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Polybenzimidazole hybrid membranes as a selective adsorbent of mercury

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ABSTRACT

Polybenzimidazole hybrid membranes (H1–H3) were prepared by incorporating different amounts (wt.%) of inorganic hetero poly acids (IHA-Si) into polybenzimidazole (PBI) matrix. Structural, morphological and thermal characteristics of all the hybrid membranes were studied by FT-IR, XRD, SEM and TGA and further investigated functional relationships between the materials structure and metal ion uptake using Hg(II), Pb(II), Y(III), and Cd(II). It was found that H3 was most selective toward Hg(II) as compared to H1 and H2 and further uptake capacity of H1–H3 was strongly dependent on mesoporous silica. The hybrid membranes with high mesoporous silica (H3) exhibited high thermal stability and high uptake capacity toward Hg(II) which was experimentally determined to be 2.48 mg g^{-1}. Desorption study for the regeneration of adsorbent was also achieved using ethylenediaminetetraacetic acid solution. Ultimately, the proposed method provided reasonable results for the determination of Hg(II) in environmental water samples.

1. Introduction

Living organism life is incomplete without water because water is needed for every cell of the organism to perform its normal function. Water is life and essential for human endurance and industrial progress. However, pollution has reduced the vitality of water in hydrosphere [1]. Water pollution is objectionable revolution in the state of water. The water sources are being incessantly spoiled worldwide by assortment of health perilous wastes. Metal ions are one of the pollutants which repeatedly liberate by different industries and instigate water pollution [2]. Therefore, introduction of easy, fast and competent method has attracted global attention for scrutinizing metal ions in the state of water.

Different analytical techniques such as atomic absorption spectrometry [3], inductively coupled plasma – optical emission spectrometry (ICP–OES) [4], anodic stripping voltammetry [5], and ion chromatography [6] have been implemented for observation and quantification of metal ions in aqueous media. However, low sensitivity and selectivity of these analytical techniques restrict them to measure metal ions at ultra trace level. Thus, a competent separation method is frequently mandatory prior to precise and interference-free measurement of metal ions [12]. Preconcentration of metal ions [7–11], liquid–liquid extraction [13], ion exchange [14], coprecipitation [15], cloud point extraction [16] and solid phase extraction (SPE) [17,18] have been utilized for the removal of metal ion. Except SPE, all other methods lost their importance due to cost, time and solvent consumption. SPE is thought-out to be the most accepted technique since its low cost, low solvent usage and less time consumption. The selectivity and sensitivity of adsorbent play important role in SPE and variety of adsorbents like alumina, C18, molecular imprinted polymers, cellulose, silica gel, activated carbon and carbon nanotubes have been used so far in effort to get adsorbent with high selectivity and up take capacity [19–25]. However the uptake capacities of all these phases for selective uptake of analytes are still not high enough. Therefore, there is still lack of adsorbents with more selectivity and high uptake capacity.

During the search of new material for high metal ion uptake, composites were found to be most promising candidate for metal ion adsorption because of its simple preparation, easy handle and low cost and excellent properties [26–29]. Nanocomposites have played efficient role in advanced applications due to their novel assets which are significantly unusual from corresponding bulk substances. Composites also presented excellent thermal, mechanical and so many other properties [30–32]. Inorganic materials have improved bio-properties, water permeability and anti-water

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absorption properties [33–35]. One of the inorganic materials is silicotungstic acid which enhances thermal, mechanical and proton conductivity of polymer [36].

In this study, PBI and H1–H3 were synthesized and characterized structurally by different characterization techniques. H1–H3 were found thermally more stable than PBI which were evaluated by TGA. In accordance, this investigation was intended to assess the utility and the analytical potential of PBI and H1–H3 on the selectivity extraction of Hg(II), Pb(II), Y(III), and Cd(II). Data obtained from the selectivity study, displayed that H3 was most selective toward Hg(II) as compared to H1 and H2. Desorption study for the reusability of H3 adsorbent was carried out using ethylenediaminetetraacetic acid solution. Finally, the newly applied method gave satisfactory results for the determination of Hg(II) in environmental water samples.

2. Experimental

2.1. Chemicals and reagents

Mercuric nitrate and yttrium nitrate were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Stock standard solutions of 1000 mg L^{-1} Cd(II) and Pb(II) were also obtained from Sigma–Aldrich. Ethylenediaminetetraacetic acid (EDTA) was purchased from Sigma–Aldrich and used as received for desorption study. Double distilled deionized water was used throughout the experiment while all reagents were used as received from Sigma Aldrich.

