) ions were dominantly adsorbed attaining equilibrium after 20 h . The results were likely due to high adsorption affinity of Hg (II), which led to substitution of already adsorbed metals on the adsorption sites. Rengaraj [17] also reported that favored adsorption of a metal onto the adsorbent can result in desorption of other metals into solution. It was concluded that even higher concentrations of Cu (II) and Pb (II) ions did not affect the efficient removal of Hg (II) dramatically, which is of significance in practical treatment of Hg (II) from aqueous solutions contaminated with other heavy metals such as Pb (II) and Cu (II).

3.3. Kinetics of mercury ions adsorption and effect of contact time

The effect of contact time on the adsorption capacity of the PVA/IL beads was investigated in the time ranges of 5 min – 24 h (Fig. 10). It was observed that initial adsorption of Hg (II) was rapid on the PVA/IL beads. The adsorption sites on the PVA/IL beads were quickly covered by Hg (II) and the adsorption rate became dependent on the rate at which the metal ions were transported from the bulk liquid phase to the actual adsorption sites [18]. Then the adsorption rate slowed down after initial 2 h of contact time. The

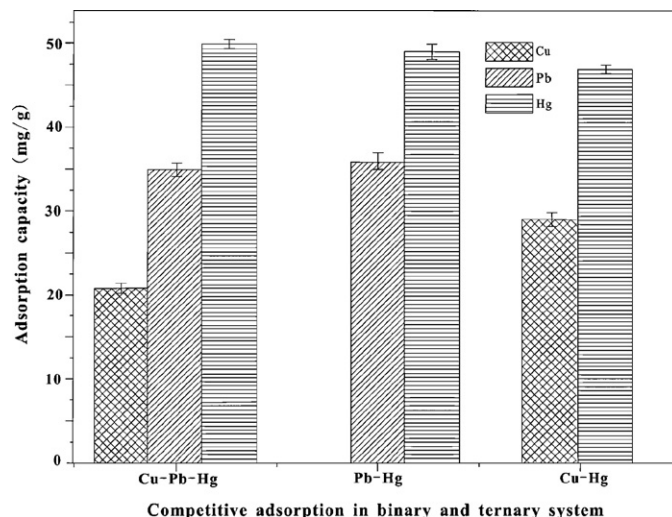


Fig. 9. Competitive adsorption for Cu(II), Pb(II) and Hg(II) on PVA/IL beads in multi-metals solutions (initial concentration of metals: $\text{Hg(II)}=50$ ppm, $\text{Cu(II)}=50$ ppm, $\text{Pb(II)}=50$ ppm; $\text{pH}=5.78$; PVA/ILs dosage = 1 g L^{-1} ; temperature = 298 K , contact time = 24 h).

maximum capacity was $49.89 (\pm 0.11) \text{ mg g}^{-1}$ at around 20 h . Thus the contact time of 24 h was used in the following sections to ensure the adsorption equilibrium.

The kinetics of Hg (II) removal could be explained using pseudo first-order, second-order and Elovich kinetic models to examine the rate controlling mechanisms of the adsorption process.

Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo-first-order equation [19]. The linear form of the pseudo first-order equation is described by Eq. (3):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_{ad}t}{2.303} \quad (3)$$

where Q_e and Q_t are the amounts of Hg (II) adsorbed (mg g^{-1}) at equilibrium time and at any instant of time, t , respectively, and k_{ad} (L min^{-1}) is the rate constant of the pseudo-first-order sorption.

