Chemical Methodologies 2(2018) 194-203

Chemical Methodologies

journal homepage: http://chemmethod.com

Original Research article

Selective Transport of Aromatic Compounds Across Parchment Supported Prussian Blue Membrane

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ARTICLE INFORMATION

Received: 10 February 2018
Received in revised: 12 March 2018
Accepted: 15 April 2018
Available online: 01 July 2018

DOI:
10.22631/chemm.2018.118847.1038

KEYWORDS

selective transport
parchment supported
aromatic molecules

ABSTRACT

The study of permeation of Aromatic compounds across parchment-supported membrane treated with Prussian blue is presented.The skin layer of the metal hexacyanoferrate membrane which consists of a network structure could be selectively used with defined pore size in the nanometer range to permeate molecules with different size molecules. In order to demonstrate a possible sieving of molecules, we have investigated the permeation of a variety of aromatic compounds such as aniline (An), phenol (Ph), and naphthalene (Np). For these neutral compounds, a size-selective transport was found. Size leads to a separation factor α(An/Ph) of 1.5 and α(An/Np) of 4 respectively. Finally, it is demonstrated that the purely inorganic membrane of Prussian Blue(PB) can be prepared upon adsorption of ferric ion and hexacyanoferrate on porous support.

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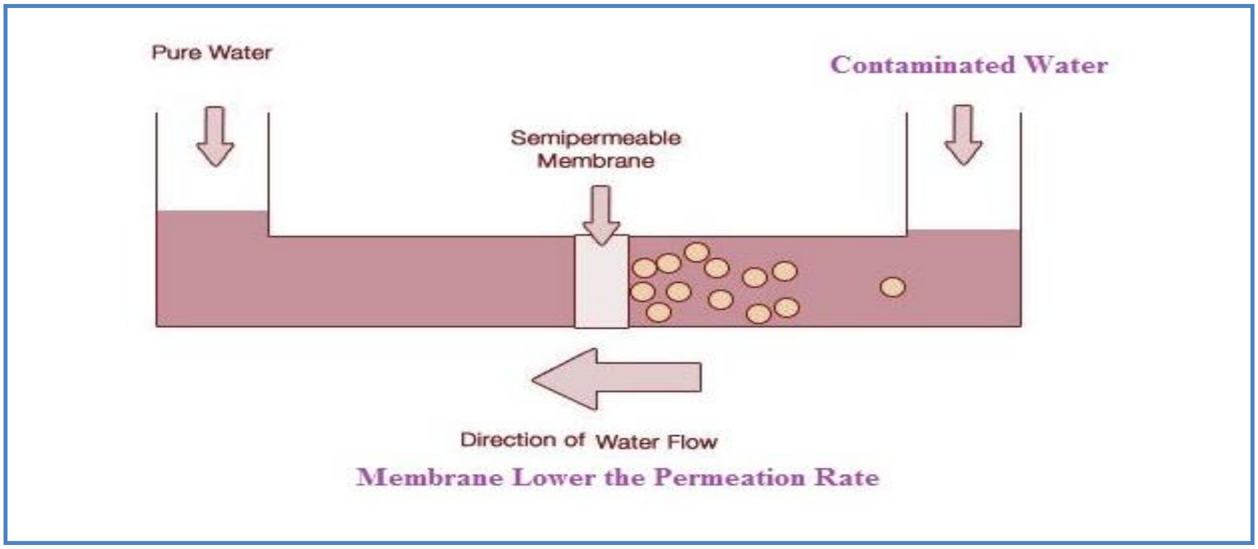
Graphical Abstract



Introduction

Heavy metals, organic compounds and other pollutants are found in wastewater from chemical manufacturing, painting and coating, mining, extractive metallurgy, nuclear and other industries [1]. These pollutants constitute serious problems to human health and environment. Therefore, the removal of these dangerous compounds from wastewater which is required for human life and environment has been extensively investigated in industries [2]. A number of separation methods are available for the removal of heavy metal and organic compounds from aqueous solutions including: ion exchange [3], solvent extraction [4], reverse osmosis [5], precipitation [6], coagulation and flocculation [7], and adsorption [8]. The membrane separation process has been the most frequently used and applied method in the industries [9-12].

