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Transport of inorganic acids through polybenzimidazole (PBI) based membranes by chemo-dialysis

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ABSTRACT

A process of chemo-dialysis involving poly(benzimidazole) (PBI) as a chemically active membrane material is proposed for the transport of inorganic acids. These membranes possessing basic nature selectively bind acid molecules present in the feed solution due to acid-base interactions. They are transported across the membrane by concentration gradient as the driving force. The transported acid molecules are stripped away from other side of the membrane surface by a suitable stripping agent or water. Effects of nature of feed acid (pK_a, molecular size), its concentration in the feed solution and the nature of stripping agent (base or water) on acid transport properties are presented. Membranes showed appreciable transport rates for three acids, viz., H_2SO_4, HCl and HNO_3. The fluxes for different acids varied from 16.1 to 140.7 g/m^2 h under different operating conditions. Most significantly, there was no transport of non-acidic solutes such as NaCl or glucose. This could be made possible since these solutes neither get sorbed in the membrane matrix, nor does the membrane exhibit any porosity for the transport to occur through pores. This resulted in practically infinite selectivity of transported acid over the non-acidic solutes. Use of water as the stripping agent allows recycling of the acid, making the process economically attractive. Moreover, possible recovery of acid and its reuse eliminated the requirement of acid neutralization and disposal; which is a routine practice followed today. Thus, this process of chemo-dialysis is economically attractive and environmentally benign.

Keywords: Acid transport; Membrane; Polybenzimidazole; Chemo-dialysis; Inorganic acids; Chemical interaction

1. Introduction

Inorganic acids are widely used in various chemical processes such as steel and metal surface treatment, metal refining, electronics, glass industry, pigments, fine chemicals, etc. [1]. The spent liquor from these processing contains acid and other metallic or organic impurities and represents a major environmental concern. As an example; steel pickling liquor contains varying amounts of Co, Ni, Fe, HCl, H_2SO_4, HNO_3 and HF; while etching waste liquor of semiconductors contains Al, Fe, Na, HNO_3, H_3PO_4 and acetic acid [2,3]. Stringent environmental legislations on the discharge of industrial effluent are being forced worldwide, which makes the acid containing effluent treatment as an important step before its discharge [4]. A neutralization-precipitation-discharge sequence is most frequently used, which poses environmental consequences related to the accumulation of toxic solid wastes.

In view of large amount of acid usage and economical benefits offered by acid recycling, (e.g., ~40% cost

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saving by acid recycling in galvanizing plant); its recovery from effluent is justified to address economical and environmental concerns [5,6].

Membrane processes based on physical separation offer several advantages such as operational simplicity, compact nature, easy scale up, no need for chemical treatment, etc. Though different membrane based techniques are demonstrated for the acid separation (e.g., electrodialysis (ED) [5], reverse osmosis (RO) and nanofiltration (NF)); they have multiple drawbacks such as high power consumption, transport of by-product salt, low process economy, regeneration of ion-exchange resins, cleaning of dialyzer, membrane fouling and thus necessity of its cleaning, etc. [1,5,7]. Though perstraction using liquid membranes for the separation of HNO_3 and organic acids is reported, it suffers from low membrane stability [7–9]. Diffusion dialysis (DD) using anion exchange membrane (AEM) provides an attractive tool for acid recovery because of energy demand only for liquids pumping, reducing operational cost, operation under common pressure without changing the state [1,10]. Various membranes are reported for the separation of organic as well as inorganic acids, viz., Neosepta, polysulfonated SB–6407, Nafion and Flemion, perfluorinated membranes (PTFE-FEP) and aminated poly(2,6-dimethyl–1,4-phenylene oxide) (PPO) [11–15]. The operation is known to be effective only at high acid and low salt concentrations, as the acid transport rate is affected by the presence of salt molecules in the feed solution and is accompanied by co-transport of salt, which is a major draw-back [10,14–17].

Neosepta is a composite membrane containing quaternary ammonium salts (anion exchange sites) and a porous PVC cloth as the reinforcing support [18]. Quaternary ammonium salts are also present in other AEMs, viz., PTFE-FEP, aminated PPO, SB-6407, etc. Nafion contains $–SO_3H$ groups, while Flemion contains perfluorocarboxylic groups [12–15].

