

Article

Hydrophobic Poly(ionic liquid) for Highly Effective Separation of Methyl Blue and Chromium Ions from Water

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Abstract: The hydrophobic poly(ionic liquid) of poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (PVI-TFSI) containing imidazolium cations and bis(trifluoromethanesulfonyl)imide anions was synthesized for the separation of methyl blue and chromium ions [Cr(VI)] from water. The adsorption of methyl blue and Cr(VI) in PVI-TFSI/water system reached equilibrium stage within 60 min and 12 h, and the maximum adsorbed percentage for methyl blue and Cr(VI) was 97.6% and 98.0%, respectively. The adsorption regime of either methyl blue or Cr(VI) for PVI-TFSI was in correspondence with the Langmuir adsorption model. The maximum adsorption capacity of PVI-TFSI for methyl blue and Cr(VI) was determined as 476.2 and 17.9 mg/g, respectively. The hydrophobic poly(ionic liquid) with a remarkable adsorbent capacity of methyl blue and Cr(VI) can be conveniently synthesized and shows potential in water treatment for the effective separation of organic dyes or heavy metal ions.

Keywords: poly(ionic liquid); adsorption; water treatment; methyl blue; chromium

1. Introduction

The removal of industrial pollutants from wastewater has attracted considerable attention in recent years [1,2]. As well known, industrial wastewater usually contains heavy metal ions [e.g., Cr(VI), Pb(II), Hg(II)] and organic pollutants (e.g., methyl blue, methyl orange). Lots of new technologies

have been employed to remove these hazardous substances, including biological treatment, adsorption, chemical oxidation, membrane filtration, coagulation and photochemical degradation [3,4]. Among the numerous treatment methods, adsorption has been widely accepted and used due to its high removal capacity, convenient operation, low cost and energy consumption. Various adsorbents including nanoporous silica, zeolite, hematite, MnO-Fe₂O₃, mesoporous TiO₂ and activated carbon with high specific surface area or plentiful ion exchange sites played an important role on the separation and purification of wastewater [5,6].

Ionic liquids (ILs), which are organic salts with melting temperature below 100 °C, have attracted significant interest due to good chemical and electro-chemical stability properties such as high ionic conductivity, polarity, heat capacity and thermal stability [7–11]. The functionality of ILs is tunable by adjusting molecular structures of the organic asymmetric cations (e.g., imidazolium, pyridinium, and tetraalkylammonium) and anions (e.g., halide, tetrafluoroborate, hexafluorophosphate, triflate, amidotriflate, dicyanamide) [12–15]. Recently, the researchers have focused on poly(ionic liquid)s (PILs) from the polymerization of IL monomers [16]. Compared to their monomers, the PILs possess good processability and membrane forming ability with potential in polymeric electrolytes, carbon dioxide absorbing materials, catalytic membranes, ionic conductive materials and microwave absorbing materials [17–24]. Different from normal water soluble polyelectrolytes, PILs can be tunable as hydrophobic but soluble in strong polar organic solvent such as DMF and DMSO by introducing the hydrophobic counter-ions (e.g., PF₆⁻, Tf₂N⁻) [25]. The hydrophobicity of PILs provides the possibility to absorb the heavy metal ions or organic pollutants from water by a convenient heterogeneous phase regime. The room temperature ionic liquids were employed as a novel media for liquid-liquid extraction [26] and the recovery of biofuels [27]. However, the usage of PILs as adsorbents to separate and remove methyl blue from water by a heterogeneous phase regime has been seldom reported up to date.

In this contribution, we report a convenient synthesis of hydrophobic PIL of poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (PVI-TFSI) via free radical polymerization. The solubility of PIL mostly depended on the type of the counter anions, so we selected bis(trifluoromethanesulfonyl)imide [(CF₃SO₂)₂N⁻] as the anion because of its hydrophobic characteristic [28,29]. Then the as-synthesized PVI-TFSI was used as adsorbent for the separation and removal of heavy-metal ions of Cr(VI) and methyl blue from their water solutions.

