

Short Communication

Development of Composite Membranes as Selective Adsorbent for Yttrium Ion

Jin-Woo Lee¹, Sher Bahadar Khan^{2,3,*}, Hadi M. Marwani^{2,3}, Kalsoom Akhtar⁴, Abdullah M. Asiri^{2,3}, Muhammad Tariq Saeed Chani², Jongchul Seo⁵, Haksoo Han^{1,*}

¹Department of Chemical and Biomolecular Engineering, Yonsei University, 262 Seongsanno, Seodaemun-gu, Seoul 120-749, South Korea

²Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia

³Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia

⁴Division of Nano Sciences and Department of Chemistry, Ewha Womans University, Seoul 120-750, South Korea

⁵Department of Packaging, Yonsei University, Wonju-si, Kangwondo 220-710, Korea

*E-mail: sbkhan@kau.edu.sa; hshan@yonsei.ac.kr

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Polybenzimidazole based composite membranes (65 TSAD, 50 TSAD and 35 TSAD) were prepared by incorporating different amounts (wt %) of inorganic hetero poly acids (IHAD) into polybenzimidazole (PBI) matrix. IHAD was synthesized by reacting silicotungstic acid with tetraethyl orthosilicate (TEOS) in the presence of acid. Structural, morphological and thermal characteristics of all the composite 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 composite membranes were more selective toward Y(III), and further uptake capacity of composite membranes is highly reliant on the amount of IHAD contents. The composite membrane containing high IHAD contents (35 TSAD) exhibited high thermal stability and high uptake capacity toward Y(III), which was experimentally determined to be 2.48 mgg⁻¹.

Keywords: Polybenzimidazole; Hybrid membranes; Metal ion uptake; Yttrium ion; Environmental applications

1. INTRODUCTION

Human life and industrial progress is highly reliant on water and water is the elementary requisite for both human and industrial survival but maximum part of water in hydrosphere is dirty and

salty [1,2]. Various polluted wastes are regularly releasing to the different source of water and thus spoil rivers and seas all over the world [3,4]. Construction industries are continuously releasing different pollutants especially metal ions which are responsible for messiness of water [5,6]. For the safety of human life and industrial evolution, monitoring of water is much more concerned and for this purpose development of effective, well-organized, simple and fast approach is instantly desirable in order to control metal ions in the environment.

Different analytical methods have been implemented to estimate the concentration level of metal ions in aqueous media [7,8], but they lost their importance because these methods can not measure metal ions at ultra-trace concentration in aqueous systems. Therefore, a talented separation step is often essential in order to determine metal ions in aqueous systems [5-7]. Solid phase extraction (SPE) is known as one of the utmost widespread techniques because it reduces solvent usage and exposure, disposal costs, and extraction time for sample preparation. Several adsorbent have been used for selective extraction of analytes [6-8].

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. Composites also presented excellent thermal, mechanical and so many other properties [9-14]. The addition of inorganic support material to the polymer matrix is also one of the methods to increase the stability and metal adsorption of polymers [7,8]. One of the inorganic material is silicotungstic acid which is highly conductive material in the crystalline form with the structure of $H_4[W_{12}SiO_{40}].nH_2O$ [15]. Inorganic materials have improved various properties of polymers, such as, thermal, mechanical and proton conductivity [16-19].

In this study, PBI was prepared by simple polymerization reaction and composite membranes were synthesized by doping with different amount of IHAD. Both PBI and composite membranes were characterized by Fourier transform infrared spectroscopy whereas the morphologies were confirmed via X-ray diffraction. Composite membranes showed high thermal stability as compared to PBI which were confirmed by TGA. Further, we explored the utility and analytical potential of composite membrane phases on the selectivity and adsorption capacity of Hg(II), Pb(II), Y(III), and Cd(II) prior to their determination by ICP-OES. The selectivity of composite membranes toward different metal ions was investigated in order to explore the effectiveness of PBI and composite membranes on the extraction of selected metal ions. Data obtained from the selectivity study, displayed that composite membrane phases were most selective toward Y(III).

