

Preparation and Formation Mechanism of Porous Polyurea by Reaction of Toluene Diisocyanate with Water and Its Application as Adsorbent for Anionic Dye Removal*

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Abstract A novel and easy one-step protocol for preparation of a new porous material, polyurea (PPU), is reported, which is accomplished through a precipitation polymerization of toluene diisocyanate (TDI) in mixed solvent of H₂O-acetone without need for surfactant and porogen. Effects of TDI concentration, mechanical stirring, solvent composition and TDI addition rate on PPU structure are studied. Surface morphology and pore structure of PPU are characterized by scanning electron microscopy and Hg intrusion. Chemical structure of the PPU polymer is investigated using NMR, XRD and FTIR. Mechanism of pore formation is discussed. The obtained PPU is used as adsorbent for anionic dyes adsorption investigation. Two anionic dyes, remazol brilliant blue R and acid fuchsine, are tested. The results indicate that the as-prepared PPU is of high performance in dye adsorption and recycled use. This study provided therefore a facile route to the preparation of a novel and attractive adsorbent candidate for removal of anionic dyes from wastewaters.

Keywords: Precipitation polymerization; Porous polyurea; Toluene diisocyanate; Anionic dyes adsorption.

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INTRODUCTION

Porous materials are a series of network structure materials consisting of inter-permeated or closed pores. They are classified as microporous (pore size < 2 nm), mesoporous (pore size 2–50 nm) and macroporous (pore size > 50 nm) materials, respectively, according to their pore size. These porous materials may be inorganic^[1], natural^[2] and synthetic polymer^[3, 4] or their combinations^[5, 6]. By virtue of the easy control of their specific surface area and their designable pore structure and functionalization, porous polymers are widely applied to various fields, such as ion-exchange^[7], adsorption^[8], catalysis^[9], chromatography^[10, 11], solid phase extraction^[12], new energy^[13], biological technology and tissue engineering^[3, 14, 15], active substance carrier^[16], microreactor^[17] and sensor technology^[6, 18] etc.

The methods for preparation of porous polymer materials commonly include, for examples, suspension polymerization, high internal phase emulsion^[19] or dispersion polymerization^[20] and a variety of emulsion polymerization^[21, 22]. All these are often labeled as heterogeneous polymerization, surfactants and stabilizers are

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needed to ensure the formation of the pores in the outcome polymer and the stability of the polymerization. In addition, prior to their practical application, the porous materials thus obtained are usually subjected to a chemical modification in order to endow them with functional groups, such as amine, sulfonate, hydroxyl, carboxyl, imine^[23–26], thiol and amidoxime^[26, 27] *etc.*, which are essential for specific applications. This means that, for the preparation of functional porous polymers, multiple steps, including polymer synthesis and surface modification, are needed, and each step is more or less sophisticated with long-lasting and high energy consuming. And the surface modification often leads to adverse effects on the porous materials^[27]. Furthermore, the organic porogens, surfactants and stabilizers commonly used in these processes, hard to be full removed, are unpleasant, particularly for applications in biomedical fields.

Recently, our studies have been focused on the preparation of monodisperse polymer microspheres by precipitation polymerizations, through free radical polymerization^[28–30] or step-growth polymerization of diisocyanate with amine^[31–34]. Based on isophorone diisocyanate (IPDI), highly uniform polyurea microspheres were prepared at high yields^[31–33]. A porous polyurea (PPU) was also prepared through a facile one-step precipitation polymerization using toluene diisocyanate (TDI) instead of IPDI as the sole monomer without any additives such as porogen, surfactant or stabilizer^[34, 35]. In this paper, preparation of the PPU materials was optimized, and mechanism of the pore formation was proposed. Furthermore, two anionic dyes, remazol brilliant blue R (RBBR) and acid fuchsine (AF), were selected to test the adsorption performance of PPU and its reusability.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI, industrial grade, Beijing Keju Chemical Materials Co. Ltd.), acetone (AR, Laiyang Fine Chemicals), and ethanol (AR, Tianjin Fuyu Fine Chemicals) are all domestic products. The dyes used in this work are remazol brilliant blue R (RBBR, AR, Sigma) and acid fuchsine (AF, AR, Tianjin Damao Chemicals). Their structures are given in Fig. S1 in Supporting Information. All the chemicals were used as received without further purification.

Preparation of PPU

In a typical process for PPU preparation, 90.0 g of H₂O-acetone mixture at mass ratio of 3/7 was first located into a round bottom flask of 250 mL, and immersed in a water bath at 30 °C. Under stirring at 300 r·min⁻¹, 10.0 g of TDI (10 wt% in the polymerization system) was supplied at a rate of 20 mL·h⁻¹. The polymerization was allowed to continue for 2 h after completion of TDI addition, followed by centrifugation and filtration. The filtrate was dried at 70 °C under vacuum for 12 h to collect the white powdery product. Based on this process, different PPU materials were prepared by varying TDI concentration, solvent composition and stirring rate during the synthesis.

Characterization of PPU

Morphology of PPU was examined using a scanning electron microscope (SEM, Quanta FEG-250). Surface area and pore volume were tested by mercury (Hg) intrusion porosimetry (AutoPore IV 9500). Spectrophotometric determination for dye concentration in adsorption and desorption tests was carried out on a UV-Vis spectrometer (Perkin-Elmer, Lambda 35). Fourier transform infrared analysis (FTIR) was done using Spectrum GX of Perkin-Elmer. For high-resolution NMR analysis, PPU was dissolved in DMSO-d₆, the tests were carried out on a Brüker instrument (Advance III) at 400 MHz for ¹H and 100 MHz for ¹³C. Spectra were obtained with a 5-mm-QNP probe at 298 K with tetramethylsilane as the internal reference. Powder X-ray diffraction (XRD) was recorded on a diffractometer (Brüker D8 Focus) in the 2θ range from 6° to 60° using a Cu-K radiation source. DSC (Differential scanning calorimetry) was conducted, from 30 °C to 450 °C at a heating rate of 5 K·min⁻¹, using a Mettler-Toledo instrument (DSC 822) in a nitrogen atmosphere. DTA (Differential thermal analysis) and TGA (thermogravimetric analysis) were conducted using a Perkin-Elmer equipment (Pyris Diamond TG/DTA) with the temperature range scanned from 30 °C to 500 °C at a heating rate of 10 K·min⁻¹ in a nitrogen atmosphere.