All these membranes rely on the presence of either quaternary ammonium or acidic ($–SO_3H$ or –COOH) group as a functionality responsible for the acid transport, though they have different polymer backbone, membrane symmetry (asymmetric, composites) or porosity (porous or nonporous). To our knowledge, acid transport through basic membranes possessing free amine functionality is not reported in the literature, though a strong binding of acid with basic amine containing sorbents (small organics or polymer) is known [7,19,20]. A crucial application of polybenzimidazole (PBI) as a proton exchange membrane in fuel cell works only when PBI is highly doped with H_3PO_4. It is reported that acid doped PBI membranes looses acid by leaching during PEMFC shutdown and cold start operations or in contact with water [19]. It is also known that while in contact with water, major quantity of doped acid leaches out through the membrane within less than 10 min [21]. Intuitively it was thought that combination of these two phenomena (high acid sorption and its fast release/leaching) could be effectively used for the transport of acid through PBI based membranes. When solution containing acid would be contacted with feed side of the membrane, only acid molecules would get sorbed and transported across the membrane by concentration gradient as the driving force. This transported acid could be stripped away by a suitable stripping agent. In the present work, this approach is examined by investigating transport properties of inorganic acids (H_2SO_4, HNO_3 and HCl) through PBI membrane. Effect of some of the crucial parameters, viz., nature of feed acid and its concentration, nature of stripping agent (water/aqueous alkali solution) on the transport properties are evaluated.

2. Experimental

2.1. Materials

3,3′-diaminobenzidine (DAB), isophthalic acid (IPA) were procured from Aldrich Chemicals. Polyphosphoric acid (PPA, ca. 84% as P_2O_5) was procured from Lancaster. D-glucose was procured from Qualigens Fine Chemicals. *N,N*-dimethyl acetamide (DMAc), acids (HCl, HNO_3 and H_2SO_4), bases (NaOH and $NaHCO_3$), NaCl, $CaCl_2$ and phenolphthalein (AR/LR grade) were obtained from Merck. All these chemicals were used without further purification.

2.2. Synthesis of PBI, dense membrane preparation and their stability

Polybenzimidazole (PBI) based on DAB and IPA was synthesized by solution polycondensation in PPA as reported earlier [22]. Typically, a three-neck round bottom flask equipped with a mechanical stirrer, N_2 inlet and an outlet fitted with $CaCl_2$ drying tube was charged with 450 g of PPA and heated up to 120°C under constant flow of N_2. 15 g (0.07009 mol) of DAB and 0.07009 mol of IPA was added to the reaction mixture, temperature was raised to 170°C and maintained for 5 h. The temperature was further raised to 200°C and maintained for 12 h. The polymer was obtained by pouring reaction mixture into stirred water. The precipitated polymer was sequentially washed with water, $NaHCO_3$ solution and again water, till pH of the filtrate was neutral. The polymer was dried at 100°C under vacuum (a week). It was purified by dissolving in DMAc at 80°C, centrifugation at 3000 rpm (2 h) and precipitation in water. Obtained polymer was dried at 100°C under vacuum (a week). Structure of monomers and polymer are given in Fig. 1.

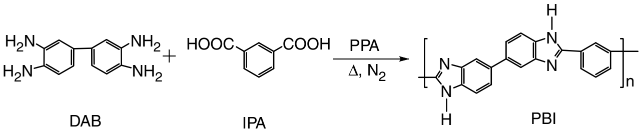

Fig. 1. Synthesis of poly(benzimidazole) (PBI).

Obtained PBI was characterized by Fourier transfer infrared (FT-IR) spectra, recorded on Perkin Elmer-16-PC FT-IR spectrophotometer. Its thermogravimetric analysis (TGA) was performed on TGA-5000 (TA instruments) under N_2 atmosphere with a heating rate of 10°C/min. Inherent viscosity of the PBI was determined using 0.2 g/dl of polymer solution in 98% H_2SO_4 at 35°C. Dense membranes were prepared by the solution casting method on a flat glass surface using 2% w/v DMAc solution at 80°C for 18 h under dry conditions. After initial evaporation of the solvent, formed membrane was peeled off from the glass plate. Membranes with varying thickness (10–40 ± 4 μm) were prepared. They were treated with water at 60°C for 3 days in order to remove traces of the solvent and dried under vacuum at 100°C for a week. They were preserved in the desiccator until use. Stability of these membranes towards acids and bases was assessed by immersing membrane samples (3 × 3 cm^2) in 10 M H_2SO_4, 6 M HNO_3 and 2.5 M NaOH solutions and the visual observation on membrane integrity was noted. The scanning electron microscopic (SEM) image of the membrane surface was recorded on FEI QUANTA 200 3D operated at 20 kV with LFD detector.