2. Experimental Section

2.1. Materials

The 1-vinylimidazole (99%), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 98%), 2,2'-azobis(isobutyronitrile) (AIBN, 99%) were purchased from J&K Tech. (Shanghai, China). The bromoethane (Alfa Aesar, 98%, Tianjin, China), *N,N*-dimethylformamide (DMF), methanol were supplied by Alfa Aesar (Tianjin, China). DMSO-*d*₆ was purchased from J&K Tech., Shanghai, China, and used as a solvent for nuclear magnetic resonance (NMR) measurement. Potassium chromate (K₂CrO₄, 99%) and methyl blue (99%) were used as received without further treatment.

2.2. Synthesis of Poly(1-vinylimidazole)

Poly(1-vinylimidazole) (PVI) was synthesized via free radical polymerization in solution as described as follows. The 1-vinylimidazole (1.0 g, 10.6 mmol), AIBN (0.01 g, 0.061 mmol) and DMF (3 mL) were charged into a 25 mL flame-dried Schlenk flask equipped with thermometer and stir bar. The solution was stirred and kept at 70 °C for 24 h. Then, the mixture was precipitated into toluene. The precipitate was dried at 30 °C under vacuum until constant weight. The product of PVI was a faint yellow solid with a yield of 90%. ¹H NMR (400MHz, DMSO-*d*₆, δ): 1.98 (2H, -CH₂-CH-N-), 3.04 (1H, -CH₂-CH-N-), 6.83 (2H, -N-CH=CH-N), 7.09 (1H, -N-CH-N-).

2.3. Synthesis of Hydrophobic PVI-TFSI

The hydrophobic PVI-TFSI was synthesized via anion exchange of poly(3-ethyl-1-vinylimidazolium bromide) (PVI-Br) and Li-TFSI. The bromoethane (2.4 g, 22 mmol) was added drop-wise into a 25 mL flask charged with PVI (1.0 g, 11 mmol, in terms of molar mass of monomer) and methanol (5 mL). Then, the mixture was refluxed at 60 °C for 20 h. After the methanol and unreacted bromoethane were completely evaporated from the solution, poly(1-ethyl-3-vinylimidazolium bromide) was dried under vacuum at 30 °C until constant weight (88.9% yield). PVI-Br (1.0 g) was dissolved in an aqueous solution (10 mL) with slight excess of Li-TFSI (2.8 g, 9.76 mmol) and stirred for 24 h at ambient temperature. The resultant poly(ionic liquid) phase was separated from the aqueous phase and washed with water. Here, the PVI-TFSI was washed with much water in order to remove the unreacted reactants and the by-product of LiBr. Then the AgNO₃ solution was added, where the emergence of AgBr precipitation indicated that bromide salts were eliminated from the PVI-TFSI. After completely evaporating the residual water and being dried under vacuum at 50 °C, the resulting poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (PVI-TFSI) was obtained as a light yellow solid with a yield of 80%. ¹H-NMR (400MHz, DMSO-*d*₆, δ): 1.42 (3H, -N-CH₂-CH₃), 2.32 (2H, -CH₂-CH-N-), 3.65 (2H, -N-CH₂-CH₃), 4.12 (1H, -CH₂-CH-N-), 7.03 (1H, -N-CH=CH-N-), 7.64 (1H, -N-CH=CH-N-), 9.09 (1H, -N-CH-N-).

2.4. Characterization

Nuclear magnetic resonance (NMR) measurement was carried on an INOVA-400 spectrometer (Varian, Palo Alto, CA, USA) in DMSO-*d*₆. Chemical shifts were referenced with tetramethylsilane (TMS). Water static contact angle was determined using the Rame-hart Model 250-F1 Standard Goniometer (Rame-hart, Succasunna, NJ, USA) with DROP image Advanced 2.1 at ambient temperature. A drop of ion-exchanged water (3 μL) was placed on the surface using microsyringe apparatus. Six parallel measurements were carried on for each sample, and the average value of contact angle was taken as the result for one sample. Thermogravimetric analysis (TGA) was conducted on a Netzsch STA449C F3 instrument (Netzsch GmbH & Co., Selb, Germany) at a heating rate of 10 K/min under argon atmosphere. The concentration of solution during the adsorption process was measured on an UV spectrophotometer (Shimadzu UV2550, Tokyo, Japan).