The values of first order rate constants k_{ad} and Q_e for the initial Hg^{2+} concentration of 50 ppm by keeping the adsorbent amount constant (1 g L^{-1}) at 298 K are calculated and listed in Table 1. The coefficient of determination (R^2) is found to be 0.919 and the true value of Q_e obtained from experiment, $49.89 (\pm 0.11) \text{ mg g}^{-1}$, is not

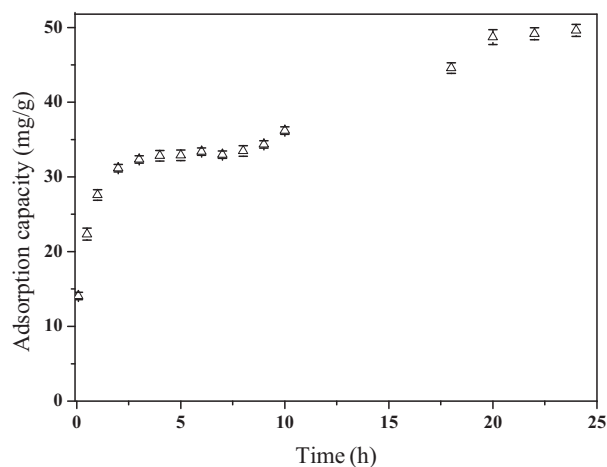


Fig. 10. Effect of contact time on adsorption of Hg (II) onto the PVA/IL beads (Hg^{2+} concentration: 50 mg L^{-1} ; $\text{pH}=5.8$, PVA/ILs dosage = 1 g L^{-1} ; temperature: 298 K , contact time: 24 h ; volume of solution: 100 mL).

Table 1
Comparison of pseudo-first-order, pseudo-second-order and Elovich kinetic model for Hg (II) adsorption by PVA/IL beads.

Kinetic model	Parameters		
Pseudo-first-order	k_{ad} (min^{-1}) 2.303×10^{-3}	$Q_{e1,cal}$ (mg g^{-1}) 43.9	R^2 0.919
Pseudo-second-order	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) 4.82×10^{-4}	$Q_{e2,cal}$ (mg g^{-1}) 50.7	R^2 0.999
Elovich model	α 10.2	β 1.09	R^2 0.988

in agreement with the predicted values as given in Table 1. So the plot of $\log(Q_e - Q_t)$ versus t for the pseudo-first-order adsorption kinetics was not given here.

Ho [20] developed a pseudo-second-order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat, which is described in the following linear form:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{h} \quad (4)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the second-order rate constant, $h = k_2 Q_e^2$ can be regarded as the initial sorption rate as t approaches 0.

The application of the second-order kinetics by plotting t/Q_t versus t as shown in Fig. 11(a) yielded the second-order rate constant, k_2 , Q_e and the coefficient of determination (R^2). As can be seen from Table 1, the calculated Q_e value shows a good agreement with the experimental value and the obtained value for the coefficient of determination (R^2) is more than 0.995, which indicates that the second-order kinetic model describes the removal of Hg^{2+} by PVA/IL beads as solid extractants well.

Elovich equation is a rate equation based on the adsorption capacity describing adsorption on highly heterogeneous adsorbents which is commonly expressed as Eq. (5) [21]:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (5)$$

where α ($\text{mg g}^{-1} \text{min}^{-1}$) is the initial adsorption rate and β (g mg^{-1}) is the desorption constant.

Fig. 11(b) represents the application of the linear form of Elovich kinetic equation. The constants α and β are obtained from the intercept and the slope, respectively. The coefficient of determination (R^2) obtained is 0.9882, which is found to be less than the value calculated using second-order kinetic model as shown in Table 1. Thus it may lead to the conclusion that there were three stages in the adsorption process: an external surface adsorption stage; the gradual adsorption stage where intraparticle diffusion was rate-controlled; the final equilibrium stage where intraparticle diffusion started to slow down due to the extremely low adsorbate concentrations in solution. Overall, these observations suggest that metal sorption by PVA/IL beads followed the second-order reaction indicating that the process controlling the rate may be a chemical sorption and the correlation coefficients of Elovich equation (above 0.98) at pH 5.8 also may confirm the predominant chemical nature of Hg (II) adsorption on PVA/IL beads.