2.3. Acid transport

PBI membranes were initially soaked in the feed acid solution for 3 days and then mounted in a plate and frame module thermostated at 40 (±0.1)°C (Fig. 2). The flow directions on both sides of membrane were cross flow. On feed side of the membrane, 300 ml of aqueous solution of inorganic acid was circulated; while on the stripping side, 1500 ml of stripping agent (base solution or water) was circulated. The acid solutions chosen were HNO_3 (1, 4 or 6 M), 1 M HCl or 0.5 M H_2SO_4; while stripping agent was either NaOH (0.24 or 0.5 M) or water. Flow rates on both sides of the membrane were maintained at ~1.6 ml/min. The active membrane area was 102 cm^2.

For analysis, 1 ml of sample was taken at various time intervals from both the containers (feed and permeate side), diluted to 10 ml and titrated. The feed side of the membrane was also separately charged with 0.1% NaCl and 10% glucose solution as the representative of inorganic and organic solutes of smaller molecular weights. Glucose analysis was done by DNSA method, while concentration of NaCl was determined by conductometric titration against aqueous $AgNO_3$. Acid flux of the membrane was calculated as;

$$J = \frac{M}{A \cdot t} \tag{1}$$

where J is the flux through membrane (g/m^2 h), M is the mass of transported acid (g) across the membrane of cross-sectional area A (m^2) within the duration t (h).

Acid flux through the membrane can be given by integration of Fick's law in the limit of the permeant concentrations at membrane-liquid interfaces on feed and stripping side [23]:

$$J = \frac{D_i \cdot K_i}{l}(C_{if} - C_{is}) \tag{2}$$

where l is thickness of the membrane, C_{if} and C_{is} are the concentration of permeant at feed and stripping side solutions. They can be correlated with $C_{if(m)}$ and $C_{is(m)}$

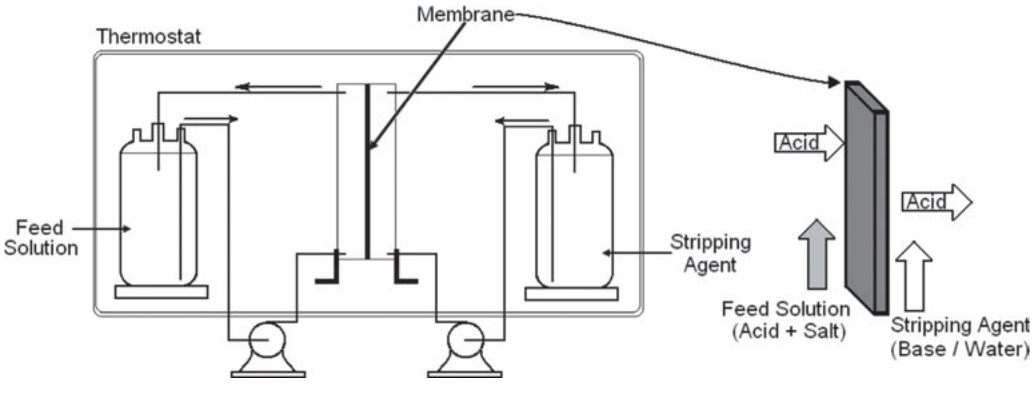

Fig. 2. Schematic representation of the chemo-dialysis process.

Table 1
Effect of stripping agent on the transport of inorganic acids

Feed solution	Average thickness (μm)	Flux (g/m^2 h)	Permeability (m^2/sec)
A) With NaOH solution (0.24 N) as the stripping agent			
0.5 M H_2SO_4	36.37	48.3	4.62×10^{-11}
1 M HNO_3	21.92	24.5	0.48×10^{-11}
1 M HCl	13.38	19.4	0.57×10^{-11}
B) With water as the stripping agent			
0.5 M H_2SO_4	36.37	23.3	1.88×10^{-11}
1 M HNO_3	21.92	20.8	0.35×10^{-11}
1 M HCl	13.38	16.1	0.48×10^{-11}