2.5. Adsorption Experiment

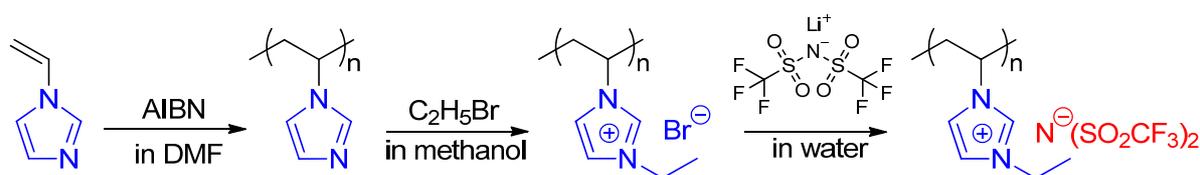
For the adsorption experiment, the water solutions that contained methyl blue (30 mL, 200 mg/L) and Cr(VI) ions (30 mL, 30 mg/L) were prepared. The K_2CrO_4 was used as the source of Cr(VI) ions. A certain amount of PVI-TFSI (20 or 50 mg) was added to the as-prepared solution under stirring for a certain time at room temperature. At each time interval, a sample of the suspension (2 mL) was removed and centrifuged to remove the solid adsorbent. The concentration of solution during the adsorption process was measured on an UV spectrophotometer. For the study of adsorption isotherm, the 10 mL solution of methyl blue or Cr(VI) with different concentrations was mixed with 10 or 50 mg of PVI-TFSI for a certain time, *i.e.*, 60 min and 12 h, respectively. The initial concentration of solution for methyl blue and Cr(VI) was 60 and 5 mg/L, respectively. After the adsorption, the hydrophobic solids of PVI-TFSI were easily separated by centrifugation. The concentration of residue solution was measured again on a UV spectrophotometer using a Beer's law plot constructed from a standard solution [6,30].

3. Results and Discussion

3.1. Synthesis of Hydrophobic Poly(ionic liquid)

The hydrophobic imidazolium-based poly(ionic liquid), *i.e.*, PVI-TFSI, was designed and synthesized as illustrated in Scheme 1. Here, we employed a polymerization route to prepare PVI-TFSI, *i.e.*, the polymerization of 1-vinylimidazolium with subsequent anion exchange. The anion exchange process was conducted by adding excessive lithium bis(trifluoromethylsulfonyl)imide into a poly(3-ethyl-1-vinylimidazolium bromide) solution to ensure the hydrophobicity of PVI-TFSI in a bulk state.

Scheme 1. Synthetic route of poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide) using a polymerization route.



In the 1H -NMR spectrum of PVI (Figure 1a), the resonance of protons in the imidazolium ring (Hc, Hd, and He) was clearly observed in the range of 6.6–7.6 ppm similar with the starting monomer of 1-vinylimidazolium. Obviously, the new peaks of Ha and Hb at 1.6–2.4 ppm and 2.8–3.3 ppm can be assigned to the protons on ethylene from the polymerization of vinyl group of 1-vinylimidazolium. Accordingly, the physical state of PVI turned to be solid state from liquid state of monomers due to the increase of molecular weight. After the reaction between PVI and bromoethane, the resonance of protons in the imidazolium ring (Hc, Hd, and He) shifted to 7.0–9.6 ppm due to the ethyl substitute with the resonance at 1.4 and 4.2 ppm (Hg and Hf) as shown in Figure 1b. According to the integral area of the peak of Hg and the peaks of Hc, Hd, He, about 70% of imidazolium rings was bonded with ethyl groups. Subsequently, to prepare the hydrophobic poly(ionic liquid), the bromide ions on PVI-Br

were further exchanged by bis(trifluoromethanesulfonyl)imide anions. From the $^1\text{H-NMR}$ spectrum in Figure 2, compared to PVI-Br, the chemical shifts of PVI-TFSI were eventually maintained except the protons of Hc and Hf, whose chemical shifts depended strongly on the nature of the near anion of bis(trifluoromethanesulfonyl)imide.

