Removal efficiency of Pb(II) from aqueous solution by 1-alkyl-3-methylimidazolium bromide ionic liquid mediated mesoporous silica

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A B S T R A C T

In this research, mesoporous silica was synthesized via modified sol–gel technique using a series of 1-alky-3-methylimidazolium bromide [(C$_n$MIM)Br (n = 4, 10, 16)], one kind of amphiphilic room temperature ionic liquids (RTILs), as a template. Subsequently, the material was characterized and identified by various techniques such as N$_2$ adsorption–desorption isotherm, SEM, TGA and FT-IR analysis. To obtain the optimum condition, different variables such as adsorbent dose, contact time, initial concentration, temperature and pH were studied, and the optimum conditions were found to be 0.7 g/100 mL, 30 min, 10 mg L^{-1}, 40 °C and pH of 6.0, respectively, for the adsorption of lead ions from aqueous solution. The results showed that the RTIL bearing longer alkyl chain 1-hexadecyl-3-methylimidazolium bromide [(C$_{16}$MIM)Br] was a suitable adsorbent for Pb(II) removal among all the adsorbents. The adsorption of lead ions follows pseudo-second-order rate equation, and the equilibrium data fitted well with the Freundlich model with maximum adsorption capacity 5.18 mg g^{-1}. Various thermodynamic parameters were calculated, and the results showed that the adsorption of lead ions on the material was feasible and endothermic in nature. The results from the adsorption–desorption cycles showed that the material held good desorption and reusability. It is concluded from the results that the material can be used to remove the Pb(II) from contaminated water to permissible limit.

Introduction

Heavy metals such as lead, arsenic, cadmium, mercury, etc. pose major environmental problems worldwide because of their toxicity. These metals enter into the food chain by industrial activities and cause serious disorders by attacking several functions of human systems [1–3]. Lead is one of the most common heavy metals used widely in industrial activities such as metal plating, oil refining and battery manufacturing. Drinking water of 10, 10, 15 and 10 ppb of lead is considered to be safe by the World Health Organization (WHO), the European Union (EU), the United States Environmental Protection Agency (USEPA) and Guidelines for Canadian Drinking Water Quality, respectively [4,5]. Hence the removal of Pb(II) ions from the water and waste water is highly paramount in terms of safety of health and environment. To bring Pb(II) to permissible limits, a wide variety of techniques are reported in the literature such as ion exchange, reverse osmosis, nanofiltration, precipitation, selective liquid–liquid extraction, photochemical process, coagulation/co-precipitation and adsorption [6,7]. Among all, adsorption process is one of the most popular methods used because of its ease and low cost for the removal of Pb(II) ions in contaminated water.

Room temperature ionic liquids (RTILs) have gained a lot of interest for their promising role as an alternative media in the synthesis, separation and electro-chemistry as a result of their unique chemical and physical properties such as low vapor pressures, nonvolatility, nonflammability, wide electrochemical windows and higher ionic conductivity [8,9]. Recently, research efforts have intensified on utilization of ionic liquids as green chemical compounds for removal of heavy metals from various aqueous and nonaqueous samples [10]. In these directions, use of RTILs in single drop micro-extraction as well as liquid–liquids extraction techniques of various metal ions has been reported in the literature [11–13]. However, the major disadvantage in using RTILs for removal of metal ions from various matrices is mainly based on finding suitable chelating compounds that can bind metal ions as well as transfer them from their matrices to the ILs medium after the complexation step. These limitations have motivated our attention to establish a new sorbent mediated from the various ILs as a template for removal of heavy metals.

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Mesoporous materials have attracted a great deal of attention of chemists and material scientists with properties such as the presence of large uniform pores, accessible adsorption sites, good thermal and structural stability; and high metal removal efficiency to become an efficient adsorbent for heavy metal ions [14,15]. The synthesis of mesoporous materials depends on a supramolecular templating mechanism with amphiphilic molecules, that is, surfactants work as a structure directing agent. Recently, several researchers have focused on the use of a new class of amphiphiles based ionic liquids (ILs) on their interesting properties of high thermal stability, very low flammability and negligible vapor pressure to produce shape-selective mesostructured materials [16]. For example, Viau et al. synthesized several sets of silica ionogels from imidazolium and pyridinium ILs with typical anions like tetrafluoroborate, hexafluorophosphate, bis(trifluoromethyl-sulfonyl)imide, chloride and acetate, using either water (pure H_2O or acid aqueous solutions) or formic acid (FA) as a reactant with tetraethyl orthosilicate [17]. Li et al. used a series of 1-alky-3-methylimidazolium bromide (C_nMIM)Br (n = 12, 14, 16), a kind of amphiphilic room temperature ionic liquids, as a template via a sol–gel nanocasting technique to prepare mesoporous silica [18]. ILs derived from 1-alkyl-3-methylimidazolium series are of particular interest because, by changing the alkyl chain length or the anion, wide varieties of properties such as hydrophobicity, viscosity, density can be obtained [19]. The long-chain ILs have shown a stronger tendency toward self-aggregation and supramolecular templating in the preparation of porous silica [20–22]. Though highly porous silica materials can be synthesized, which is the highlight of this paper, a systematic study of synthesis of mesoporous silica using various types of ILs with different alkyl chain length and their subsequent use as a potential adsorbent for heavy metal removal has not been reported.