2. EXPERIMENTAL

2.1. Chemicals and reagents

$H_4[SiW_{12}O_{40}].nH_2O$, 99.99% purity TEOS from Sigma Aldrich were used as received. Mercuric nitrate $[Hg(NO_3)_2]$ and yttrium nitrate $[Y(NO_3)_3]$ were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Stock standard solutions of 1000 mgL^{-1} Pb(II) and Cd(II) were also obtained

from Sigma-Aldrich. All reagents used were of high purity and of spectral purity grade. Doubly distilled deionized water was used throughout the experiments.

2.1.1. Synthesis of 2,5-Polybenzimidazole

PBI was synthesized by simple polymerization process in the presence of polyphosphoric acid using 3,3-diaminobenzidine and pyridine-2,5-dicarboxylic acid as a reactants. Both the reactants were mixed in a round-bottom flask and stirred in the presence of polyphosphoric acid until homogeneity was reached. The temperature of the mixture was raised up to 220 °C in the presence of nitrogen. The product was transferred into de-ionized water and neutralized using KOH (1mol/L) after stirring for about 30 hours at 220 °C. The product is washed and dried at 120 °C for 24 hours. The complete procedure was described in previous report [15].

2.2. Preparation of inorganic heteropoly acid materials

Inorganic heteropoly acid (IHAD), composed of silicotungstic acid and TEOS 65:35 (IHAD), was synthesized by treating silicotungstic acid with TEOS/silica. For IHAD, the essential quantity of TEOS was spread in ethanol and added 8 wt% of HNO₃. Silicotungstic acid was then added dropped wise into the mixture with continuous stirring. The mixture solution was titrated with 1N NaOH solution and stirred for three hours until suspension was formed. The product was dried and ground to get fine powder. The fine powders were further dried at 100 °C for 24 hours.

2.3. Preparation of composite membranes

For the synthesis of composite membranes, PBI was first dissolved in methane-sulfonic acid and then added different wt % of IHAD (35, 50 and 60 wt%) into PBI solution. The mixture was stirred day and night and then casted by spin coater on a flat glass. Films of 50~80 µm thickness were obtained after drying. Composite membranes containing 65, 50, 35 wt% of PBI and 35, 50, 65 wt% of IHAD are noted as 65 TSAD, 50 TSAD and 35 TSAD, respectively.

2.5. Characterization of silica composite materials and membranes.

PBI and composite membranes were characterized using various spectroscopic techniques while thermal properties were studied by TGA using Q50 (TA instrument) [15].

2.5.1. FT-IR Analysis

FT-IR analysis was performed for both the samples of inorganic heteropoly acid and composite membranes. Tested samples were located on the test table with KBr dispersion IR radiation reflection with Varian resolution Pro in the wave number range of 500 to 4000cm⁻¹.

2.5.2. Thermal Gravimetric Analysis (TGA)

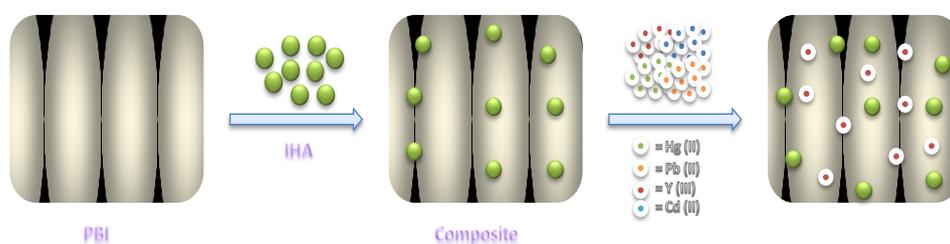
Thermal gravimetric analysis was performed in the temperature range of 30 to 700 °C using Q50 (TA instrument) in nitrogen atmosphere with the scanning rate of 20 °C/min.

2.5.3. X-ray Diffraction Analysis (XRD)

X-ray diffraction analysis was performed with a Philips X-Pert diffractometer using a Cu-K α radiation.