Dye Adsorption

PPU of known mass (m) was added to a glass bottle of 25 mL, followed by addition of 20.00 mL of dye aqueous solution (V), with known concentration (c_0 , $\text{mg}\cdot\text{mL}^{-1}$) and pre-adjusted pH. The bottle was fixed on a reciprocating oscillator (SHZ-88, Jintan Medical Instruments, Jiangsu, China) in water bath with temperature set at 30 °C and shaken for 4 h at 120 $\text{osc}\cdot\text{min}^{-1}$. The content was centrifuged at 12000 $\text{r}\cdot\text{min}^{-1}$ (HC-3514, Zonkia) for 5 min to separate the PPU out of the dye solution, the supernatant was taken and analyzed using a spectrophotometer (Perkin-Elmer, Lambda 35) at 592 nm wavelength for RBBR and 540 nm for AF. Through the working curves of each dye absorbance at corresponding wavelength versus its concentration established prior to the test, dye concentration (c_e , $\text{mg}\cdot\text{mL}^{-1}$) in the supernatant was obtained. Dye amount adsorbed per gram of PPU (q_e) and its percentage relative to the initial amount (adsorption rate E , %) were calculated by Eqs. (1) and (2):

$$q_e = \frac{(c_0 - c_e) \times V}{m} \quad (1)$$

$$E(\%) = \frac{(c_0 - c_e)}{c_0} \times 100\% \quad (2)$$

Dye Desorption and Regeneration

For the desorption test of each dye, PPU of known mass after equilibrated adsorption was separated, dried up under vacuum at 70 °C and packed into a glass column (ϕ 10 mm $\times$ 200 mm). 200 mL of the desorption solvent (H_2O , NaOH solution of 0.01 $\text{mol}\cdot\text{L}^{-1}$ and equal volume mixture of H_2O -ethanol, or H_2O -EtOH) was flowed as the eluent through the column at rate of 100 $\text{mL}\cdot\text{h}^{-1}$. The eluent was collected at the outlet. Dye concentration in the eluent was detected by spectrophotometry as described above in dye adsorption test, and dye desorption rate was calculated. The PPU after dye elution was filtrated and rinsed several times with deionized water to fully remove the eluent, dried in a vacuum oven at 70 °C, and reused for the adsorption and desorption in the subsequent cycles of tests.

RESULTS AND DISCUSSION

Chemical Reactions in PPU Preparation and Its Porous Characteristics

As described above, PPU was prepared through reaction of isocyanate groups (NCO) with water, using TDI as the only monomer, water and acetone as solvent. Experiments show that TDI was 100% converted to polymer thanks to the step polymerization mechanism involved^[32, 34] as schematized in Fig. 1. NCO of TDI first reacts with water in the mixed solvent to produce carbon dioxide and amine. The amine generated will further react with NCO to form polyurea. It is believed that the PPU as prepared is consisting of only linear polyurea, the hydrogen on the *in situ* formed carbamido is unlikely to react with NCO groups, because specific conditions (high temperature, catalyst) are reportedly required for this reaction to occur^[36].

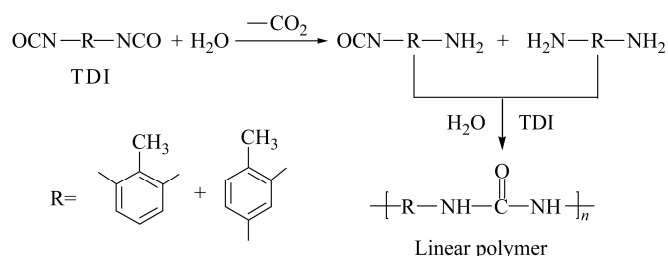


Fig. 1 Schematic presentation of PPU synthesis through precipitation polymerization of TDI with water

Pore volume and pore size distribution curves from Hg intrusion test of a sample, prepared with 10 wt% of TDI in H_2O /acetone mass ratio of 3/7 and at 300 $\text{r}\cdot\text{min}^{-1}$ stirring, are given in Fig. 2. At start of the test at low

pressure, larger pores were first filled with Hg, followed gradually by Hg intrusion in the pores of smaller size with pressure increase. Figure 2 demonstrates that the accumulated pore volume was in constant increase in the tested range of the pore size (3 nm to 130 μm), indicating the presence of the pores with continuous size variation in the tested span. The largest contribution to pore volume was by large pores with size varying from 10 μm to 40 μm , followed by those from 3 nm to 100 nm, indicating the abundant presence of the pores size within these ranges. To visualize the structure and morphology of this material, SEM photos of this sample are given in Fig. 3, one at low magnification for a general view and another at high magnification to show the general porous structure of this PPU.

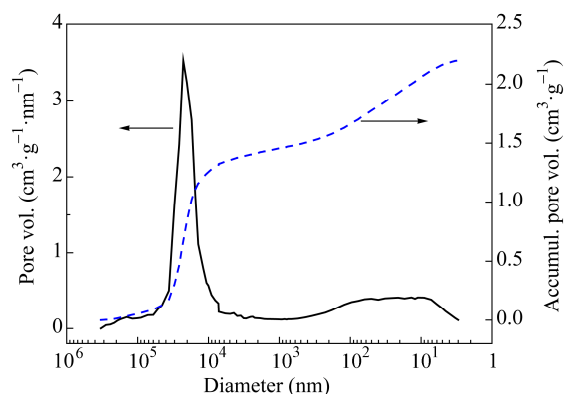


Fig. 2 Accumulated pore volume and pore size distribution of PPU prepared with 10 wt% of TDI and H_2O /acetone mass ratio of 3/7 under $300 \text{ r} \cdot \text{min}^{-1}$ stirring

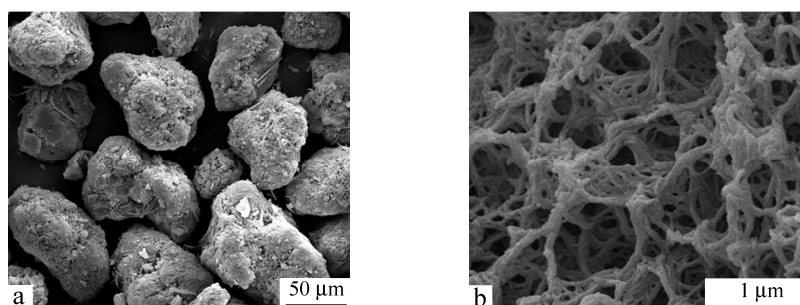


Fig. 3 SEM photos of PPU prepared with 10 wt% of TDI and H_2O /acetone of 3/7 under $300 \text{ r} \cdot \text{min}^{-1}$ stirring

Effect of Monomer Concentration

In a first set of polymerizations, the effect of monomer concentration on the morphology of PPU was explored with TDI concentration varied from 2.5 wt% to 40.0 wt%. SEM pictures of selected PPU samples are given in Fig. 4.