Figure 1. $^1\text{H-NMR}$ spectra of (a) PVI and (b) PVI-Br in $\text{DMSO-}d_6$ at 25 °C.

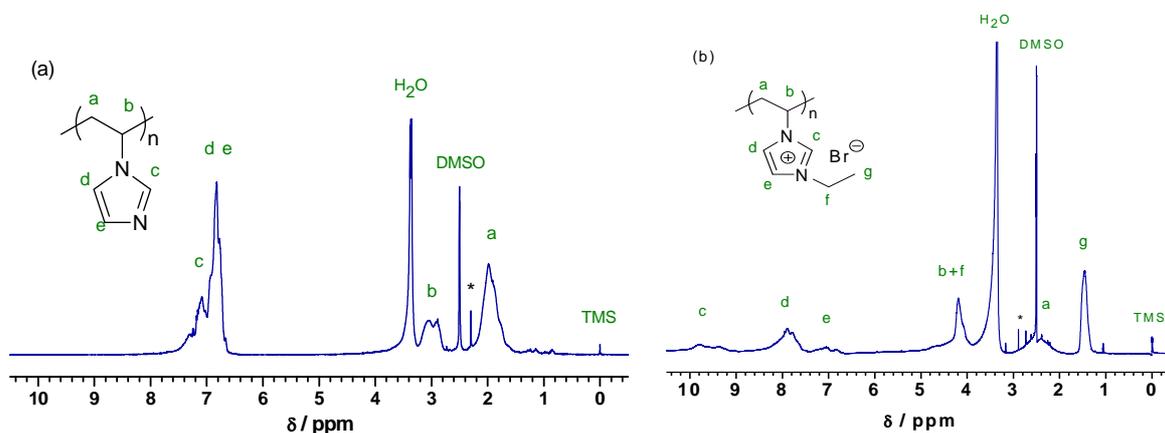
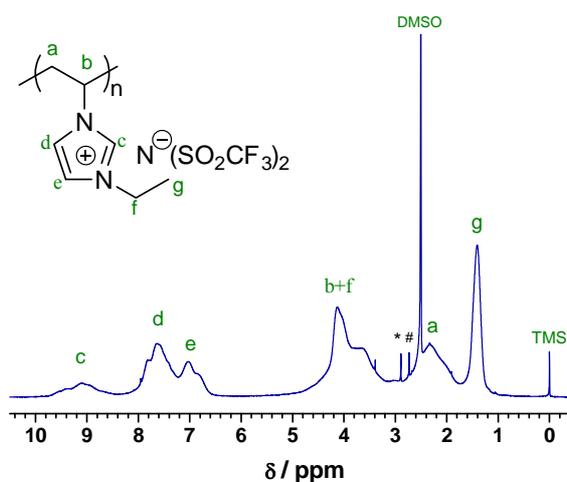


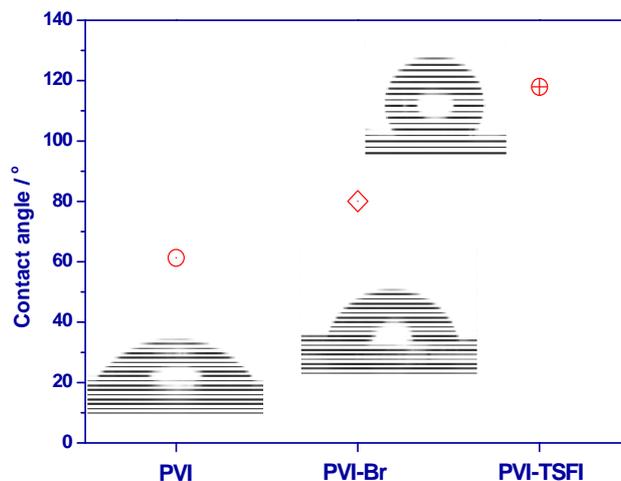
Figure 2. $^1\text{H-NMR}$ spectrum of PVI-TFSI in $\text{DMSO-}d_6$ at 25 °C.



