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Electrically driven separation of cresol from water using PVDF/IL-silica composite membrane

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Abstract

A novel PVDF-Sil-IL membrane was created and applied to isolate cresol in solution with an electrically driven device. The effects of several variables such as the type of salts, voltage, time, pH and temperature were experimentally evaluated. The FT-IR proved the PVDF-Sil-IL membrane was successfully prepared. And under the optimized condition (20V of voltage, 20min of isolation, neutral pH and 40^{o}C of system), 90% of cresol was isolated. This finding can facilitate the development of PVDF membrane as an efficient electrochemistry tool for the isolation of phenols compounds from water samples.

Keywords: ionic liquid-based silica, PVDF, membrane, electrical drive, cresol

Introduction

Phenol is an organic substance which is used in several manufacturing processes such as for the manufacture of phenolic resin and other phenol derivative chemicals. It is also used as a solvent, as an antiseptic and as additive in disinfectant [1, 2]. Phenolic compounds are also used widely in many industrial processes, such as petroleum refineries, pharmaceutical, and chemical industries. However, they are highly toxic to human and environment even at low concentrations [3].

In order to remove them, various treatment methods like fenton, ozonation, distillation, liquid-liquid extraction, adsorption, pervaporation, membrane extraction, biological based processes and different kinds of electrochemical methods were currently practiced for phenolic compounds [4-7], especially the application of ionic liquids (ILs). ILs are well-known green reaction Medias with excellent chemical properties. Their hydrophobicity, miscibility with several inorganic/organic solvents, and π-π interactions between functional groups are allow ILs to be widely applied. Balasubramanian *et al*. [3] extracted five phenolic compounds (phenol, p-chlorophenol (CP), 2, 4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP)) by [BMIM][PF6] in tributyl phosphate (TBP) to obtain an IL mixed carrier (ILMC). The IL was investigated and different volumes in TBP were performed. The result was observed that 0.02% (v/v) of [BMIM][PF6] in TBP can remove 99.5% of phenols. As the IL concentration increased to 0.15% (v/v), the phenol removal decreased to 98%.

However, the extraction method expended large amount of organic solvents in process. So, in recent times membrane technology has emerged as an efficient process for concentration and purification of species in aqueous solutions. Many researchers are putting their consistent effort to develop an efficient IL introduced membrane separation process for the treatment of target compounds. Ng *et al*. [2] used liquid membranes with three ILs [BMIM][PF_6], [BMIM][Tf2N] and [BMIM][FAP] to extract phenol which is a common organic compound used in many manufacturing processes and chemical solvents. [BMIM][Tf_2N] with the highest efficiency and the lowest viscosity was selected. In addition, when the pH was higher than 6.6 the extraction efficiency was decreased. After optimizing several parameters, the extraction efficiency was higher than 96.2% with a recovery of 94.4%. Other researchers reported liquid membrane in separation. Chakrabarty *et al*. [8] tested the extraction and recovery of lignosulfonate by a low viscous liquid membrane containing trioctylamine (TOA) as carrier. The maximum separation occurs at feed phase pH of 2 and carrier concentration of 4 vol. %. Cichy *et al*. [9] studied the extraction and perstraction of phenol through a bulk liquid membrane with Cyanex 923 as a carrier. The concentration of the phenol complex in the membrane phase increased to 1.5 g/dm^3 when Cyanex 923 was used and the NaOH concentration was 0.05 mol/dm^3.

Poly (Vinylidene fluoride) (PVDF) as a linear, semi-crystalline and high molecular weight polymer has been the subject of much investigation [10]. PVDF membranes have been extensively applied in distillation, ion exchange, ultrafiltration, and microfiltration owing to its excellent chemical resistance and good stability. Nevertheless, the hydrophobic property of PVDF membranes results in low water permeability and severe membrane fouling when treating an aqueous solution [11]. This inevitably depresses the lifetime of the membrane so some modifications are needed. In this research, an ionic liquid-based silica complexes PVDF membrane was created and it was used to evaluate the separation efficiency of cresol with the help of electric drive.