Transport of organic compounds is of fundamental interest and importance for potential applications such as water purification, and separation of chemical compounds. Up to now, only a few studies were concerned with the permeation of organic compounds across precipitated membrane [13]. Jin et al. have proved a size-selective transport of neutral and charged aromatic compounds across PSS/PDADMAC and PSS/PAH membranes. It is worth mentioning that their method is based on molecular sieving according to the different nanopore size of the polyelectrolyte complex membrane [14].

The crucial point of this work is the preparation of homogeneous and selective separating membranes with high constant flux and optimum separation capability. Therefore, the principal purpose of this work was to introduce new selective Prussian blue membranes to be utilized as a biological model.

Experimental

All compounds used in this study were of analytical grade and used without further purification.

Preparation of membrane

The deposition of complex salts (Prussian Blue) on porous parchment paper by Potassium hexacyanoferrate(III), $K_3[Fe(CN)_6].3H_2O$ (HCF) and ferric chloride,$FeCl_3.6H_2O$ were prepared by the method of interaction suggested by Siddiqi [15]. First, a parchment paper was tied carefully to the home-made apparatus as described in Figure 1. 0.2 M solution of $FeCl_3$ and HCF was filled in the two sides of apparatus for about 72 h at 25^{o}C.The two solutions have interchanged and kept for another 72 h. After a fine deposition of Hexacyanoferrate$Fe^{III}HCF^{III}$ was obtained on the porous of the parchment paper, the membrane was, then, washed with Milli-Q-water for the removal of the free ions.

Permeation measurements

Permeation measurements of organic compounds were carried out using a home-made apparatus as described in Figure 1. The concentration c_p of the aromatic compounds in the permeate chamber was detected spectrophotometrically. For the UV measurement, a small amount of the permeate solution (about 3 ml) was periodically collected and the concentration of the permeate was determined by measuring the peak absorbance in a UV/Vis spectrometer. After measurement, each sample was immediately returned to the permeate solution chamber (which took about 2-3 min)[16].

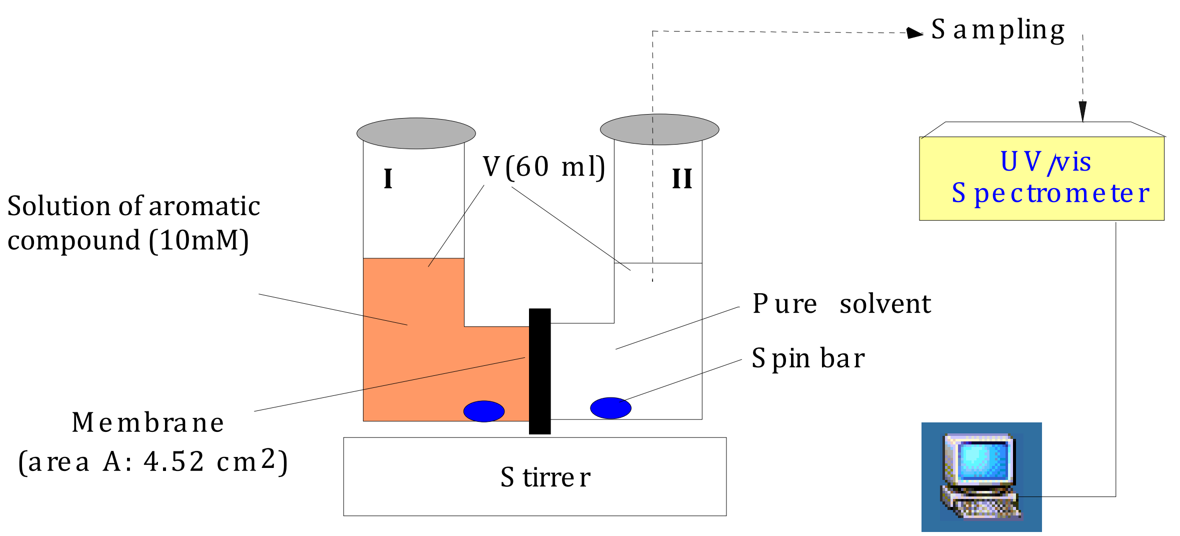


Figure 1. Schematic representation of the cell used for measurement of the transport of aromatic compounds [16].