2.6. Metal ion uptake experiment

The preparation of stock solutions of Hg(II), Pb(II), Y(III), and Cd(II) and their uptake experiments were carried out in a similar fashion as we published earlier [1,2]. For evaluating the selectivity of PBI and composite membranes toward metal ions, standard solutions of 2 mgL⁻¹ of each metal ion were prepared, adjusted to pH value of 5.0 with 0.1 molL⁻¹ CH₃COOH/CH₃COONa and individually mixed with 5 mg PBI and composite membranes. For investigation of Y(III) uptake capacity, standard solutions of 0, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 mgL⁻¹ [Y(III)] were prepared, adjusted to pH 5.0 and individually mixed with 5 mg PBI and composite membranes. All mixtures were mechanically shaken for 1 h at room temperature. 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) (Scheme 1).



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

3. RESULTS AND DISCUSSION

3.1. Structural Characterization

All the composite membranes were structurally characterized by FT-IR. FT-IR spectrum of 2,5-polybenzimidazole exhibited a band at 3410 cm⁻¹ which is specified for N-H stretching. It also

displayed a band at 1643 cm^{-1} which is owing to C=C bond stretching. Similarly, it exhibited stretching band for C-C bond (1070 cm^{-1}), C-N (1306 cm^{-1}) and C=N band (1606 cm^{-1}). All composite membranes showed similar peaks showing absorption bands at 692, 816, 1089 which are owing to W-O, W-O-W, Si-O and Si-O-Si stretching, respectively, indicating that composites were successfully synthesized [15]. All composites showed similar spectrum trend. Therefore, for comparison with PBI, we have only shown 50 TSAD in Fig. 1.

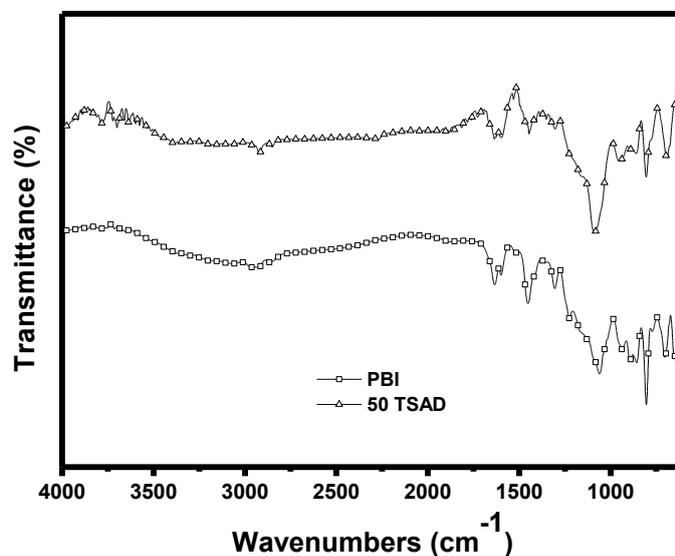


Figure 1. Typical FT-IR spectrum of PBI and 50 TSAD.

3.2. Morphological characterization

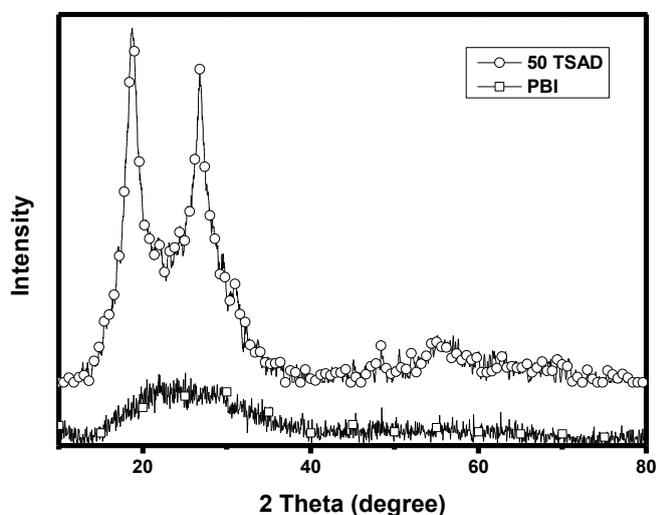


Figure 2. Typical XRD spectrum of PBI and 50 TSAD.