2. Materials and methods

2.1 Materials and instruments

Silica (40 μm), (3-chloropropyl) trimethylsilyl, imidazole, cresol and all inorganic salts (NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$, Na_2HPO_4 and NaH_2PO_4) were purchased from Aladdin Inc. (Shanghai, China) and all grades of purity were higher than 98.0%. Organic solvents such as methanol, acetone, ethanol, toluene *et al*. were supported by Brazilian Company (Tianjing, China) and purities were higher than 99.0%. Ultrapure water was produced by a purification machine (UPH-I-5, Youpu, China) and all organic solvents should be filtered before use. PVDF powder was supported from Dr. W. Xiao. The DYY-2C DC electrical power was purchased from LIUYI Biotechnology Co. Ltd (Beijing, China). All solutions were detected by UV spectrophotometer (752N, YOKE Instrument Co. Ltd, Shanghai, China) with a 270 nm wavelength.

2.2 Preparation of membranes and electrically driven device

Firstly, ionic liquid-based silica was prepared. Silica was activated by stirring in 10.0% vol HCl aqueous solution for 24 hr and washed by water until pH=7.0. Then the activated silica was synthesized by following steps shown in Fig. 1. 30.0 g of activated silica, 40.0 mL of (3-chloropropyl) trimethoxysilane and 80.0 mL of toluene were well stirred and heated to 100 °C in a flask for 12 hr. The obtained powder (3-chloropropyl based silica, Sil-Cl) was then washed with ethanol and fully dried. Then the obtained Sil-Cl, 25.0 g of imidazole and 80.0 mL of toluene were mixed and synthesized in a flask for 8hr under 100 °C. After washing by diluted water, ethanol and acetone, the imidazole IL-based silica (Sil-IL) was obtained and the powder was fully dried in an oven.

Secondly, membranes were prepared on filter paper (Fig. 1). According to the property of PVDF, 1.5 g of the powder was fully dissolved in 10 mL of acetone. Then the solution was dropped on filter paper (pore size: 20-30 μm) and after acetone volatilized the PVDF membrane was obtained. 1.5 g of PVDF and 1.5 g of Sil-IL mixed in acetone and after the same step the PVDF-Sil-IL membrane was obtained.

Finally, the electrically driven device was set up (Fig. 1). The membranes were fixed in the middle of tank, and two graphite electrodes were hold on both inside walls. Impermeability of the device needed to be checked before using.

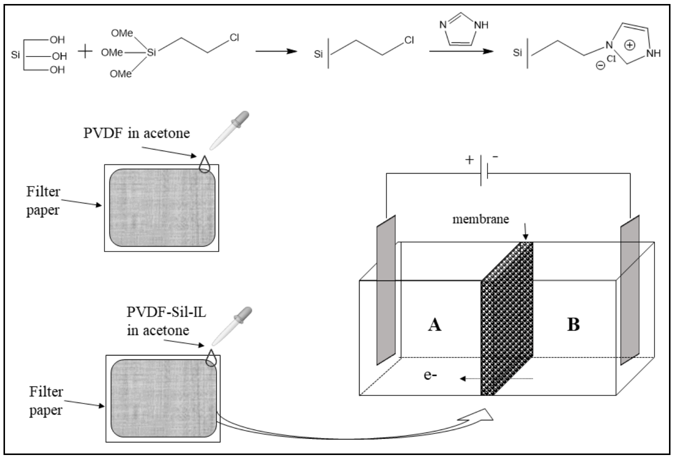

Fig 1: Preparation of Sil-IL, membranes and the electrically driven device.

2.3 Electrical conductivity testing of different salts in water

50.0 mL and variable concentrations of NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$, Na_2HPO_4 and NaH_2PO_4 aqueous solution were prepared and 5 mL of each solution was pour into tank without membrane. Then the DC electrical source was entered to circuit and different voltages were adjusted.

2.4 Investigation of different conditions

The membranes were involved to isolate cresol in solution. In the tank, same volumes of cresol solution were added in part A and B, after electrically driven under variable conditions such as voltage, electrical time, pH and temperature, the concentrations of cresol in A and B were detected by UV spectrophotometer.

3. Results & Discussion

3.1 Characterization

The characteristics of all obtained IL based silicas were analyzed by FT-IR (Nicolet 6700, Thermo Fisher, Waltham, USA) in the range of 400-4000 cm-1 with a scan rate of 20 scans/min. In Fig. 2, silica exhibits a conspicuous peak in the range of 3200-3250 cm^{-1} and it belongs to the finger print region of the -OH group. In Sil-IL, -OH peak is obviously decreased and a new peak emerged around 1517.6 cm^{-1}. The characteristic region of the amide bands ranged from 1500 to 1600 cm^{-1}, indicating the replacement of-OH groups by imidazole groups. More peaks appear on PVDF-Sil-IL, 1180.7 cm^{-1} and 1399.9 cm^{-1} are the finger print region of $-CF_2-$ and $-CH_2-$ from PVDF, also the shoulder peaks between 2883 cm^{-1} and 2981 cm^{-1} are belong to -CH-. The above results showed that the complex PVDF-Sil-IL membrane was successfully created.