The permeation rate P_R of the aromatic compounds in the permeate chamber was calculated according to formula (1)

$$P_R = \left(\frac{\Delta c_p}{\Delta t}\right) V_0 (A c_f)^{-1}, \qquad (1)\ [16]$$

With Δc_p being the change in solute concentration in the permeate chamber during the time period Δt of the permeation measurement, the value of $\Delta c_p/\Delta t$ was obtained from the plot of c_p against t. V_0, A and c_f represent the initial volume of the feed and permeate solution, the area of the membrane and the solute concentration of the feed solution, respectively. The separation factor α is defined as the ratio of the P_R values of corresponding compounds.

Results and Discussion

Since it was already proven in our lab [17-22] that precipitation of inorganic salts on porous support such as the parchment paper are suited for preparation of selective membrane, the aromatic compounds were chosen because their concentration in the permeate could be easily detected upon UV-spectroscopy.

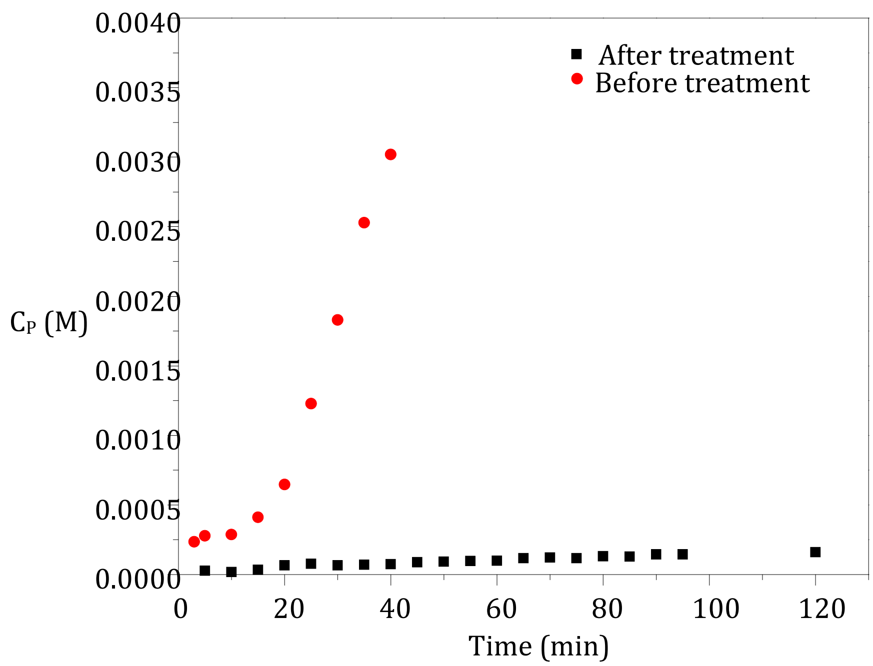


Figure 2. Plot of concentration C_p of aniline in permeate vs. time t of the permeation measurement before and after treatment with Prussian blue (Fe^{III} HCF^{III})

First, the permeation of 10 mmol. L^{-1} of aniline (An) in ethanol through the bare parchment substrate (before treatment) was studied as shown in figure 2. This permeation rate dropped sharply down when the porous was coated with Fe^{III} HCF^{III} (after treatment with Prussian blue). However, the experiment indicates that we succeeded to minimize the size of the porous in the parchment paper and enough to reduce the permeation rate by about 90%, so that the transport is controlled by the pore size.