Micron-sized pores are clearly seen in the porous PPU prepared with TDI concentrations below 30.0 wt%, especially at 5.0 wt% (Fig. 4b) and 10.0 wt% (Fig. 3b). The porous materials were fiber-like polymers. The data from mercury intrusion are listed in Table 1. The results show clearly that, at lower TDI concentration, mainly large pores were formed. The sample prepared with 2.5 wt% of TDI showed therefore the largest pore volume ($5.65 \text{ cm}^3 \cdot \text{g}^{-1}$) and the lowest specific surface area ($26.91 \text{ m}^2 \cdot \text{g}^{-1}$) among all the samples. With TDI concentration increased to 10 wt%, a sharp increase in the specific surface area was observed with an obvious decrease in pore volume, indicating that the number of the large pores was decreasing, while that of small ones were increasing. Alternatively speaking, the sizes of all the pores became smaller at higher TDI concentrations. However, with further increase in TDI concentration up to 20 wt% or higher, the specific surface area remained relatively constant or slightly changed while the pore volume was in gradual decline, making the values for the

specific surface area at 10 wt% of TDI the highest among all the samples. These observations strongly suggest that the pore formation mechanism is closely associated with TDI concentration.

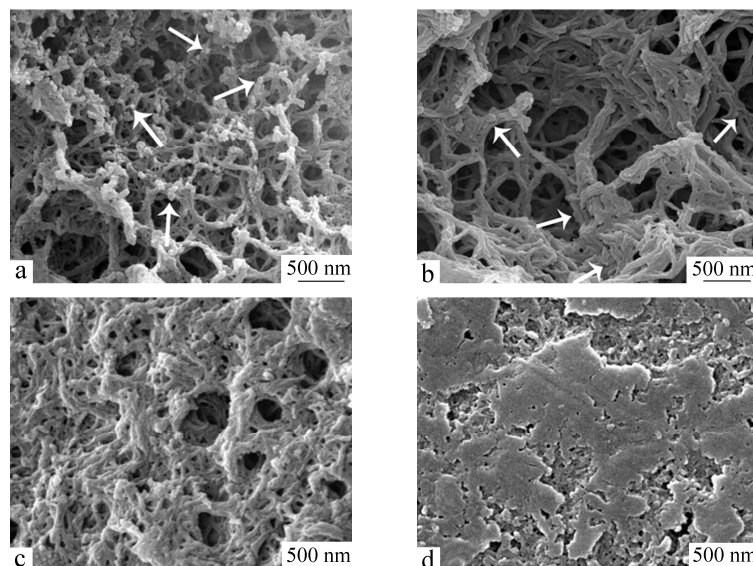


Fig. 4 SEM images of PPU obtained with varied TDI concentrations: (a) 2.5 wt%, (b) 5.0 wt%, (c) 20 wt% and (d) 30 wt%

Table 1. Pore parameters of PPU prepared with varied TDI concentration

TDI (wt%)	Specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)
2.5	26.91	5.65
10.0	161.68	2.20
20.0	154.39	1.44
30.0	156.00	1.08

Formation Mechanism of the Porous Material

It is to point out that the process is a veritable precipitation polymerization like the one with IPDI^[31, 32]. And it is particularly important to note that TDI was added at a constant rate of $20 \text{ mL} \cdot \text{h}^{-1}$, which means that the polymerization at higher TDI concentration was in fact an extension of the one at lower concentration. For example, the run with 10 wt% of TDI (TDI feeding time about 30 min) with a quarter of TDI added was exactly the same as that of 2.5 wt% (about 7.5 min of TDI feeding); And the run with 2.5 wt% of TDI was exactly identical to that with 10 wt% of TDI if actual TDI feeding time was extended to 30 min (to reach 10 wt% for TDI). Based on this point, it is conceivable that the morphology and properties of the PPU prepared with higher TDI was the further developed form of those prepared with lower TDI concentration.

Up to date, precipitation polymerization has been often used as an effective means for preparation of uniform microspheres^[28–32, 37]. The correlative mechanism proposed by Stöver *et al.*^[37] is commonly accepted, which suggests there are two steps in the process with regard to microsphere production: the nucleation of the primary particles and their growth. The nucleation occurs once the oligomers reach their critical length, where they become insoluble in the solvent; the growth of these particles is accomplished through an “entropy process”. Namely, particle growth is accomplished either by polymerization of oligomers adsorbed on the surface of the primary particles regardless of their length, or by direct polymerization of monomers with reactive groups available on the same surface. During the polymerization, the stability of the particles is assured by the presence of a hairy layer consisting of soluble chain terminals with reactive functional groups chemically bonded to the particle surface. These soluble chain ends tend to extend towards the solvent phase to maximize the entropy of the system, as defined by the mechanism, and to protect the particles from collision and aggregation. Their continuous reaction with oligomers or monomers contributes to the particle growth.

In the present polymerization, no microspheres were produced, which indicates that, either there was no particles formed, or primary particles were formed but their aggregation occurred soon after their formation, leading to the porous materials as observed. Based on the chemical structure of TDI, it is easy to understand that the oligomers (rich in aromatic rings) must be highly rigid, and are prone to precipitate out once formed. The particles thus nucleated, hardly to be spherical because of the chain's rigidity, were most probably not having the flexible chain ends required to maintain their stability, and a quick aggregation of the particles would take place. With progress of the polymerization, further aggregation between the aggregated primary particles was not excluded, producing the porous materials in large blocks of several dozens of microns.

This is quite similar to the phase separation commonly seen in preparation of porous materials. It is well known that phase separation of the polymer from the solvent leads to the formation of large pores^[38, 39], and so does the partial aggregation of small particles, particularly with polymers and primary particles of high rigidity, which do not allow them to rearrange their shape, causing the final materials with low space packing and with pore size much larger than that of the interstices when the particles are closely packed. Based on these analyses and taking into accounts of TDI structure and the experimental observation, it is likely that the polyurea oligomers would have precipitated out quite soon after their formation to generate small primary particles, which in turn would quickly aggregate short of the flexible polymer chains terminals. It is believed that the polymer chain ends, though their number is not large enough to protect the particles from aggregation, were acting, together with the monomer and the oligomers available for surface reaction, as adhesive to stick together the primary particles and the subsequent aggregates, resulting in PPU with large pore and low specific surface area at lower TDI concentration.