(concentrations of permeant within the membranes at feed and stripping side interface) by $C_{if(m)} = K_i \times C_{if}$ and $C_{is(m)} = K_i \times C_{is}$ D_i is the diffusion coefficient and K_i is sorption coefficient. $D_i \times K_i$ is normally referred as the permeability coefficient, P_i.

$$J = \frac{P_i}{l}(C_{if} - C_{is}) \tag{3}$$

Thus

$$P_i = \frac{J \cdot l}{(C_{if} - C_{is})} \tag{4}$$

For many systems, D_i, K_i and thus P_i are concentration dependent. Thus, Eq. (4) implies the use of D_i, K_i and P_i values averaged over membrane thickness. The flux and permeability values (by averaging over the duration of experiment) for various acids are presented in Table 1 (variation of ±10%).

3. Results and discussion

3.1. PBI synthesis and physical characteristics

PBI was synthesized by solution condensation of diaminobenzidene (DAB) and isophthalic acid (IPA) in polyphosphoric acid (PPA) as the solvent. The duration of reaction required at 200°C was 12 h, which was in agreement with our earlier work [22]. The recovery of polymer by precipitation of reaction mixture in stirred water and next processing to remove phosphoric acid were similar as that of reported earlier. Inherent viscosity of the formed PBI was found to be 1.2 dl/g. FT-IR spectra of this PBI showed absorption bands at 1432, 1586 and 1608 cm^{-1} (Fig. 3), attributable to C=C and C=N vibrations of imidazole ring [22]. A broad band at ~2500–3700 cm^{-1} was due to hydrogen bonding of N-H/N type and non-hydrogen bonded N-H stretching [22]. A small band at ~3060 cm^{-1} could be attributable to the aromatic C-H bond vibration. Initial decomposition temperature (IDT) of PBI as analyzed by TGA was found to be 604°C, which was reported earlier to be 600°C [22]. Since IR bands and TGA matched with our earlier results, further spectroscopic analysis of PBI by ^{1}H-NMR was not performed.

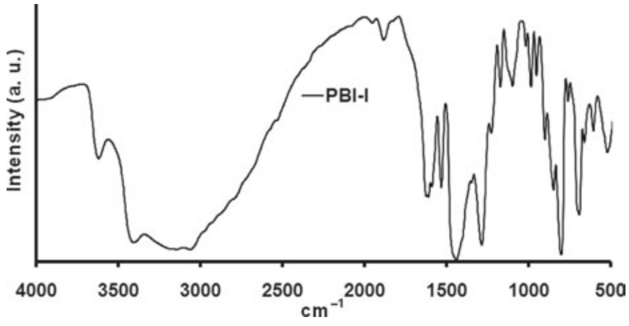

Fig. 3. FT-IR spectra of the synthesized PBI.

3.2. Stability of PBI towards strong acids and bases

For the application of PBI as a membrane material for acid recovery, it was necessary to determine the stability of membrane and its integrity in presence of acids and bases. PBI membrane samples were immersed in 10 M H_2SO_4, 6 M HNO_3 and 2.5 M NaOH at ambient. Membranes were found to be stable for minimum a month in above solutions; except a greenish tinge developed to H_2SO_4 treated membranes. SEM image of the surface of H_2SO_4 treated membrane sample is given in Fig. 4, which is free from any defect. The original light brown color of these samples was regained back after immersing in water for 3 days, without any physical change to the membrane (retained integrity).

This observation is in accordance with the excellent chemical stability of PBI towards various acids and bases reported in the literature [19,24,25]. Present investigations performed for a longer duration indicated that PBI could be suitable candidate for continuous acid separation or recovery applications. At the same time, base can be used as a stripping agent to remove transported acid from the membrane surface.

3.3. Transport properties

3.3.1. Investigations with non-acidic molecules

Spent liquors from various industrial streams contain inorganic [2,3] as well as organic solutes [2,26,27]. For effective acid removal, recycle and its reuse; the permeated acid should be free of any impurity. In order to establish applicability of PBI as an acid transporting