3.2. Wettability of Poly(ionic liquids)

To demonstrate the wettability of PILs after the anion exchange, the static water contact angles (CAs) on the surface of PILs film are presented in Figure 3, where the corresponding water droplet shapes are enclosed. The CA of PVI and PVI-Br is about 61° and 79° , respectively. It indicates their hydrophilic nature because the polarity of either imidazole ring or bromide. However, after the anion exchange, the hydrophobic bis(trifluoromethanesulfonyl)imides were introduced into the pendent groups of PVI-TSFI as illustrated in Scheme 1. Thus, the bulk film of PVI-TSFI shows hydrophobicity with a CA of 115° . The hydrophobicity nature of PVI-TFSI provides the possibility for it to absorb heavy metal ions or organic pollutants from water by a convenient heterogeneous phase regime.

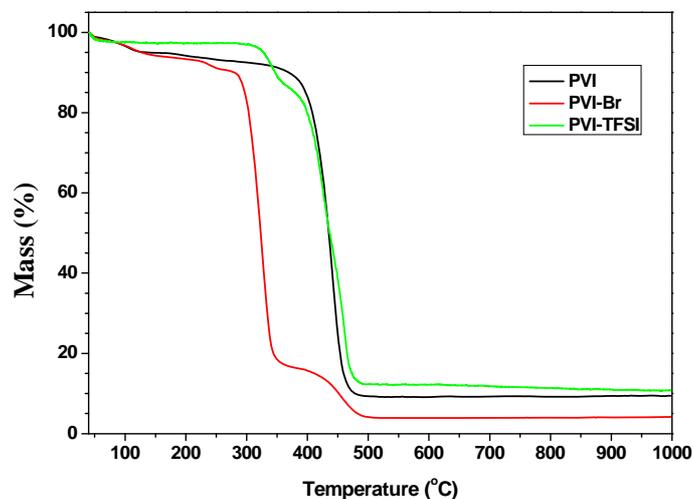
Figure 3. The static water contact angles and enclosed water droplet shapes of PVI, PVI-Br and PVI-TFSI.



3.3. Thermal Analysis of Poly(ionic liquid)s

The TGA curves of polymers including PVI, PVI-Br and PVI-TFSI are shown in Figure 4. The PVI shows great weight loss between 400 and 500 °C and the final mass loss is 90.6%. The PVI-Br exhibits earlier weight loss at 240 °C and possesses great weight loss of 95.8% up to a temperature of 1000 °C, which is attributed to the gaseous ethyl groups connecting on the imidazole ring. The PVI-TFSI exhibits an initial mass loss of about 15% at 375 °C due to the cleavage of the ethyl group connecting on the imidazole ring. The final mass loss about 89.2% of PVI-TFSI is more than those of PVI and PVI-Br because the strong electrostatic bonding force between $(CF_3SO_2)_2N^-$ and imidazole cation can decrease the volatilization of gaseous small molecules [e.g., H_2 , CH_4 and hydrocarbons CH_x ($x = 2-3$)] and the distillation of oligomer fragments during the heating.

Figure 4. TGA curves of PVI, PVI-Br and PVI-TFSI scanning from 40 to 1000 °C at a heating rate of 10 K/min under argon atmosphere.