With more TDI addition at constant rate after the formation of primary particles, and particularly after the formation of PPU with large pores (as the case with TDI concentration of 2.5 wt%), different reactions could occur for TDI. One is the reaction with water; the other is that with the amine *in situ* produced from TDI reaction with water. It is commonly accepted that the reactivity of TDI with amine is much higher than that with water^[40, 41]. In a previous study on precipitation polymerization of IPDI, it was revealed that the reaction of isocyanate with water was quite slow at start of the reaction, and it was significantly accelerated with more than doubled reaction rate after a period of time, which was ascribed to the presence of the *in situ* formed amine groups^[41]. It is therefore rational to believe that TDI added after PPU formation reacted preferentially with amines rather than with water. It is to note that the amine groups were mainly present on the surface of the precipitated polymer particles at this stage of polymerization, and that the solvent trapped inside the pores was probably consisting of more acetone than that in the continuous solvent phase because acetone is more compatible with the polymer. All these enable one to believe that newly added TDI was driven thermodynamically towards existing PPU, particularly inside the pores. And there its reactions took place, filling up the larger pores formed at early stage where low TDI amount was added (low TDI concentration). Keeping in mind that TDI itself and the oligomers are of high rigidity, the adherence under any form onto the interface of PPU-solvent is alike a simple pileup, particularly when PPU surface is rough, because these rigid oligomers lack sufficient conformational flexibility to allow them to rearrange their shape to pack space efficiently. Under this circumstance, there will be solvent trapped between the new pileup and the existing PPU. Evaporation of the trapped solvent molecules will leave micron-sized pores. This is very similar to the process for fabrication of microporous materials by direct synthesis method^[39] and that for fabrication of materials of intrinsic microporosity^[42, 43], where commonly used monomers are of high rigidity consisting of aromatic rings, like TDI in this work.

The data listed in Table 1 are well understood with above interpretation. At low (2.5 wt%) TDI concentration, only large pores were produced, along with a low specific surface area. This indicates that the large pores were formed mainly by aggregation of primary particles, and eventually by further aggregation of the aggregated primary particles. Careful examination on the SEM photos (Figs. 4a and 4b) indicated that a few tiny particles were in fact present as pointed by the white arrows. With TDI concentration increased to 10 wt%, a significant increase in the specific surface areas (to 161.68 m²·g⁻¹) occurred, ascribable to the formation of a

large amount of small pores of nanometer scale, and that the large pores, observed in the sample with 2.5 wt% of TDI concentration, were mostly filled up by rigid polymers formed by post-added TDI. The distinct decrease in pore volume (from $5.65 \text{ cm}^3 \cdot \text{g}^{-1}$ with 2.5 wt% of TDI to $2.20 \text{ cm}^3 \cdot \text{g}^{-1}$ with 10.0 wt% of TDI) was in accord with this interpretation. Further increase in TDI concentration entrained only a slight decrease in pore volume, whereas the specific surface areas remained relatively constant. More addition above 10.0 wt% of TDI contributed to fill the rest of the large pores. While this caused a slight decline in pore volume, the effect on specific surface area was not obvious. All these are in good agreements with the morphology evolution of PPU with TDI concentration as shown by SEM photos given in Fig. 4 and with the results shown in Table 1. This mechanism of pore formation is schematically presented by Fig. 5.

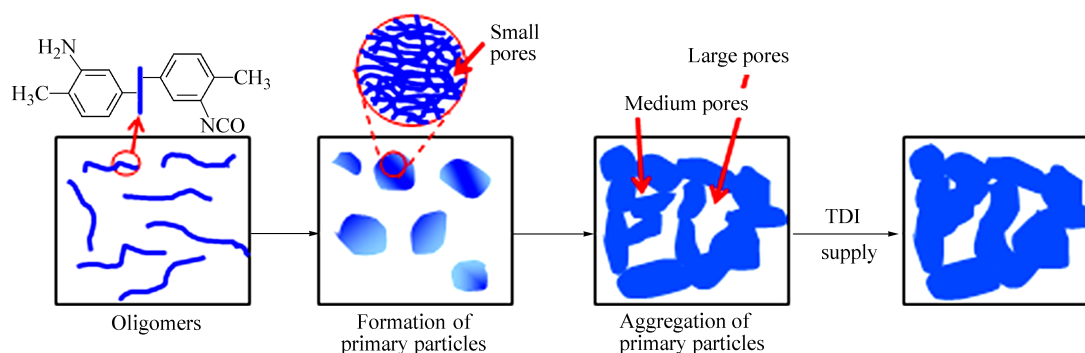


Fig. 5 Schematic presentation of pore formation in porous polyurea produced by precipitation polymerization of TDI in H_2O -acetone

Effect of Mechanical Stirring

It is known that mechanical stirring plays an important role in the formation of porous materials. PPU was then prepared with 10 wt% of TDI concentration at varied stirring rates from $100 \text{ r} \cdot \text{min}^{-1}$ to $500 \text{ r} \cdot \text{min}^{-1}$. The porous characteristics of the PPU are listed in Table 2. Compared with the sample prepared at $300 \text{ r} \cdot \text{min}^{-1}$, the data for the sample prepared with reduced stirring at $100 \text{ r} \cdot \text{min}^{-1}$ demonstrate clearly that, the specific surface area of PPU was dramatically declined (from $161.68 \text{ m}^2 \cdot \text{g}^{-1}$ to $14.54 \text{ m}^2 \cdot \text{g}^{-1}$, concomitantly with an obvious increase in pore volume (from $2.20 \text{ cm}^3 \cdot \text{g}^{-1}$ to $4.06 \text{ cm}^3 \cdot \text{g}^{-1}$). With stirring rate raised from $300 \text{ r} \cdot \text{min}^{-1}$ to $500 \text{ r} \cdot \text{min}^{-1}$, the specific surface area was slightly increased, along with also a moderate decrease in the pore volume. These data indicate that, to prepare a good porous polyurea by this process, a stirring of $300 \text{ r} \cdot \text{min}^{-1}$ or higher was necessary. For a run without any stirring, phase separation was observed shortly after the start of the polymerization with a clear top layer. The polymers settled as sediment and were presented in the form of a solid block when dried up.

Table 2. Pore parameters of PPU prepared with varied mechanical stirring

Stirring ($\text{r} \cdot \text{min}^{-1}$)	Specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Porosity (%)
100	14.54	4.06	52.03
300	161.68	2.20	71.77
500	162.99	1.79	49.42

Effect of Solvent Composition

In precipitation polymerization, the composition of the binary solvent usually imposes great influence on the polymerization process and the morphology of the final polymers^[28–32]. PPU was therefore prepared with fixed TDI concentration but different H_2O /acetone mass ratios. Hg intrusion test was carried out for the samples, and the results are given in Table 3. The data show that, amongst all the samples, the largest specific surface area with the highest pore volume was observed for PPU prepared with H_2O /acetone mass ratio of 3/7. While reducing water content in the solvent to 1/9 caused declines in both specific surface area and pore volume; the decline in specific surface area was much more significant for PPU synthesized at higher H_2O /acetone ratios (*i.e.*

5/5 and 7/3). From Fig. 2, it is known that the sample prepared with H₂O/acetone ratio of 3/7 possessed both large (10 μ m to 100 μ m) and small pores (10 nm to 100 nm). By examining the pore size distribution of the samples prepared with a lower H₂O/acetone ratio (1/9, see Fig. S2 in Supporting Information), it was seen that the large pores remained, the small pores shifted to smaller side, and both with reduced intensity in pore volume; At higher H₂O/acetone ratio (*i.e.* 7/3), the large pores were detected, while the small pores disappeared. TDI and its oligomers are known to be more soluble in acetone than in water. More acetone in the solvent would increase the flexibility of the oligomers and it was easier for them to adopt themselves so that to achieve a more compact packing both for the oligomers and for the aggregated primary particles, leading to therefore a decrease in the pore volume for both the large and the small pores.