In this paper, we have synthesized the mesoporous silica materials using RTILs having different alkyl chain lengths like 1-butyl-3-methylimidazolium bromide, 1-octyl-3-methylimidazolium bromide and 1-hexadecyl-3-methyl-imidazolium bromide as templates. The silica materials were characterized by SEM, FT-IR, TGA and N_2 adsorption–desorption measurements. The objective of the work is to find the preferred RTIL among all the above ILs for the synthesis of silica materials which could show higher removal efficiency for Pb(II) ions from water solution.

Materials and methods

Chemicals

1-Methylimidazole, 1-bromobutane, 1-bromooctane, 1-bromo-hexadecane were purchased from Sigma–Aldrich. Sodium hydroxide, lead nitrate and hydrochloric acid were purchased from HiMedia. A stock solution of Pb(II) was prepared by dissolving 1.598 g of lead nitrate in 1 L de-ionized water. The required concentration of lead solution was prepared by proper dilution of the stock solutions. The pH of the solution was maintained by the addition of required amount of 0.1 M HCl and 0.1 M NaOH.

Adsorbent preparation

Synthesis of mesoporous silica

1-Butyl-3-methylimidazolium bromide, 1-octyl-3-methylimidazolium bromide and 1-hexadecyl-3-methylimidazolium bromide were synthesized according to the literature and further used for synthesizing porous silica [19,23,24]. The ionic liquid was dissolved under stirring with formic acid (FA) at room temperature for 10 min before adding TEOS (molar ratio: 1 TEOS/0.5 IL/7.8 FA). The resulting solution was stirred for additional 10 min at room temperature. Syntheses were performed by using 6.72 mmol of

silica. The final products were then dried in oven at 100 °C and finally calcined at 550 °C for 6 h to get rid of ionic liquids.

Characterization of the mesoporous silica

The surface morphology of materials was investigated using scanning electron microscope (SEM), and qualitative element composition was analyzed using energy dispersive X-ray (EDX) operated at an accelerating voltage of 20 keV (JOEL model JSM-6480LV (Japan)). The surface area was calculated by using the BET (Brunauer–Emmet–Teller) equation in QUANTACHROME AUTO-SORB (IQ) model ASIQM0000-4. The pore size distribution and pore volume were obtained by applying the BJH (Barrett–Joyner–Halenda) method. The samples were degassed in vacuum at 150 °C. Helium was used as a carrier gas, and surface area was measured by N_2 adsorption–desorption method. Thermogravimetric (TG) analysis was carried out using NETZSCH STA 449C, Germany. FT-IR spectra of the samples were obtained by using PerkinElmer FT-IR Spectrometer Spectrum RX-I. The spectrum was scanned from 4000 to 400 cm^{-1}. After adsorption the concentration of the Pb(II) in the filtrate was determined by using atomic absorption spectrometer (AAS, VARIAN, AA240) using standard method.

Adsorption experiments

In order to know the Pb(II) removal ability of mesoporous materials, a set of adsorption experiments were performed by shaking a fixed amount of mesoporous silica in 100 mL of 10 mg L^{-1} Pb(II) solution in Polylab plastic bottles at 250 rpm using a temperature-controlled water bath with shaker. The pH of the solution to the desired value for these experiments was adjusted by the addition of required 0.1 M HCl/0.1 M NaOH solution. A number of experimental parameters such as adsorbent dose (0.1–1 g), contact time (10–60 min), initial concentration of adsorbate (10–100 mg L^{-1}), pH (2–12) and temperature (10–60 °C) were studied to investigate the removal process. After the predetermined period, the adsorbent solution mixture was filtered through Whatman-42 filter paper to obtain the filtrate and that was used for the analysis of Pb(II) ion concentration in the solution. The percentage of metal removal (R%) was calculated as follows:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 and C_e are the initial and final concentrations of Pb(II) in the aqueous solutions, respectively.

Desorption experiment

After the adsorption of lead ions on mesoporous silica, the adsorbent was regenerated with 0.1 M HCl and then washed with distilled water. The regenerated adsorbent was reused, and adsorption experiment was carried out for five consecutive cycles.

Results and discussion

As reported in literature, the long-chain ILs displayed significantly stronger tendency toward self-aggregation and supramolecular templating in the preparation of porous silica [25]. The porosity and surface morphology can be controlled by changing the alkyl chain lengths. Keeping this in mind, we synthesized various 1-alkyl-3-methylimidazolium based ionic liquids with different chain lengths (C_nMIM)Br (n = 4, 10, 16). These materials were studied for Pb(II) removal from water solutions. The adsorption capacities for Pb(II) by those materials are represented in Table 1. From Table 1 it can be confirmed that the mesoporous silica prepared via modified sol–gel route using 1-hexadecy-3-