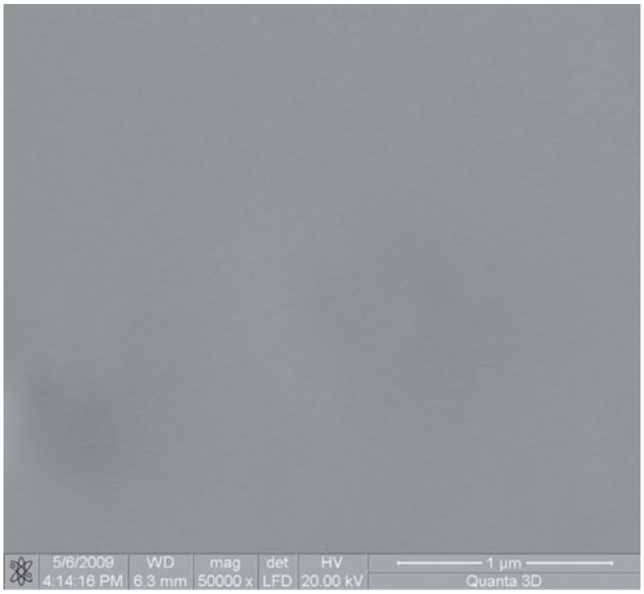

Fig. 4. Surface SEM of PBI-I membrane after stability investigations.

membrane (which is not known in the literature), it was necessary to investigate transport of not only the acids, but also organic/inorganic solutes through PBI membranes. We selected NaCl and glucose as representative of inorganic and organic solutes, respectively. A solution containing either 0.0171 M NaCl (0.1% w/v) or 0.555 M glucose (10% w/v) was circulated on the feed side of the membrane while water was used as the stripping agent. Though these concentrations do not imitate any real life industrial solutions, but have a practical significance. A 0.555 M glucose is the concentration present in a fermentation broth at its beginning. The salt concentration was taken as 0.0171 M, which was high enough to be detectable. No transport of either of these solutes could be detected after a continuous circulation of the respective solution for 72 h on feed side of the PBI membrane. This infers that these membranes are impermeable to non-acidic moieties. This could be explained on the basis of membrane type, nature of PBI and the process parameters. The membranes used in this study were dense membranes (~35 μm thick) prepared by solution casting method, and thus are nonporous. Since there is no porosity, transport through pores is absent. Secondly, PBI is anticipated to have negligible sorption of anions and cations of a salt (here NaCl), as it is non-ionic polymer. In the absence of sorption of a salt, it would not be transported. When PBI membrane was immersed in 0.555 M glucose solution for 72 h, no weight gain could be noted. Thus, sorption of glucose is almost nil in PBI. Moreover, current process uses no external stimuli such as pressure and the driving force is only the concentration gradient. Owing to all these reasons, no transport of salt or glucose could be detected. This observation has a great practical significance and conveys that the proposed process would not allow transport of even small molecular weight inorganic salt or organic molecule.

3.3.2. Transport of acids

The membrane was dipped into the feed solution for 72 h prior to mounting into a plate and frame module. This period is known to be more than enough for the acid sorption to take place in PBI matrix [22]. Initially, acid solution (concentration of 1 N for each acid, i.e. 1 M for HCl and HNO_3 while 0.5 M for H_2SO_4; 300 ml) was circulated on the feed side and 0.24 M aqueous NaOH or water (1500 ml) was circulated as the stripping agent on permeate side. In case of use of NaOH as a stripping agent, amount of acid transported on the permeate side was deduced from the amount of NaOH consumed by titration; while, in case of use of water as a stripping agent, amount of acid transported on the permeate side was deduced by titrating a sample against NaOH.

The feed side acid concentration gradually decreased, as determined by the titration analysis. The decrease in NaOH concentration on the permeate side was correlated with the formation of salt, as represented in the Fig. 5.

Since the amount of NaOH taken on the permeate side was in excess (1.2 M equivalents) to amount of acid present in the feed solution, all H_2SO_4 could be transported within 48 h (Fig. 5a). In case of HNO_3 and HCl, even after 72 h, all the acid could not be transported (Fig. 5b and c). The average flux and permeability values (obtained by normalizing flux with membrane thickness and concentration gradient) are given in Table 1. As could be seen from this Table, permeability of H_2SO_4 is much higher than that of other two acids. Similar behavior was observed when water (1500 ml) was used as the stripping agent (Fig. 6), while maintaining the acid quantity equal to the earlier case.

Since the thickness of membrane used in each case was different, a better understanding of the transport behavior of these acids could be obtained based on permeability rather than the flux. It could be seen that the permeability of dibasic H_2SO_4 was considerably higher than the permeability of monobasic HNO_3 or HCl in both the cases of stripping agent used. The transport could occur due to interaction of acid molecules with the basic PBI matrix. As could be seen from Fig. 1, each PBI has 4 basic sites ('N' atoms bearing lone pair of electrons). These sites in the polymer backbone would lead to selective sorption of acid molecules present in the feed. This sorption would have its own effect on the acid permeation properties. Due to the dibasic nature of H_2SO_4, its H-bond interactions are anticipated to be more than that of monobasic HNO_3 and HCl.

