Polyurea Materials and Their Environmental Applications

Xiaojing Dong, Xubao Jiang, Shusheng Li and Xiang Zheng Kong

College of Chemistry and Chemical Engineering, University of Jinan, Jinan, China
Email: xzkong@ujn.edu.cn

Abstract. With the rapid economy development, environmental pollution becomes an urgent issue. Porous polymer materials have been a main player to this issue because their structures are easy to be designed to address these issues. Here we present different protocols for preparations of a variety of polyureas (PU), all through polymerization of a diisocyanate with a diamine in aqueous phase, added in water or in-situ formed from the reaction of water with the disocyanate involved. Two PU materials of different types are discussed in this study: (1), PU under form of microspheres was prepared through precipitation polymerization using isophorone diisocyanate as the monomer in a mixed solvent of water-acetonitrile. Aldehyde groups were attached to the surface of the PU microspheres. Immobilized of an enzyme, laccase, was carried out. The immobilized enzyme was used as biocatalyst in the process of degradation of organic dyes, and demonstrated high performance with good reusability. (2), porous PU (PPU) was also prepared through precipitation polymerization of toluene diisocyanate with a diamine or via the reaction of water. PPU was used directly to adsorb organic dyes and metal ions from aqueous systems with high performance and high selectivity.

1. Introduction

With the fast growth of chemical, textile and manufacture industries, environmental pollution has become an urgent challenge [1]. Among a vast variety of pollutants, heavy metal ions and organic dyes are the most common ones [2, 3, 4], and great efforts have been never ceased for their removal from polluted environment. Up to date, the main strategies to deal with these issues include adsorption separation, membrane separation, catalytic degradation, ion exchange and chemical precipitation etc [5,6]. In all the related studies or industrialized processes, polymers materials have been playing important roles because of their high specific surface area and low density, and in particular the easiness of control for their pore size and functionalization by a great variety of groups [7]. Separations by adsorption on an adsorbent have been the most widely used for metal ions and dye removals. For this purpose, diverse polymer porous absorbents have been prepared. The preparation involves generally two steps, namely, the synthesis of the base polymer and its chemical modification, which are usually comprised of several steps. The whole process is in general complicated and also time and energy consuming.

Uniform microspheres of polyurea (PU) have been fabricated with a high yield, through a process of precipitation polymerization of isophorone diisocyanate (IPDI) as the only monomer in a binary mixture of water-acetone [8,9]. The study demonstrated that the microspheres thus prepared were highly thermally stable with good resistance against common organic solvents. In this study, the preparation of PU microspheres is optimized in a binary mixture of water-acetonitrile (H₂O-AN). In order to make a biocatalyst for degradation of dyes molecules, immobilization of enzyme laccase was conducted on the surface of these microspheres, and the immobilized enzyme was used as biocatalyst in the degradation of dye molecules. Porous polyurea (PPU) was successfully prepared also through a one-step process, either by precipitation polymerization of toluene diisocyanate (TDI) with its diamine
counterpart derived from its reaction with water when only TDI was present as the monomer, or by its copolymerization with ethylene diamine (EDA) in a mixed solvent of H₂O-AN (acetonitrile). PPU as-prepared was employed as an absorbent for dyes molecules; high adsorption performance and good reusability were observed. This PPU was also used as adsorbent for a selected group of metal ions. The adsorption selectivity and the reusability were also investigated.

2. Experimental

2.1. Synthesis of Polyurea Microspheres and Immobilization of Laccase

A typical protocol for the preparation of PU microspheres is as following: To a reaction bottle, a binary mixture of H₂O/AN (20/80 by mass) was charged, followed by introduction of isophorone diisocyanate (IPDI). The bottle was sealed, shaken by hand to make sure that the mixture was homogenized and installed in a water bath set at 30 °C for 2 h, without any stirring or shaking. The microspheres were separated by centrifugation, rinsed twice with H₂O/AN mixture of 20/80 mass ratio, and dried up for 12 h in a vacuum oven at 80 °C. Microspheres were also prepared at different polymerization temperature or with changed IPDI concentration and in solvent of different H₂O/AN ratio. For laccase immobilization, the microspheres suspension was first mixed with an aqueous solution of glutaraldehyde (GA) to attach aldehyde functional groups onto the surface of the microspheres, through the reaction between amine on the microspheres and aldehyde group of GA, followed by enzyme immobilization by the reaction between the newly attached aldehyde groups from GA with the amine groups of laccase, a common practice. Catalytic activity of the immobilized laccase was tested in the degradation of organic dyes, and the performance was compared with the free laccase.