3.4. Adsorption equilibrium isotherms and effect of initial Hg^{2+} concentration

The initial Hg (II) concentration was adjusted in the range of 10–50 mg L^{-1} for Hg (II) adsorption under a pH of 5.8 as shown in Fig. 12. The removal amount of Hg (II) increased rapidly with increase in the Hg (II) concentration. As the mercury ions concentration was higher than 30 mg L^{-1} it became slow. When the Hg (II) concentration was 30 mg L^{-1} , the amount of Hg (II) absorbed

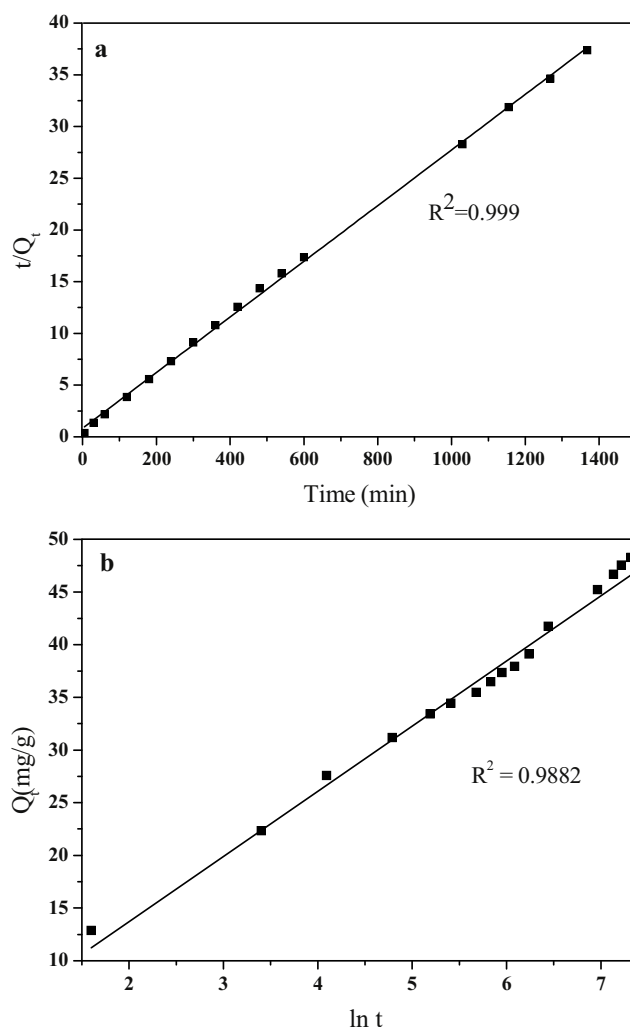


Fig. 11. Pseudo-second-order (a) and Elovich (b) kinetic model plot for the adsorption of Hg^{2+} using PVA/IL beads (pH 5.8, PVA/IL dosage = 1 g L^{-1} , temperature: 298 K, contact time: 24 h).

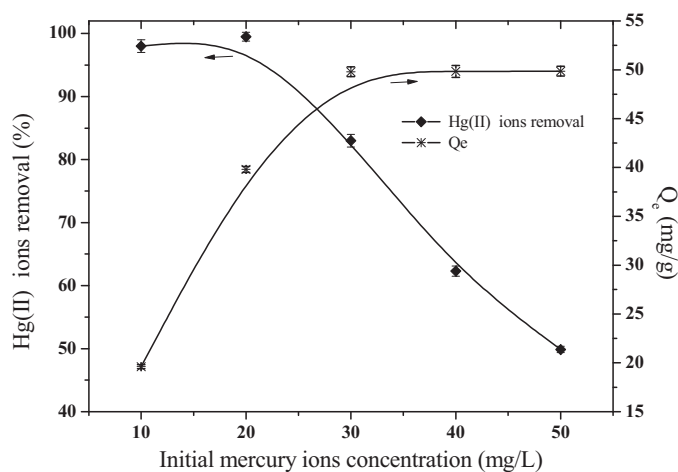


Fig. 12. Effect of initial Hg^{2+} concentration on adsorption of Hg^{2+} using PVA/IL beads (pH 5.8; PVA/ILs dosage = 0.5 g L^{-1} , temperature: 298 K, contact time: 24 h).