Figure 3. Plot of concentration C_p of phenol in permeate vs. time t of the permeation measurement before and after treatment with Prussian blue (Fe^{III} HCF^{III})

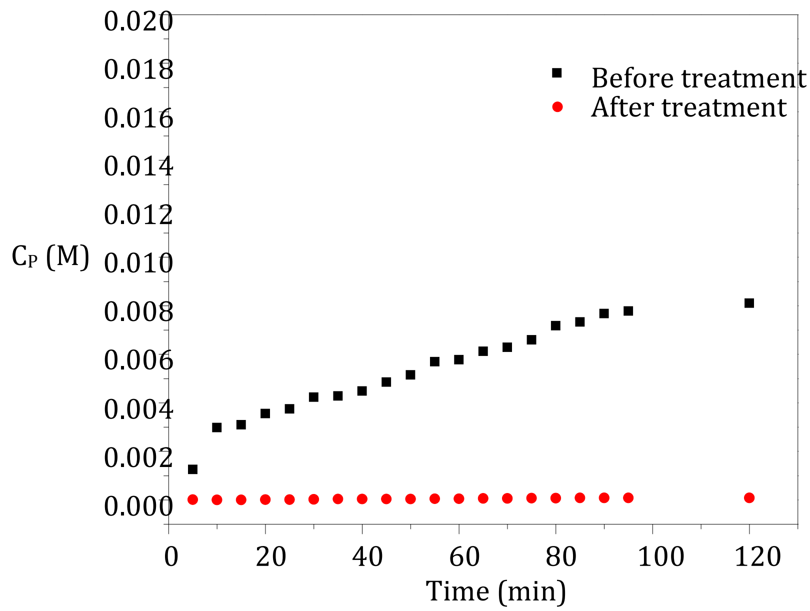


Figure 4. Plot of concentration C_p of naphthalene in permeate vs. time t of the permeation measurement before and after treatment with Prussian blue (Fe^{III} HCF^{III})

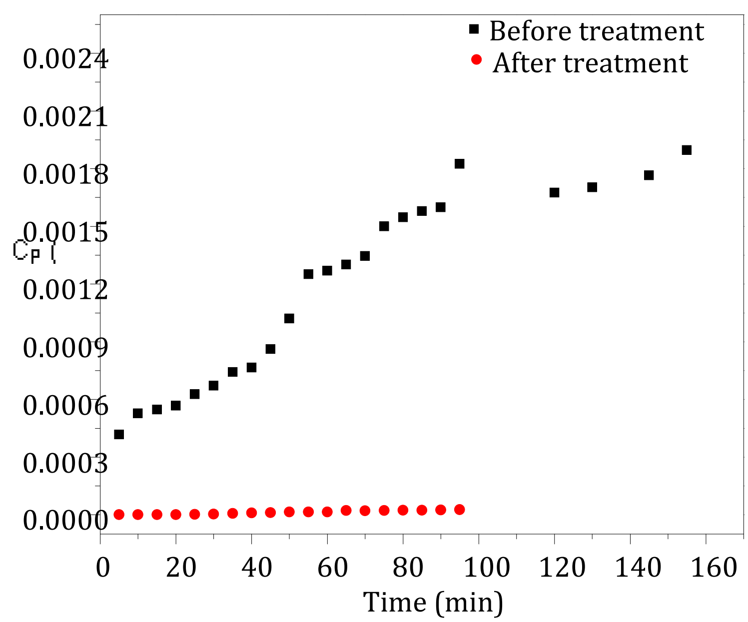
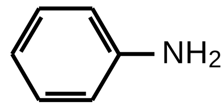
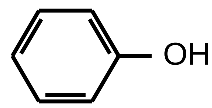
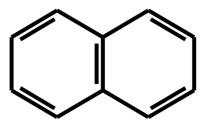


Table 1. Structures and sizes of organic compounds and abbreviations used in this study

Abbreviation	Compounds	Chemical Formula	Longest axis (nm)
An	Aniline		0.5886
Ph	Phenol		0.5573
Np	Naphthalene		0.7184

In order to obtain further information on transport mechanism and selectivity, the permeation of another aromatic compounds with different size such as phenol (Ph) and naphthalene (Np) in ethanol was investigated (Table 1) and Figure 3 and 4 show low permeation rates of Ph and Np, while An exhibits a much higher value. From the P_R values, theoretical separation factors α(An/Ph) and α′(An/Np) of 6 and 14, respectively, could be calculated.