Table 3. Pore parameters of PPU prepared with varied H₂O/acetone mass ratios

H ₂ O/acetone (mass ratio)	Specific surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Porosity (%)
1/9	126.78	2.02	71.20
3/7	161.68	2.20	71.77
5/5	45.53	2.07	48.17
7/3	61.41	1.70	65.66

At higher H₂O/acetone ratio, the disappearance of the small sized pores may indicate that the oligomers precipitated out earlier with lower degree of polymerization, and so was the aggregation of the primary particles and pore formation. This advancement in pore formation would lead to more TDI available for post-reactions after pore formation. In addition, these post-reactions were more likely to occur in the pores than in the solvent phase because TDI is less compatible to the solvent of high water content. As afore mentioned, the solvent trapped inside the pores is probably consisting of more acetone than that in the continuous phase, which would facilitate TDI reactions to occur inside the pores, making the pores being filled up by the newly formed polymers. Obviously, the possibility to have TDI reactions in the pores of smaller size is higher, leading to disappearance of these pores (< 100 nm, for instance), and the large pores becoming smaller. These results demonstrate that solvent composition has important impact on the resulting materials. PPU with high specific surface and broad pore size distribution were achieved with the binary solvent at H₂O/acetone mass ratio of 3/7, specific surface area and pore volume were decreased no matter this ratio was increased or decreased.

PPU Structures Characterization

A sample, prepared with 10 wt% of TDI and H₂O/acetone mass ratio of 3/7 with stirring at 300 r·min⁻¹, was subjected to FTIR analysis (For the spectra, see Fig. S3 in Supporting Information). The spectra showed strong absorption peaks at 3303 cm⁻¹ (stretching vibration of N—H bond in urea group), 1296 cm⁻¹ and 1222 cm⁻¹ (both owing to vibration of N—C in aromatic amines). The peaks at 1645 cm⁻¹ (stretching vibration of carbonyl, —C=O, in urea group) and at 1536 cm⁻¹ (bending vibration of N—H in urea group) were also present. All these indicate PPU with presence of abundant amine groups was obtained as expected.

The same sample of PPU used for FTIR analysis was also subjected to NMR (¹³C, ¹H) tests with purpose to further illustrate its chemical structure. The corresponding spectra are displayed in Fig. 6. To facilitate the chemical assignment, the same tests were also done for TDI and 2,4-TDA (the spectra are given in Fig. S4 for ¹³C-NMR).

From ¹³C-NMR spectrum in Fig. 6, one can see clearly that, the peaks, assigned to the carbon atoms attached to NCO in TDI spectrum at 132.55 and 132.83 (Fig. S4 in Supporting Information), all disappeared. And the characteristic peaks of carbon atoms of NCO group in TDI at 131.30 and 124.20, also disappeared. In contrast, new peaks around 152.75 appeared, which were assigned as characteristic resonance of polyurea^[44]. These are strong indication that all NCO groups in TDI were effectively reacted. Based on the mechanism of PPU formation (Fig. 1), it is known that, the formation of a carbamido group in PPU from an NCO group is done through an intermediate product, *i.e.* a primary amine. It is well conceivable that there must be primary amines left in PPU because at the later stage of the reaction where very little amount of TDI or even no more TDI was

available. The *in situ* formed primary amine must remain. The peak at 146.9 in ^{13}C -NMR spectra of PPU, very close to those observed for the carbon atom with amine attached in toluene diamine (at 147.09 and 146.68. Fig. S4 and Table S1 in Supporting Information), was assigned to the carbon atom adjacent to this primary amine, in agreement with the mechanism of PPU formation. Noting that, with the NCO groups in TDI turning to urea, the chemical shifts of the carbon atoms in phenylene ring directly bonded to NCO groups in TDI would shift to a lower field zone in PPU because the capacities of electron attraction of amide in urea are lower than those of NCO groups. Multiple peaks around 138.07 were assigned to the carbons in phenylene ring and directly attached by a carbamido group. All these assignments are listed in Table 4.

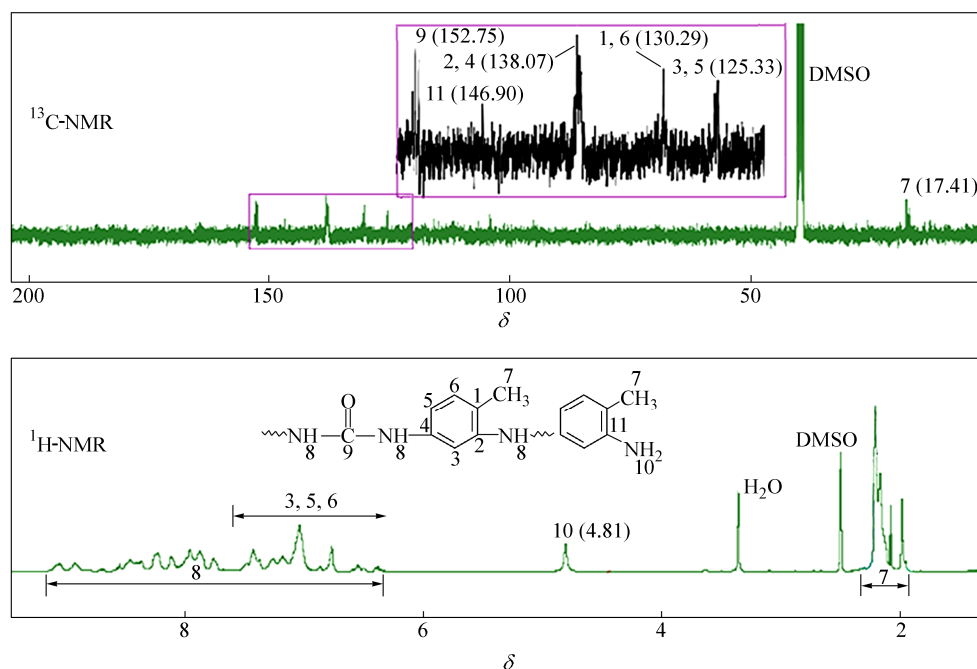


Fig. 6 ^{13}C - (Upper) and ^1H - (bottom) NMR spectra of PPU prepared with 10 wt% of TDI and H_2O /acetone mass ratio of 3/7 under $300\text{ r}\cdot\text{min}^{-1}$ stirring