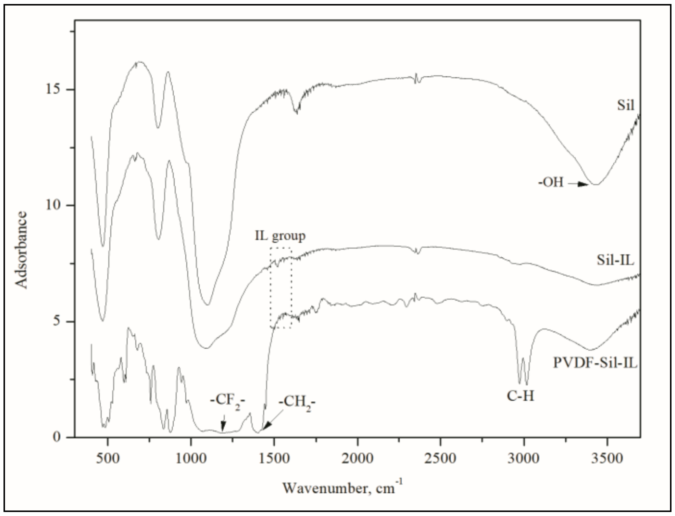

Fig 2: FT-IR of silica, PVDF and PVDF-Sil-IL

3.2 Electrical conductivity of salts

When the voltage was fixed as 5V and time as 20 min, with the concentrations of salt increasing the current of aqueous solution increased. In Fig. 3 the results showed that currents of Na_2HPO_4 and NaH_2PO_4 were quite higher than other salts. In addition, when the concentration of all salts higher than 0.6 mol/L, large amounts of $MgCl_2$, Na_2SO_4 and $MgSO_4$ were precipitated as crystallizations. Moreover, although the current of Na_2HPO_4 is a little higher than NaH_2PO_4, it seeded out more amount than NaH_2PO_4 under high concentration. In this case, an equal amount of these two salts were mixed and prepared as 0.5mol/L for further experiments.

Then in the tank the PVDF and PVDF-Sil-IL membranes were involved and the tank was isolated to part A and part B which the volumes of them were same. Under the same condition of 5V and concentrations of salts, the detected currents were as the same as previous. Therefore, the membranes did not weaken the electrical conductivity and aqueous solution contained Na_2HPO_4 and NaH_2PO_4 would be used as media liquid.

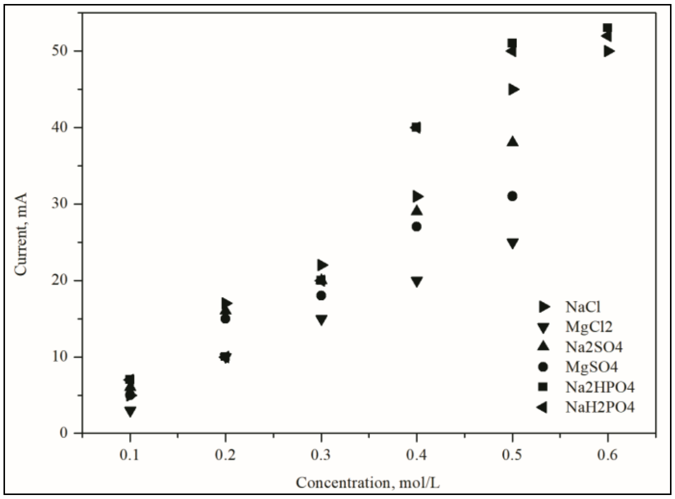

Fig 3: Current of aqueous solution with different salts and concentrations

3.3 Effect of PVDF and PVDF-Sil-IL membranes

First of all, the calibration curves were constructed using the absorbance measured at seven increasing concentrations ranging from 0.0001-0.01 mg/mL. Good linearity was obtained and the correlation equation was $y=183.2x+0.09$ ($R^2=0.995$) (y is absorbance and x is the concentration in solution).

In order to evaluate the effect of membranes, 0.001 mg/mL of cresol in 0.5 mol/L Na_2HPO_4/NaH_2PO_4 solution was used, and 5.0 mL of the solution was pour into A and B of tank simultaneously with 5V and 20 min. Cresol in solution showed electronegativity because of the hydrolysis of hydrogen, so it would move from B to A.