XRD pattern of all composite membranes exhibited semi-crystalline peaks which demonstrate that synthesized composite membranes are semi-crystalline in nature [15-18]. XRD spectrum of 2,5-polybenzimidazole membrane exhibit amorphous peak. After composition with IHAD, the XRD spectrum showed semi-crystalline peaks, providing that the IHAD were homogeneously dispersed in the 2,5-polybenzimidazole membrane lacking agglomeration or aggregation. All composites showed similar pattern. Therefore, we have shown only 50 TSAD in Fig. 2 for comparison with PBI.

3.3. Thermal Properties.

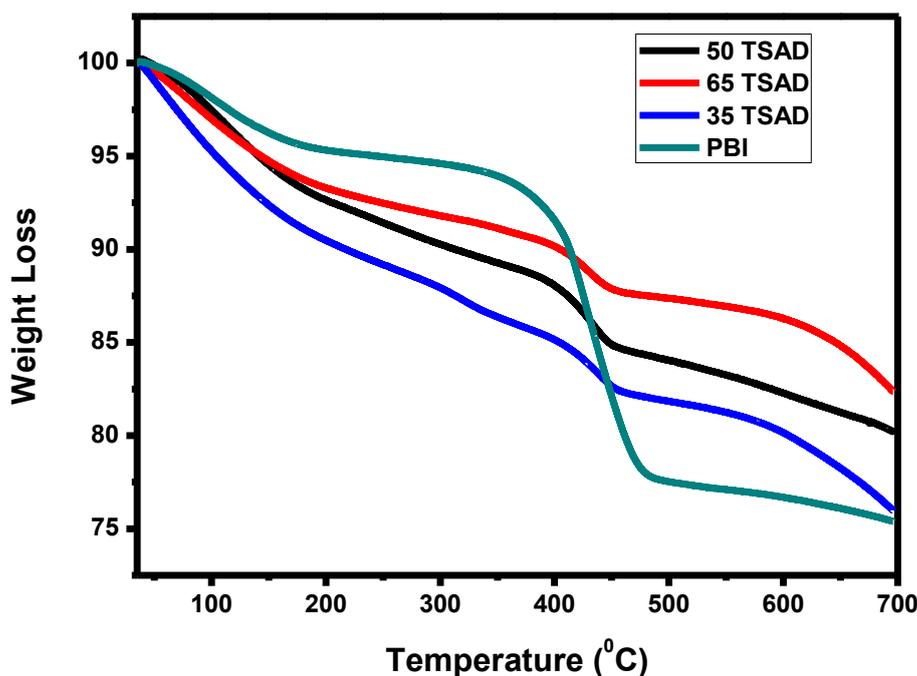


Figure 3. Typical TGA curves of PBI and composite membranes.

The influence of IHAD on the thermal stability of PBI membrane was examined under nitrogen atmosphere, and the TGA graphs are depicted in Fig. 3. The initial weight loss in the TGA data of PBI around 100 °C is due to removal of water, other solvent or any monomer residue [9-15]. The second decomposition around 400 °C is the main decay of the polymer backbone. The composite membranes also show initial weight loss which is higher percent loss than PBI. However, the second weight lost percentage is lower than PBI but occurred at higher temperature as compared to PBI. Comparing the TGA curves of composites with PBI, composite membranes showed less thermal degradation which reflects the importance of IHAD addition on the thermal stability of the PBI matrix. Further comparing different composites, 35 TSAD showed high thermal stability because of the higher content of IHAD present in the 35 TSAD. Comparing thermal properties of composite membranes, higher the content of inorganic heteropoly acid precursors resulted in higher thermal stabilities of the organic matrix.