2.2. Preparation of Porous PU, Dyes and Metal Ions Adsorption

For the preparation of PPU adsorbent, a H₂O-acetone mixture (H₂O/acetone of 30/70 by mass) was first located into a round bottom flask (250 mL), which was then installed in a water bath at 30 °C. The polymerization was started by addition of TDI at a constant rate under constant stirring. Upon completion of TDI addition, the polymerization was allowed to continue for another 2 h, followed by separation of the microspheres by centrifugation and drying the polymer at 70 °C under vacuum. For the test of dye removal from aqueous solution by adsorption, an accurately known amount of PPU was first added into a glass bottle, followed by addition of an aqueous solution of the dye for test with known concentration at a pre-adjusted pH. The adsorption was done with the bottle located in a water bath shaker at 30 °C and shaken at 300 osc/min for 30 min. The bottle content was then centrifuged to separate PPU out from the dye solution. The amount of the no-adsorbed dyes in the solution was determined by analyzing the supernatant using a spectrophotometry at a given wavelength for a given dye. The adsorption was done for two dye molecules, anionic acid fuchsine and Remazol brilliant blue R, i.e. RBBR. For a typical process for adsorption of metal ions on PPU, a Cu²⁺ aqueous solution (using CuSO₄•5H₂O), of known concentration with pH pre-adjusted at 5.5, was first added to a glass flask of 25 mL capacity, and a known amount of PPU was added in a second step. The adsorption was allowed to proceed for 3 h at 30 °C. The content was centrifuged and the no-adsorbed Cu²⁺ in the supernatant was determined. Different adsorption processes were carried out under different experimental conditions.

3. Results and Discussions

3.1. Optimization of PU Microspheres Preparation

The preparation was optimized with regard to different experimental conditions, such as the monomer concentration, composition of the solvent (H₂O/organic solvent ratio), polymerization temperature etc. It is reported that the formation and the productivity of the uniform microspheres were closely related to the solubility of IPDI in the binary solvent. Uniform microspheres were obtained only when initial IPDI concentration was equal or below its solubility in the solvent. In this case IPDI molecules were homogeneously dissolved in, and neither IPDI droplets nor phase separation were present. The
uniformity of the outcome microspheres was deteriorated whenever the initial IPDI concentration used was higher than its solubility at that given temperature of polymerization and in the solvent concerned.

In a previous report [8], with H₂O-acetone as the binary solvent, 11 wt% of IPDI was the upper limit achieved to have uniform PU microspheres. To further increase the productivity of the uniform microspheres, polymerization was carried out by substituting acetone by different solvent in the binary mixture. Solvent selection was done with objective to find a solvent system, in which the solubility of IPDI was insoluble only in AN, THF and water. Water was straightly excluded because IPDI is not soluble in; and aggregation of the primary PU particles was always observed in early stage of the polymerization conducted in THF. Nevertheless, experiments showed that the solubility of IPDI was higher in AN than in acetone, and IPDI-based PU was insoluble in AN. Therefore, a set of polymerization was done at different temperature in H₂O/AN of different composition. Corresponding IPDI solubility, microsphere yield, their size (Dₙ) and size distribution (Dₘ/Dₙ) were determined and listed in Table 1. Preparation of PU microspheres at high yields was achieved, under experimental conditions optimized with regard to solvent composition, temperature of polymerization and IPDI concentration while keeping a high uniformity (Dₘ/Dₙ ≤1.10) for the microspheres. It was concluded that the highest productivity of the uniform microspheres was reached by polymerization at 50 °C with monomer concentration of 23 wt%, which gave 95.12% for the yield of the microspheres.

Table 1. Comparison of the Preparation of PU microspheres in H₂O-acetonitrile to that in H₂O-acetone at different polymerization temperature and IPDI concentration

| Solvent         | H₂O (wt%) | Temperature (°C) | IPDI (wt%) solubility | IPDI (wt%) concentration | Sphere yield (wt%) | Sphere size Dₙ (μm) | Dₘ/Dₙ |
|-----------------|-----------|------------------|------------------------|--------------------------|-------------------|---------------------|-------|
| H₂O-Acetone     | 30        | 50               | 8.6                    | 8.6                      | 88.75             | 6.91                | 1.006 |
| H₂O-Acetone     | 30        | 70               | 11.0                   | 11.0                     | 88.46             | 10.5                | 1.006 |
| H₂O-AN          | 20        | 30               | 17.0                   | 17.0                     | 93.68             | 7.15                | 1.008 |
| H₂O-AN          | 20        | 50               | 23.0                   | 21.0                     | 93.79             | 10.95               | 1.008 |
| H₂O-AN          | 20        | 50               | 23.0                   | 23.0                     | 95.12             | 11.22               | 1.010 |
| H₂O-AN          | 20        | 70               | 29.0                   | 21.0                     | 93.13             | 8.11                | 1.008 |