Table 4. Chemical shifts (δ) of ^{13}C - and ^1H -NMR spectra of PPU

C or H atoms	1	2, 4	3	5	6	7	8	9	10	11
$\delta(\text{C})$	130.29	138.07	125.33	125.33	130.29	17.41	—	152.75	—	146.90
$\delta(\text{H})$	—	—	6.9–7.5	6.9–7.5	6.9–7.5	1.9–2.2	6.2–9.0	—	4.8	—

The ^1H -NMR test on PPU was also carried out. The corresponding spectrum is displayed in Fig. 6, together with that of ^{13}C -NMR. ^1H -NMR spectra for TDI and 2,4-TDA are displayed in Fig. S5, and relevant assignments for the chemical shifts are given in Table S3, all in Supporting Information. With TDI turned into PPU, NCO groups in TDI were accordingly changed to either NH_2 or carbamido units in PPU polymer chains as shown in Fig. 1. It is commonly known that, owing to the electron effect, the chemical shifts of the protons on phenylene are greatly influenced by the presence of the substituents on the phenylene^[34, 45], and this influence is closely related to the type and the number of the substituents. A generally accepted concept is that a chemical group with higher capacity as electron acceptor usually moves the chemical shift of the protons on the phenylene ring towards lower fields (peaks appearing at higher chemical shift). And in the present case, the capacity as electron acceptor is in the order of $\text{NCO} > \text{carbamido} (\text{NH}-\text{CO}-\text{NH}) > \text{NH}_2$. Giving that the chemical shifts of the protons on positions 3, 5 and 6 (as indicated in Fig. S4 in Supporting Information, same to Fig. 6 and Table 4) in TDA appeared at 5.77, 5.89 and 6.56, respectively; and they slightly shifted to higher chemical shifts (low-field)

to 7.01, 7.40 and 7.18 in TDI (Table S3) because of the presence of NCO group with higher electron attraction ability. As to PPU, the chemical environment for these protons are more complicated because NCO groups become polymer segments, impact of the polymeric substituents is hard to be compared with a concrete chemical group. However, one is sure that the chemical shifts of the protons on the phenylene ring in PPU must shift to a lower value (higher fields) in comparison with TDI since NCO is of stronger electron acceptor. The groups of chemical shifts appeared between 6.9 and 7.5 were therefore assigned to the protons at positions 3, 5 and 6 (Table 4). With the similar conception, based on the fact that the chemical shift for the methyl protons in TDI was at 2.24, and those in TDA at 1.90 (Table S3, Supporting Information), the chemical shifts between 1.9 and 2.2 were assigned to the methyl protons in PPU. Based on the reported data^[46], the resonance peaks between 6.2 to about 9.0 were assigned to protons in urea unit in PPU (NH—CO—NH), and that at 4.8 to the protons in terminal NH₂ in PPU.

PPU was then characterized by XRD. The diffractogram (Fig. S6 in Supporting Information) revealed that there were diffraction peaks at 2θ equal to 16.11°, 20.92° and 25.11°, which means that crystallinity or highly ordered structures were present in PPU. Through Bragg equation, one can easily see that these 2θ values correspond to ordered interplanar spaces of 0.5497 nm, 0.4243 nm and 0.3544 nm, respectively. This is in agreements with several reports on different polyureas that crystallinity is present owing to the rigidity of the polymer chains and the heavy hydrogen bonding^[47, 48]. Under light of this information, a schematic illustration for possible chain conformation of PPU is displayed in Fig. 7.

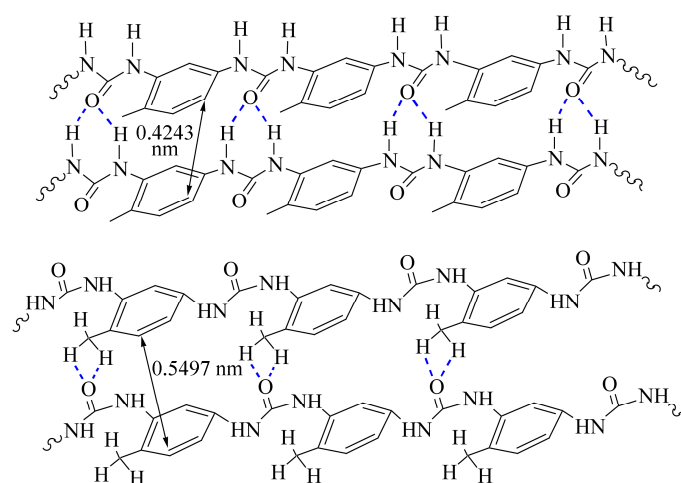


Fig. 7 Possible chain conformations in PPU owing to urea-urea (Upper) and urea-methyl interaction (Bottom)

PPU Thermal Properties Characterization

Attempt was also done to have an idea on the thermal properties of this material, with anticipation to observe also a melting point (T_m) for the crystalline portion in PPU, which was likely observed in DSC analysis (Fig. S7, Supporting Information) at 332 °C (DTA test indicated also a crystal melting at 333°C, practically at the same temperature). Similar melting points have been also reported at 370 °C and 346 °C^[47, 49]. However, in TGA test, it was seen that PPU started to have an appreciable weight loss (5%) at about 275 °C, it lost 50% of its initial mass at 322 °C. And at 336 °C, 90% of the sample was degraded. This indicates that the likely melting temperature at 332 °C detected by DSC completely superposed with the decomposition of PPU. It was therefore impossible to conclude from these tests that a melting point exists.

Dye Adsorption Using PPU as Adsorbent

From the chemical reactions involved in PPU preparation, it is known that abundant amine groups are present on the surface of the material^[41]. With the observed porous structure, it was believed that this material must be of high performance as adsorbent. Taking the sample with the highest specific surface area and largest pore volume

(prepared with 10 wt% of TDI in H₂O/acetone of 3/7 with stirring rate at 300 r·min⁻¹), its performance as adsorbent was tested with two different anionic dyes, RBBR and AF. It is commonly known that pH of the aqueous solution has important effect on dye adsorption for amines bearing materials, since it affects the degree of ionization and the surface charge of the adsorbent. The test was started at different pH at 30 °C with initial dye concentration of 100 mg·L⁻¹ and 0.25 wt% of PPU adsorbent. The adsorption was allowed for 4 h to reach a good equilibrium, and the results are shown in Fig. 8.