by the PVA/IL beads was $49.80 (\pm 0.1) \text{ mg g}^{-1}$ compared with $19.61 (\pm 0.04) \text{ mg g}^{-1}$ when 10 mg L^{-1} while the adsorption effective of Hg (II) kept constant at nearly 100%. At higher concentrations, more Hg (II) was left un-adsorbed in solution due to the saturation of binding sites. The adsorption capacity on the beads in 50 mg L^{-1} Hg (II) solution reached the maximum while the Hg (II) ions removal ($49.88 (\pm 0.06)\%$) is much lower than that in 30 mg L^{-1} ($99.92 (\pm 0.12)\%$). This indicates that PVA/IL beads are effective for being used to treat wastewater with Hg (II) of concentrations lower than 50 mg L^{-1} .

Adsorption isotherms are important to describe the adsorption mechanism for the interaction of Hg^{2+} on the adsorbent surface for the design of an adsorption process.

3.4.1. Langmuir isotherm

Langmuir model has been widely applied to many metal ions sorption process [22]. The model takes the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (6)$$

where Q_m is the quantity of adsorbate on unit mass of adsorbent (mg g^{-1}) and Q_e is the amount adsorbed on unit mass of the adsorbent (mg g^{-1}) when the equilibrium concentration is C_e (mg L^{-1}) and b (L mg^{-1}) is the Langmuir constant. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L , given by Eq. (7):

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

The isotherm data has been linearized using Eq. (6) shown in Fig. 13(a). The Langmuir constant Q_m , 50.17 mg g^{-1} , was close to the experimental data ($49.89 (\pm 0.11) \text{ mg g}^{-1}$) which indicated a good adsorption on the PVA/IL beads. The Q_m of PVA/IL beads was higher than some Q_m values of other sorbents reported by literatures (Table 2). Another constant denoting adsorption energy, b , is found to be 0.0025 L mg^{-1} . The high value of the related coefficient ($R^2 = 0.9998$) obtained indicates a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Hg^{2+} onto PVA/IL beads surface because of the macroporous structure of the PVA/IL beads. The dimensionless parameter R_L , a measure of adsorption favorability, is found in the range of $0.0025\text{--}0.0126$ ($0 < R_L < 1$) when C_0 is varying from 10 to 50 ppm. The results confirm the favorable adsorption process for Hg^{2+} removal using PVA/IL beads, especially when the initial Hg^{2+} concentration is lower than 50 ppm.

3.4.2. Freundlich isotherm

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations [30]. The linear Freundlich isotherm is commonly expressed as follows:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

where K_f ($\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$) and n (g L^{-1}) are the Freundlich constants characteristic of the system.

The Freundlich constants K_f and n are obtained by plotting the graph between $\log Q_e$ versus $\log C_e$. The values of K_f and n are 38.18 and 9.387, respectively. It is found that the coefficient of determination obtained from the Freundlich constants for PVA/IL is 0.892, which is lower than that for Langmuir isotherm model as given in