3.4. Metal ion uptake

3.3.1. Selectivity study of PBI and composite membranes

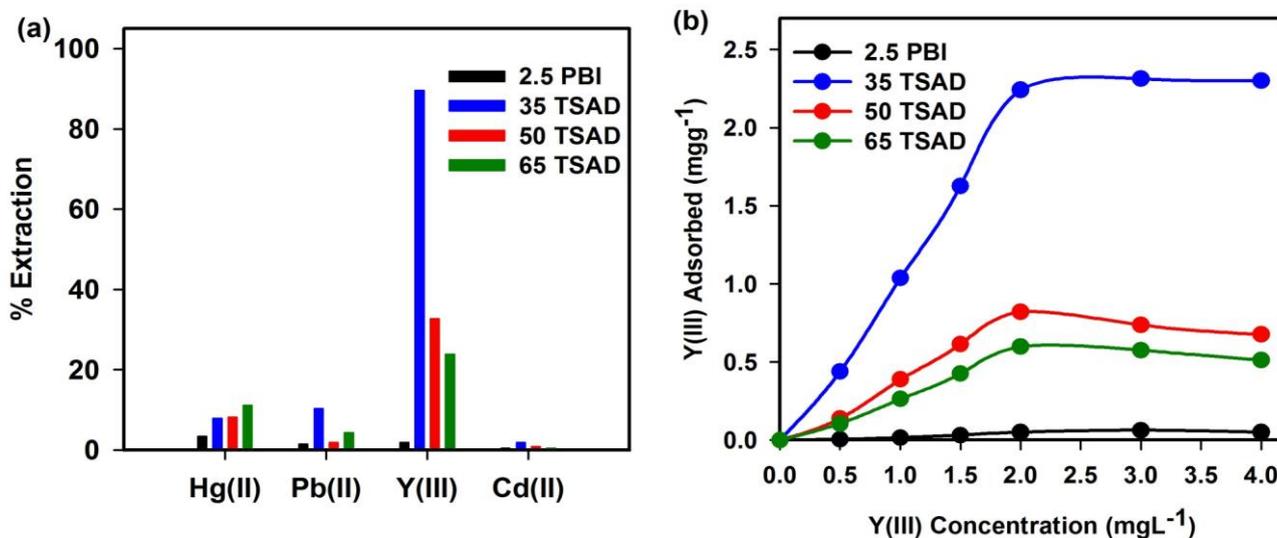


Figure 4. (a) % Extraction of different metal ions on PBI and composite membranes and (b) Adsorption profile of Y(III) on 5 mg of PBI and composite membranes in relation to the concentration at pH 5.0 and 25 °C.

The selectivity of PBI and composite membranes toward Hg(II), Pb(II), Y(III), and Cd(II) were evaluated under batch adsorption method. The percentage extraction of each metal ion was calculated based on a difference between the initial (C_o) and equilibrium (C_e) concentrations (mgL^{-1}) before and after filtration with PBI and composite membranes, respectively, as follows [5-7]:

$$\% \text{Extraction} = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

It can be clearly observed from Fig. 4a that the % extraction of composite membranes is highest for Y(III) among other selected metal ions.

3.3.2. Static adsorption capacity

For estimation of the Y(III) uptake capacities PBI and composite membranes, 25 mL sample solutions of Y(III) with different concentrations ($0\text{-}4 \text{ mgL}^{-1}$) were adjusted to pH 5.0 and individually mixed with 5 mg of PBI and composite membranes. These mixtures were mechanically shaken for 1 h at room temperature [6-8]. The static adsorption capacity was calculated using equation 2 as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where q_e denotes the adsorbed metal ion by PBI and composite membranes (mgg^{-1}), V represents the volume (L) and m refers to the weight of PBI and composite membranes (g). Fig. 4b

illustrates adsorption profiles of Y(III) on PBI and composite membranes obtained from the experiment of adsorption isotherm. The highest adsorption capacity was found for 35 TSAD, which is experimentally estimated to be 2.31 mgg^{-1} .

4. CONCLUSIONS

2,5-Polybenzimidazole and its composite membranes were synthesized and tested for selective metal ion adsorption. 2,5-polybenzimidazole was synthesized by polymerization of 3,3-diaminobenzidine and pyridine-2,5-dicarboxylic acid while their composites were synthesized by hybridization with varied weight percentage of inorganic heteropoly acid. 2,5-polybenzimidazole and composite membranes were characterized by FT-IR and XRD. Composite membranes showed high thermal behavior as compared to PBI. PBI and composite membranes were effectively applied for selective adsorption and determination of Y(III) in aqueous solution. 35 TSAD showed highest adsorption capacity for Y(III) which was found to be 2.31 mgg^{-1} . Finally, it has been concluded that composite membranes may open new aspects for a selective adsorption and determination of Y(III) in complex matrices.

ACKNOWLEDGEMENT

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