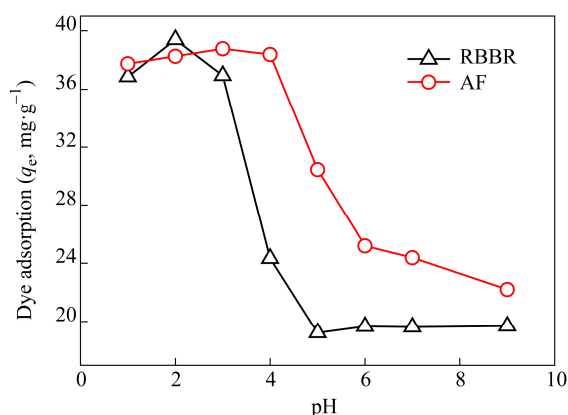


Fig. 8 Effect of pH in dye solution on adsorption of RBBR and AF on PPU

From Fig. 8, it is found that adsorptions of the two dyes were indeed significantly affected by pH of the medium. For AF, high adsorption (q_e) around 38 mg·g⁻¹ was detected with pH between 2 and 4. While a slight decrease was detected at pH = 1, and a sharp decline was seen once pH shifted to above 4, making 38.77 mg·g⁻¹ the peak value at pH = 3. RBBR demonstrated a similar adsorption profile as AF. A highest adsorption of 39.39 mg·g⁻¹ was observed at pH = 2, and slight decreases (to about 37 mg·g⁻¹) were detected with pH shifted to either direction (pH = 2 or 4). Further increase in pH above 4 caused a steep decline in RBBR adsorption.

The dye molecules are anionic owing to their dissociation in water. PPU adsorbent is positively charged at low pH owing to its abundant protonated amine groups at low pH. It is easy to conceive that the positive charges on PPU must be lessened with pH increase. The electrostatic interaction between the dye molecules and PPU was weakened, leading to a decrease in dye adsorption by consequence. Whereas when pH was adjusted to a too low pH, the dissociation of dye molecules must be impeded at certain extent owing to the abundant presence of hydrogen ions. Their electrostatic interaction with PPU is therefore reduced, causing a decreased adsorption. Similar observations have been reported^[50, 51].

Based on these results, adsorption capacities of PPU for the two dyes as function of their initial concentration were also studied with PPU amount fixed at 0.25 wt% in the aqueous medium. The dye concentration was varied from 50 mg·L⁻¹ to 500 mg·L⁻¹, whereas the pH was kept at 2 for RBBR and at 3 for AF, where their maximal adsorptions were observed as shown above. The results, including dye amount adsorbed per gram of PPU (Fig. 9a) and adsorption rate of the dyes (percentage of dye relative to the initial amount, Fig. 9b), are given in Fig. 9, which shows clearly that RBBR was nearly fully adsorbed ($\geq 98\%$) on PPU as long as its concentration was limited to 200 mg·L⁻¹. At this point, the corresponding adsorbed amount of RBBR per gram of PPU (q_e) was about 78 mg·g⁻¹, which gave 5 mg·L⁻¹ for the residual or unadsorbed RBBR concentration in the solution. With increase in RBBR initial concentration, its adsorption percentage was declining, leading to an increase in unadsorbed amount; albeit the adsorbed amount per gram of PPU (q_e) was increasing.

For AF, the results indicate that about 97% of AF was adsorbed when its concentration was at 100 mg·L⁻¹ or lower. The corresponding adsorption capacity of PPU was about 38.7 mg per gram of PPU (q_e , mg·g⁻¹). With increase in initial AF concentration, its absorbed amount was in constant increase and its adsorption percentage

(E , %) was in constant decrease, a same profile as RBBR. Figure 9 reveals clearly that RBBR demonstrated a higher adsorption than AF in the entire tested concentration span. From the molecular structures of the dyes (Fig. S1 in Supporting Information), it is believed the adsorption mechanism must be very similar one to the other for RBBR and AF, because both possess sulfonic anionic and amine groups. RBBR has a molecule weight of 626 with two sulfonic anionic groups in the molecule, and that the molecule weight of AF is 585 with three sulfonic groups. If one assumes that one single sulfonic is used to achieve the adsorption for each dye molecule, it is obvious that the adsorption of RBBR expressed in mass is higher than that of AF. Alternatively, if one assumes that all sulfonic groups were involved to interact with amine on PPU, one single sulfonic group corresponds to 313 Dalton for RBBR; whereas this value is about 195 Dalton for AF. In either case, a higher adsorption is expected for RBBR. Compared with reported studies^[50, 51], these results show that the PPU is of high performance for the adsorption of the tested dyes.

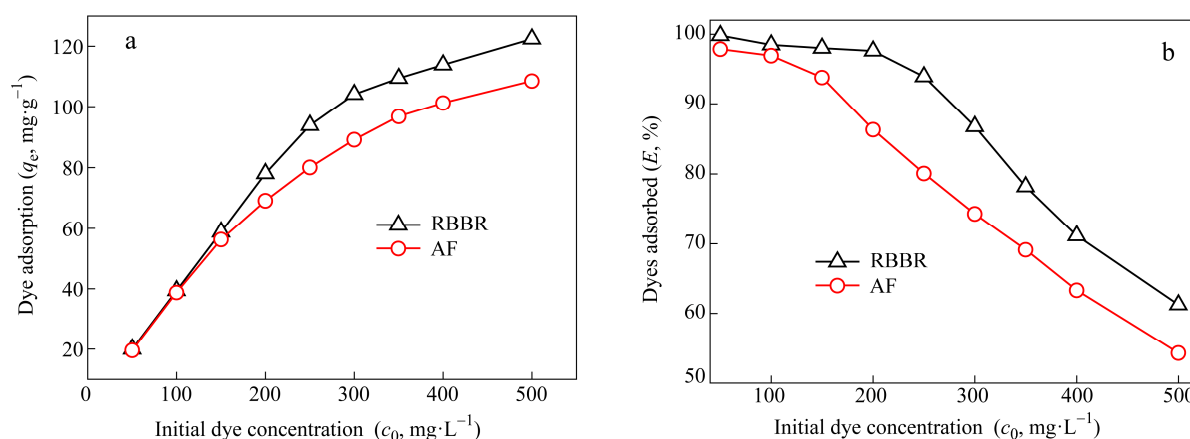


Fig. 9 Effects of initial dye concentration on their adsorption on PPU

In addition, the adsorption data were analyzed using Langmuir adsorption equation and Freundlich adsorption equation^[35]. The results demonstrated that the adsorption was better fit by Langmuir adsorption compared to Freundlich adsorption. This was also confirmed by a theoretical simulation using both Langmuir and Freundlich equations and the comparison made between the simulation and the experimental data for AF adsorption.

Desorption and Regeneration

Apart from the adsorption performance, the desorption of the adsorbate and the reusability are key properties to be taken into account in adsorbent evaluation. To this end, desorption behavior of RBBR and AF from PPU after equilibrated adsorption was tested. Three different desorption solvents, namely H_2O , NaOH solution of $0.01\text{ mol}\cdot\text{L}^{-1}$ and equal volume mixture of H_2O -EtOH, were used. Results given in Fig. 10 show that water was a poor desorption solvent, with which a low desorption far below 50% of the adsorbed RBBR and AF (17.60% and 45.99%, respectively) was detected. In contrast, the desorption, for both dyes with either NaOH solution ($0.01\text{ mol}\cdot\text{L}^{-1}$) or H_2O -EtOH mixture of equal volume as the desorption solvent, was quite effective, particularly the mixture of H_2O -EtOH. With NaOH solution of 200 mL as eluent, a maximal desorption of 75.3% of the adsorbed RBBR was obtained; and this was further increased to 95.6% with H_2O -EtOH.