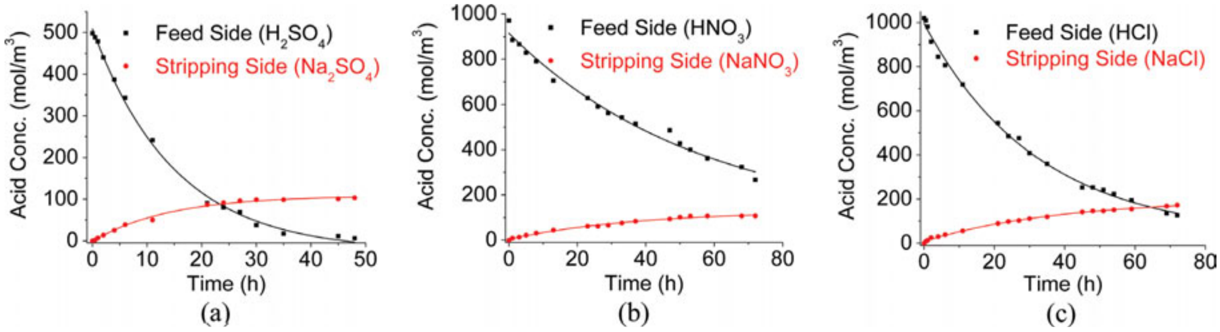

Fig. 5. Variation in acid concentration with time (aqueous NaOH as the stripping agent).

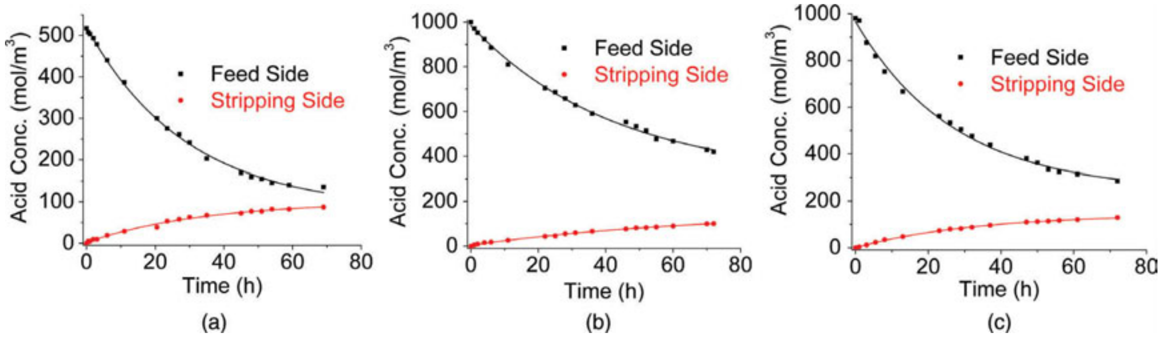

Fig. 6. Variation in acid concentration with time (water as the stripping agent), where (a) H_2SO_4, (b) HNO_3 and (c) HCl.

This may be a reason for higher observed permeability of H_2SO_4, than that of other two. HCl showed higher permeability than that of HNO_3, which could be attributable to smaller molecular size of HCl.

Transport of acid, while restricting passage of salt or glucose through basic PBI membrane indicated that interactions of solute (acid) molecules with membrane material is a primary requirement for the acid transport to occur through PBI membrane. Uptake of inorganic acids by PBI is well demonstrated in the literature [19,21,22]. Since transport could occur only due to the chemical interactions of both, solute (acid) and the membrane material (basic PBI), we propose a term as “Chemo-dialysis” for this process. Though acid transport by using various types of membranes as discussed above in ‘Introduction’ is realized, reported membranes are not basic in nature. Transport of co-solute (salt) is also a major draw-back of known membranes. Both these issues are addressed in the present process of ‘Chemo-dialysis’ where (i) basic nature of membranes transport acid via acid-base (polymer matrix) complexation and (ii) transport of co-solutes is inhibited since their sorption in membrane matrix is not realized.