When filter paper was used, because of large size of pore molecules in A and B can be frequently exchanged with or without electrical driving, so the concentration of cresol in A and B had no difference. When PVDF membrane was used, the pore size was quite smaller and with the hydrophobic property, cresol molecules moved to A was difficult diffused back to B, so the concentration in A was higher than B. The PVDF-Sil-IL membrane not only had advantage of PVDF, but also the -OH group and IL group had interactions with cresol. They were so strong that without reverse force cresol could not into part B. So using PVDF-Sil-IL membrane in further experiment could isolate cresol molecules in A with a quite high concentration.

3.4 Effect of voltage and time

Electrically driving time was evaluated first and the results showed in Table 1. Under 5V, time was increased from 5 min to 120 min and after 60 min the concentration in A did not increase. When the voltage increased to 20V or 30V, cresol molecules moved faster so the time was shortened to 30 min. However, under high voltage the dissolved salts were precipitated from solution and current decreased obviously. The phenomenon was getting worse with the voltage was higher than 30V. In this case, 20V within 30 min was selected as the optimized condition.

Table 1: Conc. (10^{-3} mg/mL) of cresol in A and B with different voltages and time.

Time (min)	5V		20V		30V		40V		50V	
	A	B	A	B	A	B	A	B	A	B
5	1.0	1.0	1.1	0.9	1.1	0.9	1.2	0.8	1.4	0.6
10	1.0	1.0	1.3	0.7	1.3	0.7	1.4	0.6	N/A	N/A
15	1.1	0.9	1.7	0.3	1.8	0.2	1.7	0.3	N/A	N/A
20	1.5	0.5	1.8	0.2	1.8	0.2	1.8	0.2	N/A	N/A
30	1.8	0.2	1.9	0.1	1.9	0.1	N/A	N/A	N/A	N/A
40	1.8	0.2	1.9	0.1	N/A	N/A	N/A	N/A	N/A	N/A
50	1.8	0.2	1.9	0.1	N/A	N/A	N/A	N/A	N/A	N/A
60	1.9	0.1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
90	1.9	0.1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
120	1.9	0.1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

N/A: not available

3.4 Effect of pH and temperature

In order to evaluate the effect of pH, phosphoric acid and sodium hydroxide were added into 0.5 mol/L Na_2HPO_4/NaH_2PO_4 solution to adjust pH from 2.0 to 12.0. Under low pH, the number of hydrogen ions increased. Although the current become higher and molecules could move faster, the hydrolysis of cresol decreased which would reduce the electrical driving force. Moreover, the negative electrode released large amount of hydrogen gas. And when pH increased to 12, the salts were precipitated more easily. So neutral pH would be selected.

Then the different temperature was evaluated. In Table 2, with the temperature increasing, the isolation time decreased. The time was shortened to 20 min under 40°C, but under higher temperature the system released too much hydrogen gas. So 40°C was decided as the optimized temperature.

Table 2: Conc. (10^{-3} mg/mL) of cresol in A and B with different temperature

Time (min)	30		35		40		45		50		60	
	A	B	A	B	A	B	A	B	A	B	A	B
5	1.1	0.9	1.1	0.9	1.1	0.9	1.2	0.8	1.3	0.7	1.5	0.5
10	1.3	0.7	1.3	0.7	1.5	0.5	1.5	0.5	1.6	0.4	N/A	N/A
15	1.7	0.3	1.7	0.3	1.8	0.2	1.7	0.3	N/A	N/A	N/A	N/A
20	1.8	0.2	1.9	0.1	1.9	0.1	N/A	N/A	N/A	N/A	N/A	N/A
30	1.9	0.1	1.9	0.1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

N/A: not available

4. Conclusion

A novel PVDF-Sil-IL membrane was successfully created and applied to isolate cresol in electrically driven device. The FT-IR proved the IL based silica was complexed with PVDF. In this method, the effects of several variables such as the type of salts, voltage, time, pH and temperature on membrane were experimentally evaluated. Finally, 20V of voltage and 20 min of isolation under neutral pH with 40°C was selected as the optimized condition. And in part B of tank, 90% of cresol was isolated to part A. The results proved that this membrane and device were potential technical and to be used as an efficient electrochemistry tool for the isolation of phenols compounds from water samples.

5. Acknowledgments

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