With regard to AF, the maximal desorption was 93.4% with NaOH solution as eluent, and it was further increased to 98.9% when H_2O -EtOH mixture was used as the desorption solvent. For both dyes, an obviously higher desorption was achieved with H_2O -EtOH mixture than with NaOH solution as the desorption eluent. In comparison to the results observed with water, the higher desorption rate observed with NaOH solution is likely attributable to the deprotonation for the amine groups on PPU at high pH, reducing therefore the electrostatic interaction between PPU and the adsorbate. The more effective desorption obtained with H_2O -EtOH mixture is

attributable to a better compatibility between PPU and ethanol than that between water and PPU, which would cause a limited swelling for PPU, facilitating therefore the desorption of the dye molecules.

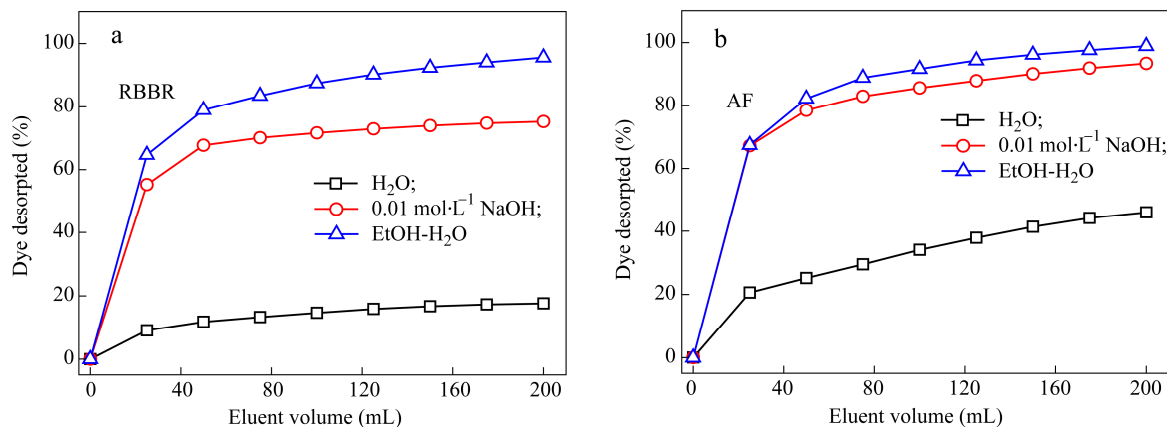


Fig. 10 Desorption of RBBR (a) and AF (b) from PPU using different desorption solvents

After dye desorption using H₂O-EtOH mixture, the regenerated PPU was anew used for readsorption of the dyes. Their amount of readsorption was compared to that in the first adsorption. The results are displayed in Fig. 11. For RBBR, it was found that the dye adsorbed in the second cycle was 97.44% of the amount in the first adsorption; this value slightly decreased to 95.04% in the third readsorption cycle, and to 93.19% in the forth cycle. For AF, very similar performance was observed. The only difference is that the readsorption of AF was slightly lower than that of RBBR. In the second reuse, readsorbed AF amount was 96.72% of that in the first adsorption against 97.44% for RBBR; in the last cycle, this readsorbed AF was 89.26% relative to that in the first adsorption against 92.35% for RBBR. These results clearly demonstrate that PPU is of good reusability in anionic dye adsorption.

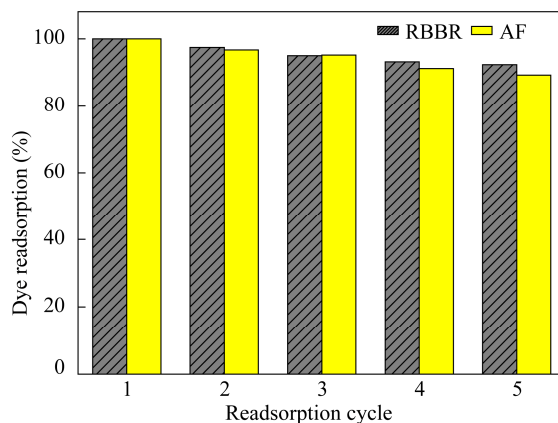


Fig. 11 Repeated adsorption of RBBR and AF on PPU

CONCLUSIONS

Based on precipitation polymerization of TDI in H₂O-acetone through step polymerization mechanism, a new porous polyurea, PPU, was prepared without need of any surfactant and porogen. Experimental conditions in PPU preparation, including TDI concentration, stirring rate and solvent composition, have important effects on the morphology and porous structure of the material. It is concluded that PPU as-prepared is featured by a broad distribution of pore size from a few nanometers to hundreds of microns. Small pores are believed to form owing

to the rigidity of the polymer chains alike the case in the formation of intrinsic micropores. Large pores are formed by aggregation of the primary particles, which are waned with continuous TDI feeding. The pore size and distribution can be adjusted by changing TDI concentration, the stirring rate during the synthesis and the composition of the solvent. Porous PPU thus prepared is rich in amine groups on surface without any chemical modification for the polymer, and was used as an adsorbent for dyes adsorption. High adsorption of up to $122.10 \text{ mg} \cdot \text{g}^{-1}$ for RBBR and $108.61 \text{ mg} \cdot \text{g}^{-1}$ for AF was achieved. The PPU was easily regenerated by solvent elution. While water was seen to be a poor eluent, H_2O -EtOH mixture at equal volume was very effective for the desorption of the dye molecules. 95.6% of the adsorbed RBBR and 98.9% of the adsorbed AF were desorbed. PPU regenerated by this elution was reused for adsorption and desorption. Good reusability was confirmed. To the fifth repeated adsorption and desorption cycle, as high as 89.26% of the AF amount adsorbed, relative to the first adsorption, was observed; and this value was 92.35% for RBBR. This work presents therefore a new route to the synthesis of a novel polyurea-based porous material. The test of the material as adsorbent demonstrates that this material is of high performance in anionic dye removal in aqueous medium and this high performance was well kept in recycled use.

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI) AVAILABLE

Structure of RBBR and AF; The pore size distribution of the samples prepared with a lower H_2O /acetone ratio of 1/9; FTIR spectra of the sample prepared with 10 wt% of TDI and H_2O /acetone mass ratio of 3/7 with stirring at $300 \text{ r} \cdot \text{min}^{-1}$; ^{13}C - and ^1H -NMR spectra and relevant assignments for the chemical shifts of TDI and 2,4-TDA; PPU XRD diffractogram; DSC analysis of PPU.

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