2.2. Synthesis of PBI and H1–H3

PBI was prepared by similar procedure published elsewhere [36]. Simply 3,3-diaminobenzidine and pyridine-2,5-dicarboxylic acid were treated in the presence of PPA and stirred at 220 °C with nitrogen flow. After one day, the resulting materials were neutralized by KOH (1 mol L^{-1}) and washed several times by H_2O and dried in vacuum oven. Hetero poly acids (HPA) composed of STA and TEOS/SiO_2 were synthesized by simple sol–gel process [36]. The hybrid membranes containing different amount of HPA and PBI were synthesized by simple stirring and made films by spin coating. The composition of hybrid membranes is given in Table 1.

2.3. Adsorption method procedure

Stock solutions of Hg(II), Pb(II), Y(III), and Cd(II) were prepared in 18.2 MΩ cm distilled deionized water and stored in the dark at 4 °C. For studying the selectivity of PBI and H1–H3 toward metal ions, standard solutions of 2 mg L^{-1} of each metal ion were prepared and adjusted to pH value of 5.0 with a buffered aqueous solution (0.1 mol L^{-1} CH_3COOH/CH_3COONa). Each standard solution was individually mixed with 5 mg PBI and H1–H3. For investigation of Hg(II) uptake capacity, standard solutions of 0, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 mg L^{-1} were prepared as above, adjusted to pH value of 5.0 and individually mixed with 5 mg PBI and H1–H3. The pH value of 5 was chosen as the optimal pH because the highest % extraction and selectivity of H3 toward Hg(II) was observed at this specified pH value. All mixtures were mechanically shaken for 1 h at room temperature (Scheme 1).

Table 1
Composition of H1–H3 membranes.

Sample	wt.% (HPA)	wt.% (STA)	wt.% (Si)	wt.% (PBI)
H-1	35	16.5	18.5	65
H-2	50	22.5	27.5	50
H-3	65	28.5	36.5	35

2.4. Desorption method procedure

The reversibility of adsorption of 5 mg H3 for Hg(II) was evaluated by desorption study at different concentrations (1 and 3 mg L^{-1}) of Hg(II). In this study, the saturated H3 with Hg(II) was removed from the solution and transferred to 25 mL of (1–3 × 10^{-3} mol L^{-1}) EDTA solution once equilibrium was reached. The mixture was mechanically shaken for 2 h at 150 rpm and room temperature using a mechanical shaker. The H3 adsorbent was then removed by centrifugation, and the concentration of Hg(II) in the aqueous solution was determined by ICP–OES.

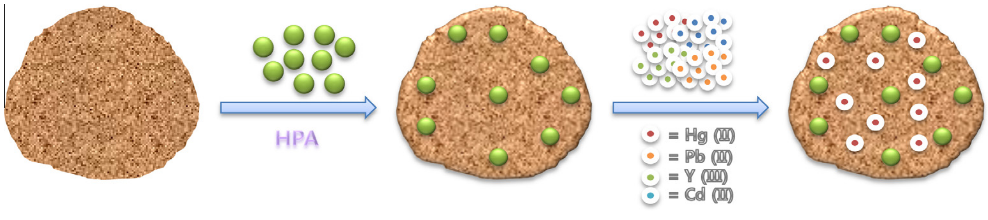
2.5. Characterization and apparatus

PBI and H1–H3 membranes were characterized using various spectroscopic techniques while thermal properties were studied by TGA using Q50 (TA instrument) [26]. ICP–OES measurements were acquired by use of a Perkin Elmer ICP–OES model Optima 4100 DV, USA. The ICP–OES instrument was optimized daily before measurement and operated as recommended by the manufacturers. The ICP–OES spectrometer was used with following parameters: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 L min^{-1}; auxiliary gas (Ar) flow, 0.2 L min^{-1}; nebulizer gas (Ar) flow, 0.8 L min^{-1}; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.5 mL min^{-1}; integration time, 3 s; replicates, 3; wavelength range of monochromator 165–460 nm. Selected metal ions were measured at wavelengths of 194.17 nm for Hg(II), 220.35 nm for Pb(II), 371.03 nm for Y(III) and 228.80 nm for Cd(II).

3. Results and discussion

3.1. Structural characterization

Hybrid membranes were structurally characterized by FT-IR and the data is shown in Fig. 1a. FT-IR spectra of all hybrid membranes displayed peaks of both PBI and HPA which is the indication of effective synthesis of hybrid membranes. H1–H3 exhibited absorption bands at 698, 772, 808, 852, 946, 1043 cm^{-1} which comes from HPA exist in hybrid membranes. These peaks are accountable for W—O, W—O—W bonds, Si—O and Si—O—Si bonds [36,37]. FT-IR spectra of hybrid membranes also exhibited all PBI



Scheme 1. Schematic view of hybrid membranes preparation and metal uptake mechanism.