By comparing the permeation rates for three compounds; as in Figure 5, one recognizes that after treatment the parchment paper with HCF the P_R values of the three compounds are lower than before, and that decrease is especially strong for larger compound.

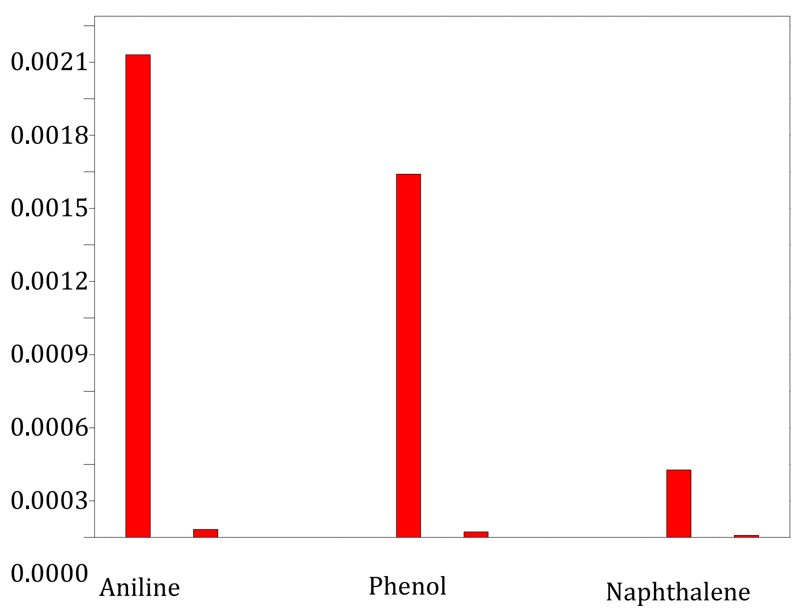


Figure 5. Permeation rates of different aromatic compounds (10 $mmolL^{-1}$ in ethanol) across Prussian blue (Fe^{III} HCF^{III}) membrane.

In Addition, the difference in permeation rates of An and Ph; as in figure 5, must have another reason. It could probably be attributed to the formation of phenol clusters occurring after dissolution in ethanol. Clearly, the size of the clusters will be an important factor determining the permeation rates through the membrane. When ethanol is used as solvent, a type of layered structure is favoured for Ph as shown in Figure 6[23].

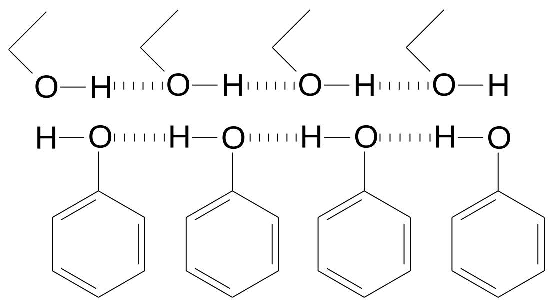


Figure 6. Schematic diagram of the phenol clustering in ethanol [23]

The ethanol and phenol layers will interact via electrostatic and/or hydrogen-bonding interactions forming phenol clusters of different size. The same phenomenon will also occur in the solvation of aniline, but with lower stability and smaller size of the clusters, due to a lower charge density of aniline. Furthermore, the H-bonds between phenol and solvent must be polarized; the electrostatic interaction among the polarized H-bond can support the stacking structure. The fact that aniline only functions as an acceptor for H-bonds also suggests that the stacking-type structure will be small. This means that the number of phenol molecules in the polarized cluster will be much larger than the number of aniline molecules in their clusters. Accordingly, the permeation rates of phenol and aniline will encounter with the size of the clusters. The extremely low permeation rates of naphthalene ($0.0354 \cdot 10^{-6}$ cm s^{-1}) as compared to aniline are attributed to the larger size of the molecules (Table 1) so that they are rejected.