The sorbed acid molecules are transported across the membrane by concentration gradient and are stripped away by aqueous NaOH or water as the stripping agent on other side of the membrane. NaOH would convert the acid to its Na-salt and thus maintain the concentration of acid on the permeate side as practically zero, at any given time. This assists in maintaining the concentration gradient essentially similar as that of feed side acid concentration. The major draw-back of using NaOH here is that it would convert acid to its salt on the permeate side and the recovery of transported molecule in its original ‘acid’ form is not feasible. In other words, re-use of acid is difficult. Use of water as the stripping agent would allow acid recovery, with a draw-back that all the acid would not be transported. As could be seen from Fig. 6, volume of water used would determine the amount of acid transported on the permeate side. The ultimate process requirement (use of water or base as the stripping agent) would be decided by the desired application.

3.3.3. Effect of feed concentration

Effect of feed concentration on the acid transport rate was studied with 1, 4 and 6 M of HNO_3 in the feed, while maintaining 0.5 M aqueous NaOH (1500 ml) as the stripping agent. The results are shown in Fig. 7.

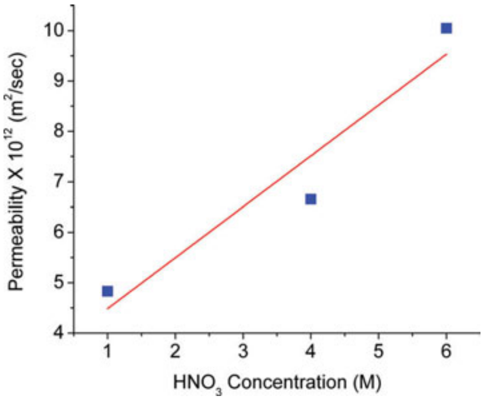

Fig. 7. Effect of concentration on the transport of HNO_3.

The increase in permeability of acid was almost linear with that of feed acid concentration. This is made possible with the increased driving force (feed acid concentration). Moreover, increased acid sorption in PBI matrix with increasing feed concentration could also be responsible for elevating the acid permeability. It is known that acid uptake in PBI matrix increases with the bath concentration [21,22].

Present study indicated that the acid permeation through a basic polymer membrane consisted three predominant steps, viz.; i) sorption of acid on feed side of the membrane by interaction between acid molecules and basic 'N' of PBI, ii) its diffusion through the membrane matrix due to concentration gradient and iii) its desorption on the other (permeate) side by a stripping agent. This is similar to the solution-diffusion model, in which permeant dissolves in the membrane material and then diffuses through the membrane by concentration gradient [23]. A separation is achieved between different permeants because of the difference in quantity of permeants that dissolve in the membrane matrix and the rate at which they diffuse through the membrane. Similarly, in current process of chemo-dialysis, the permeant (acid) is sorbed in the membrane matrix due to the interaction between permeant (acid molecule) and the membrane material (basic PBI). This sorption is followed by the diffusion of permeant across the membrane by concentration gradient as the driving force. The transported acid is stripped away from permeate side of the membrane by a suitable stripping agent. Hence the transport mechanism for chemo-dialysis can be termed as 'solution-diffusion' with some distinct differences than perstraction as: (i) the membrane material is solid polymer rather than a liquid membrane demonstrated in perstraction, (ii) easy desorption and recovery of transported acid and (iii) no transport of co-solutes (glucose/NaCl) leading to practically infinite selectivity. These findings need to be substantiated with further studies on acid-polymer interactions, sorption characteristics, intrinsic polymer properties such as chain flexibility, interchain spacing, swelling characteristics, etc. and their inter-relations; which is the aim of our next study.

4. Conclusions

A new membrane process, termed as 'Chemo-dialysis' is proposed for the recovery of acids; which works on the basis of chemical interactions of the membrane material (polybenzimidazole, a basic polymer) and the solute acid molecules. The membrane exhibited appreciable transport rates towards acids, while transport of non-acidic solutes like salt or glucose (representative of inorganic or organic solutes) was beyond detection limits. This typical characteristic makes this process unique; as a result of successful exploitation of basic nature of polymer to transport acidic solute. The process works with concentration gradient as the driving force. It uses energy only for the circulation of solution on the feed and stripping sides and thus is highly energy efficient. Use of water as the stripping agent allows recycle of acid. This leads to additional cost benefit and most importantly, addresses environmental concern; where acids are neutralized and then disposed.

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