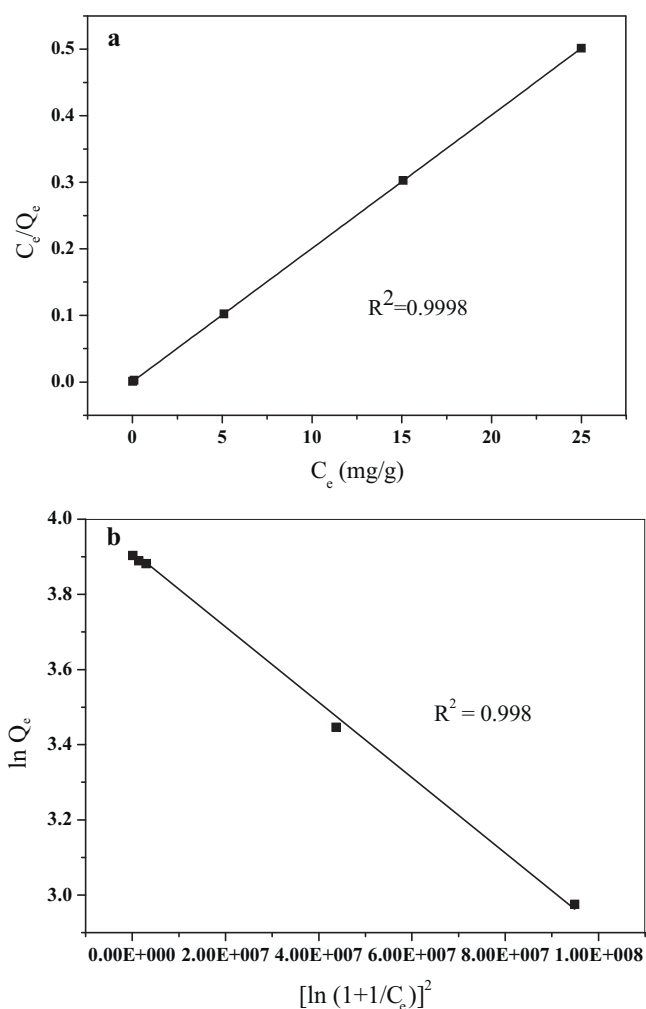


Fig. 13. Isotherm model for the Hg^{2+} adsorption onto PVA/IL beads (a: Langmuir isotherm model, b: Dubinin–Radushkevich isotherm model).

Table 3. The results indicate that the equilibrium data is not fitted well with the Freundlich isotherm model.

3.4.3. Dubinin–Radushkevich (D–R) isotherm

Dubinin and Radushkevich [31] have proposed another isotherm applied to estimate the mean free energy of adsorption (E). D–R equation is represented in a linear form by Eq. (9):

$$\ln Q_e = \ln Q_m - K\varepsilon^2 \quad (9)$$

where K ($\text{mol}^2 \text{ kJ}^{-2}$) is a constant related to mean adsorption energy; and ε is the Polanyi potential, which can be calculated from Eq. (10).

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (10)$$

The sorption energy can also be worked out using the following relationship

$$E = \frac{1}{\sqrt{-2K}} \quad (11)$$

Fig. 13(b) shows the plot $\ln Q_e$ versus ε^2 at 298 K. The constants, Q_m and K obtained are 50.88 mg g^{-1} and $9.67 \times 10^{-4} \text{ mol}^2 \text{ kJ}^{-2}$ respectively. It has been reported [32] that physisorption processes have adsorption energies less than 40 kJ mol^{-1} and relatively high values for the heat of adsorption indicate a strong interaction between sorbate and sorbent. The mean free energy of adsorption,

Table 2
Comparison of Hg (II) sorption capacity of PVA/IL beads with other typical sorbents.

Adsorbent	Operating conditions			Q_m (mg g^{-1})	References
	pH	T (K)	C_0 (mg L^{-1})		
Guava bark	9.0	303	50	3.364	Lohani et al. [23]
Hydrogel sorbents	5.0	293	50	13.46 ± 1.15	Yetimoglu et al. [24]
A cation exchanger	6.0	NA	75	32.9	Anirudhan et al. [25]
Carbonized newsprint fiber	7.0	293	100	48.3	Aoyama et al. [26]
Commercial sulfur-impregnated AC	4.8	298	100	41	Cai et al. [27]
Natural zeolites	8.5	293	NA	57.5	Chojnacki et al. [28]
PEI-attached PHEMA gel beads	5.0	293	NA	335.2	Denizli et al. [29]
PVA/IL ([A336][MTBA]) beads	5.8	298	50	49.89 ± 0.11	In this study

NA: not available.