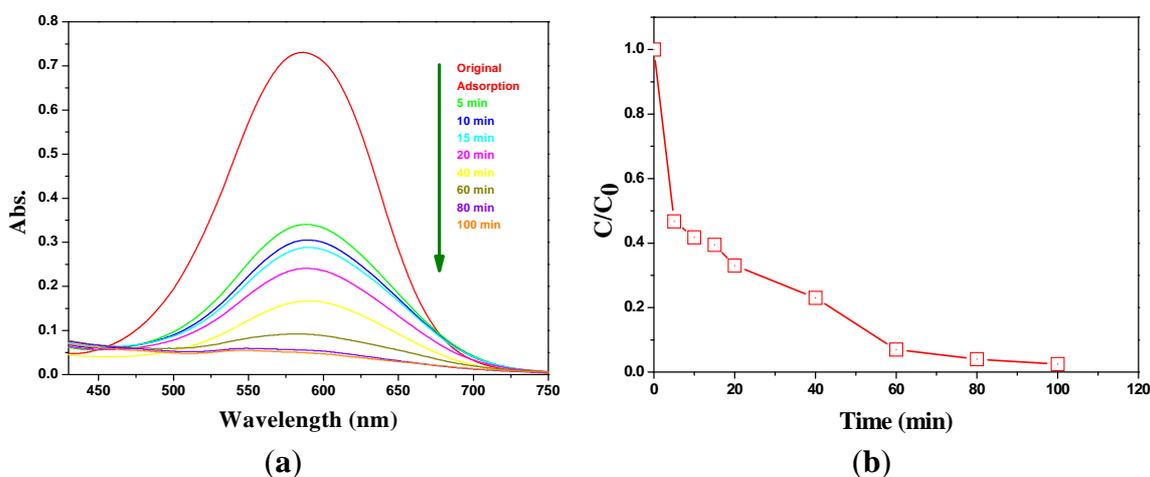


3.4. Absorption Behavior of Hydrophobic PVI-TFSI

3.4.1. Adsorption of Methyl Blue

Since the quantification of the pollutants was carried out by UV spectroscopy, the calibration curves should be prepared for methyl blue solution (Table S1 and Figure S1) and Cr(VI) solution (Table S2 and Figure S2) as shown in Supporting Information. The adsorption behavior of methyl blue and the dependence of concentration on absorption time are presented in Figure 5. The PVI-TFSI shows remarkable methyl blue-adsorption capability. The adsorption reaches equilibrium state within 60 min. The maximum adsorbed capability is 97.6%. From the photographs shown in Figure 6a, it can be obviously seen that the color of methyl blue solution is changed from dark blue to light one, indicating that the almost all of the methyl blue molecules in the solution are adsorbed after 60 min. The results indicate that more than 97% of methyl blue in the solution can be separated and removed in a short time when the PVI-TFSI is used as an adsorbent. Considering the electronegativity of methyl blue, the main reasons for the high effective absorption is the electrostatic force and van der Waals force between PVI-TFSI and methyl blue molecules.

Figure 5. The temporal evolution of UV spectral of methyl blue solution at the presence of PVI-TFSI (a) and the dependence of concentration of methyl blue on absorption time (b).



3.4.2. Adsorption of Cr(VI)

Similarly, the adsorption behavior of Cr(VI) and the dependence of concentration on adsorption time are presented in Figure 7. The PVI-TFSI exhibited highly efficient Cr(VI) separation and removal capability. The maximum adsorbed percentage for Cr(VI) is 98%. Furthermore, the PVI-TFSI shows fast adsorption rate at the initial stage, and more than 72% of Cr(VI) ions are effectively adsorbed within 6 h. Then adsorption rate decreases after 6 h and reaches equilibrium within 24 h. From the photographs in Figure 6b, the Cr(VI) solution with yellow color becomes nearly colorless after 24 h, also indicating that most of the Cr(VI) in the solution is adsorbed by the PVI-TFSI. It can be ascribed to the electrostatic force and van der Waals force between the amines on imidazole ring and the CrO_4^{2-} ions dissociating in water.

Figure 6. Photographs of the methyl blue solution (a) and Cr(VI) solution (b) adsorbed by PVI-TFSI after 100 min and 24 h, respectively.