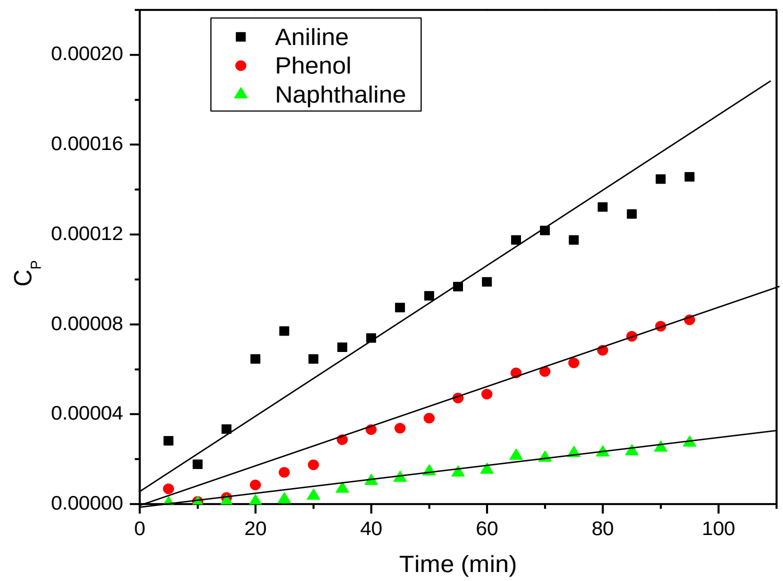


Figure 7. Permeation rates of phenol and a variety of charged aromatic compounds (10 mmol.L^{-1}) across calix8/PVA membrane.

The permeation study which demonstrates a selective transport of neutral aromatic compounds might be based on molecular sieving according to the different size of the molecules. However, as indicated in the Table 1, the size of An and Ph molecules is comparable, only Np is clearly larger.

Similar plots with a linear increase of C_p versus t were also obtained for the compounds after treatment of the membrane with very low slopes. From the slope $\Delta C_p/\Delta t$, the permeation rate P_R was calculated using the formula shown in the experimental part [24-29].

In Figure 7, the P_R values of An, Ph and Np in 10 mmol.L^{-1} ethanolic solution are represented. As can be seen, the permeation rates of aqueous An, Ph and Np across the Prussian blue membrane are very different. It can also be seen that the P_R values decrease in the series An> Ph > Np, i.e. in the direction of increasing size of the anion. The separation factors α (An/Ph) and α´ (An/Np) are 1.5 and 4, respectively. This indicates a size-selectivity in the transport of organic compounds. Thus, the permeation rates through the Prussian blue membrane depend on both the size of molecules and membrane pore size. The permeation rates decrease with increasing the size of the molecules, this phenomenon can probably be related to thickness and density of the membrane.

Conclusion

Insoluble inorganic salts of $Fe^{III}HCF^{III}$ could be easily prepared on porous parchment paper support, if suitable conditions were applied. Furthermore, the permeation of a variety of aromatic compounds was investigated. The transport of neutral compounds was controlled by the pore size of the membrane and the molecular size of the compounds. The membranes act as molecular sieves and reject compounds larger than the pore size of the membrane. The difference in permeation rates of An and Ph must have another reason. It can probably be attributed to the formation of phenol clusters occurring after dissolution in ethanol. Clearly, the size of the clusters will be an important factor determining the permeation rates through the membrane [29].

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How to cite this manuscript: Ashraf El Hashani, Nura Ben Khayal, Khaled Muftah Elsherif*. Selective transport of aromatic compounds across parchment supported prussian blue membrane. Chemical Methodologies , 2(3), 2018, 194-203. DOI: 10.22631/chemm.2018.118847.103.