Table 3
Isotherm constants and regression data for various adsorption isotherms for adsorption of Hg (II) on PVA/IL beads.

Adsorption isotherm	Isotherm parameters		R^2
Langmuir	Q_m	50.17 mg g^{-1}	0.9998
	b	0.0025 L mg^{-1}	
Freundlich	K_f	$38.18 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$	0.892
	n	9.387 g L^{-1}	
Dubinin–Radushkevich	Q_m	50.88 mg g^{-1}	0.998
	$K \times 10^{-4}$	9.67	
	E	$439.94 \text{ kJ mol}^{-1}$	

E , is calculated as $439.94 \text{ kJ mol}^{-1}$ (Table 3) indicating that the sorption process could be chemisorption because of [A336][MTBA] on the surface and inner of PVA/IL. The value of coefficient of determination ($R^2 = 0.998$) indicates that the Dubinin–Radushkevich model fits well with the equilibrium data.

Overall, the experimental data are found to be fitted well with the Langmuir and Dubinin–Radushkevich models, which confirm favorable adsorption process for Hg^{2+} removal using PVA/IL beads. This suggests that it may include both physisorption and chemisorption because of the macroporous structure and [A336][MTBA] on the surface and inner of PVA/IL beads.

4. Conclusions

The present study dealt with the removal of mercury from aqueous solutions using [A336][MTBA]-immobilized on PVA–alginate beads (PVA/IL). The work was primarily based on the principle of modification of the solid sorbents by introducing liquid extractants in inorganic materials to increase the efficiency and environmentally friendly performance. So far, a few research work on this topic has been carried out using alginate, silica and zeolite as supported materials and phosphonium-based ILs as liquid extractants. The use of PVA and [A336][MTBA] with the same purpose has not been investigated. The present study showed that PVA–alginate gel beads could entrap the ionic liquids successfully characterized by FT-IR, EDAX and TGA. It is found that the prepared PVA/IL beads can be used to remove mercury with an efficiency of more than 99% from a 50 mg L^{-1} Hg (II) solution with nearly no leakage of the ionic liquid.

Immobilized [A336][MTBA] samples with an initial [A336][MTBA] volume of 2 ml and 4 g of PVA in a 50 mL alginate solution showed the most economic adsorption for 50 mg L^{-1} of Hg (II) solutions. Experiments to characterize the PVA/IL beads including the effect of pH, the initial Hg (II) ions concentration, PVA/IL beads dosage and the contact time revealed that a pH of 5.8 and an adsorbent dosage of 1 g L^{-1} are the optimum conditions for its operation in batch mode. More than 99% of mercury ions can be removed after 20 h with the maximum adsorption capacity

of $49.89 (\pm 0.11) \text{ mg g}^{-1}$. Modelling of the sorption equilibrium performed well using the Langmuir and Dubinin–Radushkevich equations, which confirm favorable adsorption process for Hg^{2+} removal using PVA/IL beads. This suggests that it may include both physisorption and chemisorption because of the porous structure and [A336][MTBA] on the surface and inner of PVA/IL beads. The pseudo-second-order chemical reaction kinetic provided the best correlation with the experimental data as well. Moreover, the competitive experiments showed that the selectivity of the PVA/IL beads towards Hg (II), Pb (II) and Cu (II) ions was $\text{Hg} > \text{Pb} > \text{Cu}$ and even in the solutions including high concentration of Cu (II) and Pb (II) ions, PVA/IL beads kept almost the same adsorption removal efficiency of Hg (II). Thus, it can be concluded that this alternative solid-phase extractant based on [A336][MTBA] is promising to be exploited for applications in the treatment of Hg (II) polluted water. However, the repeated use of the PVA/IL beads and the column study will be the main work in future.

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