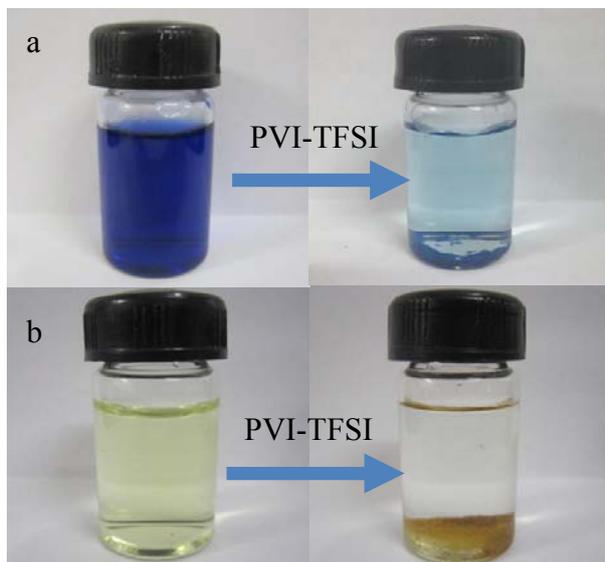
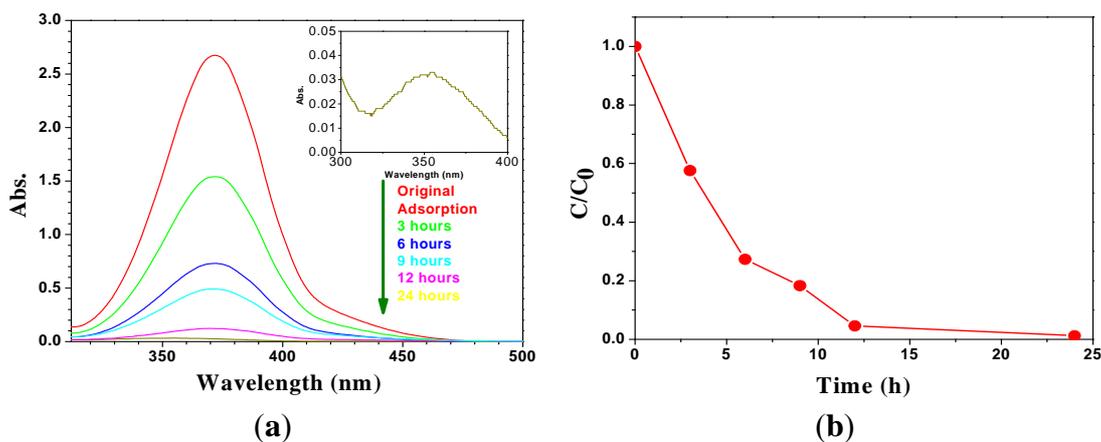


Figure 7. The temporal evolution of UV spectral of Cr(VI) solution at the presence of PVI-TFSI (a) and the dependence of concentration of methyl blue on adsorption time (b).



3.4.3. Adsorption Isotherms

The adsorption isotherms of methyl blue and Cr(VI) at different initial concentration are illustrated in Figure 8. In the low concentration range, the adsorption capacity for both methyl blue and Cr(VI) linearly increased with the increase of concentration. In the high concentration range, the increasing trend of adsorption capacity was slow. Since the linear growth of the adsorption capacities was retarded in the high concentration region and there is a trend to flatten, the highest determined concentration of Cr(VI) solution was set as 30 mg/mL. The Langmuir adsorption model can be used in this experimental [31], which represents the relationship between the equilibrium concentration of the solute (C_e , mg/L) and the amount of methyl blue and Cr(VI) adsorbed at equilibrium (q_e , mg/g).

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{1}$$

In Equation (1) [32], C_e is the equilibrium concentration (mg/L), q_e is the equilibrium adsorption capacity (mg/g), b is the Langmuir adsorption equilibrium constant (L/mg) and q_m is the maximum adsorption capacity (mg/g).

As illustrated in Figure 9, the linear relationship was obtained for either methyl blue or Cr(VI). The according correlation coefficient (R^2) is 0.991 and 0.943, respectively. It indicates that our experimental data fit with the Langmuir adsorption model well. According to the adsorption isotherms, the maximum methyl blue adsorption capacity and Cr(VI) adsorption capacity of PVI-TFSI was estimated to be 476.2 and 17.9 mg/g, respectively. It indicates that PVI-TFSI possesses potential as an important adsorbent for the purification of water containing methyl blue and Cr(VI) ions.

Figure 8. The adsorption isotherms for methyl blue (a) and Cr(VI) solution (b) by PVI-TFSI.

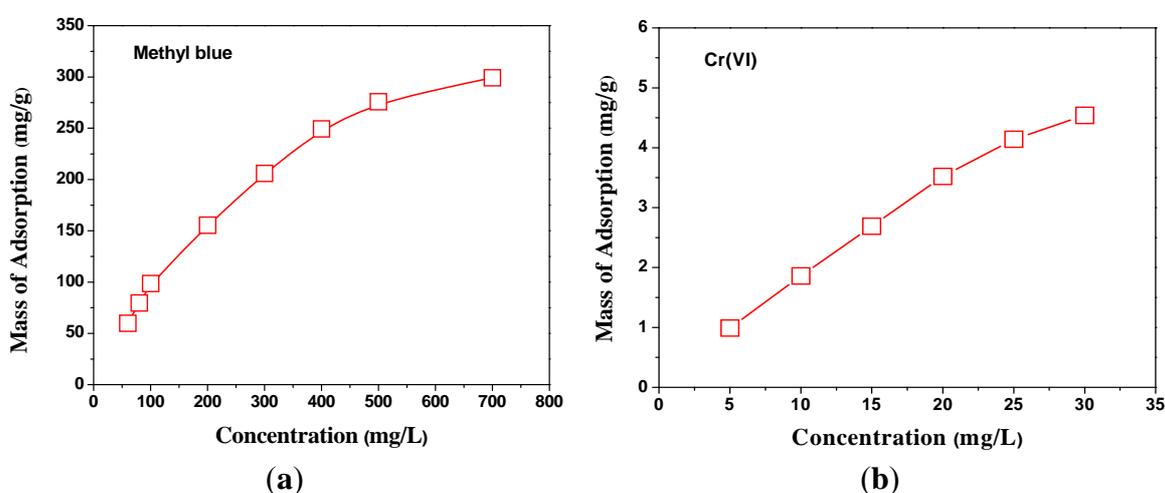
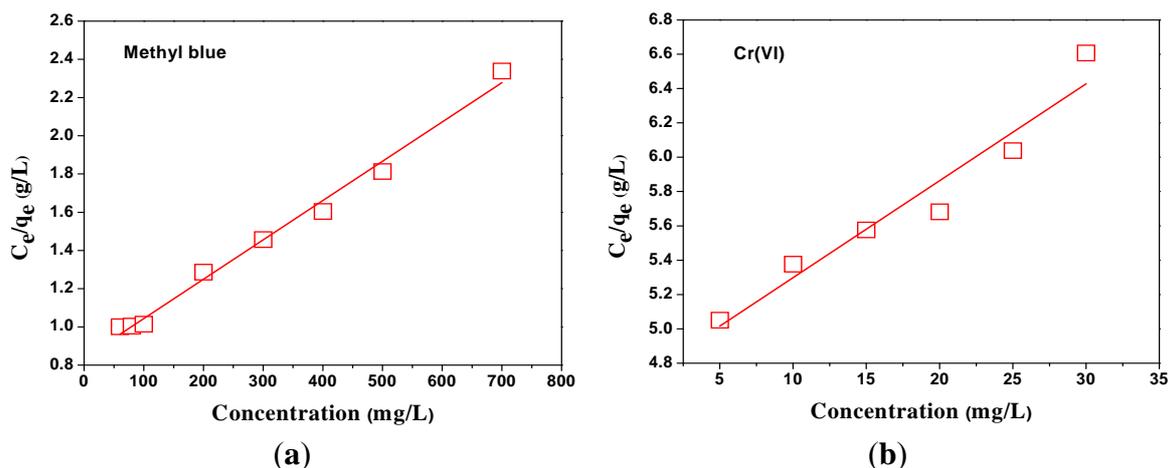


Figure 9. Langmuir adsorption isotherms for methyl blue solution (a) and Cr(VI) solution (b) by PVI-TFS.



4. Conclusions

In summary, the hydrophobic PVI-TFSI was conveniently synthesized by free radical polymerization and subsequent anion exchange. The bis(trifluoromethanesulfonyl) anion is a key factor to obtaining hydrophobic PVI-TFSI, which is an effective adsorbent for methyl blue and Cr(VI) in

water solution and exhibits high adsorption capacity. The Langmuir adsorption model is suitable to describe the methyl blue and Cr(VI) adsorption with the maximum adsorption capacity of 476.2 and 17.9 mg/g at ambient temperature, respectively. Due to the high adsorption capacity and convenient heterogeneous phase regime, hydrophobic poly(ionic liquid) has potential in the separation and removal of organic dyes or heavy metal ions from water.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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