3.2. Immobilization of Laccase on PU Microspheres and Catalytic Activity in Dyes Degradation

Following their preparation, PU microspheres in this work were directly used as the support for immobilization of laccase. The microspheres were firstly activated using GA to attach aldehyde groups on their surface, as described in previous section. As a typical result, immobilization of 20.63 mg of laccase was achieved for each gram of the microspheres. The activity of the immobilized enzyme was determined at different pH and temperature, and compared with that of the free laccase. A highest activity was observed at 50 °C for the immobilized enzyme, whereas a highest activity was detected at 40 °C for the free laccase. This shift toward higher temperature for the activity of the immobilized enzyme was attributed to its increased activation energy to adopt an optimal conformation for the enzyme when it was immobilized on the support. The optimum pH for the activity was observed at 3.0 for both the free and the immobilized laccase. It was found that free enzyme was more sensitive to pH than the immobilized counterpart, in particular in alkaline medium. When pH was below 5.5, a lower activity was observed for the immobilized laccase than for the free enzyme; this activity was inversely with pH was increased to above 5.5. For instances, the activity of the free laccase was 32.0 U/mg at pH 3.0, and it was 8.3 U/mg for the immobilized laccase, i.e. only 25.9% of activity was retained after immobilization; whereas at pH 7.2, the activity of immobilized enzyme was 3.09 U/mg, which was 3.8 times higher than that of the free laccase (0.64 U/mg) at this pH. In addition, a much better alkali resistance was also observed for the immobilized laccase.

Thermostability at 55 °C was also measured for both the free and the immobilized enzyme (Fig. 1). After 120 min of incubation, 89% of the initial activity was retained for the immobilized one, whereas only 27% of the initial activity was retained for the free laccase, a thermal stability significantly lower than the immobilized enzyme. This was attributed to a more restricted conformational mobility for the
enzyme in their immobilized form. The immobilized enzyme showed also higher storage stability than the free one. For the free enzyme, 63% of its initial activity was lost after storage of 10 day and 80% after storage of 30 days, always at room temperature. In contrast, for the immobilized enzyme, the corresponding values were found to be 40% and 60%, respectively.

The immobilized enzyme was employed as catalyst for RBBR degradation (decolorization). The test results are shown in Fig. 2 for both the free and the immobilized enzyme. To assure that this decolorization was due to the catalytic effect of the enzymes, a reference test was also done, in which exactly the same procedure for RBBR degradation was followed, using the virgin PU microspheres as-prepared prior to their activation by GA and enzyme immobilization. It is clearly seen that no any sign of RBBR decolorization was detected in the blank test, excluding therefore possible catalytic activity of PU microspheres. The results in Fig. 2 demonstrate that the immobilized enzyme was performing better in the whole degradation process of RBBR. With the immobilized enzyme, 64.1% of RBBR was degraded at 300 min, while only about 54.7% of RBBR was decolorized at the same time with the free enzyme.

![Figure 1. Thermostability of the immobilized and the free laccase at 55 °C.](image)

![Figure 2. Comparison of degradation of RBBR by free laccase to that by immobilized laccase.](image)

The importance and interest of enzyme immobilization are the reusability because this will reduce significantly the cost of the enzyme. The reusability of the immobilized laccase was tested through the same procedure, which demonstrated that, in comparison with the amount of RBBR degraded in a first run with freshly prepared immobilized enzyme, 92% of the initial degradation was obtained in the
third consecutive recycled use of the immobilized enzyme, and about 65% of the initial degradation was detected in the seventh recycled use. From these results, it was concluded that the immobilized laccase was of fair reusability as a catalyst in RBBR degradation.

3.3. Direct Adsorption of Organic Dyes and Copper Ions on Porous PU

Porous PU (PPU) was prepared using the process described above in Experimental section. The chemical structure and morphology were characterization to show that this material is a typical porous material. As described above, the surface of PPU is rich in amine groups. It is therefore believed that this PPU may be used as an adsorbent for organic dyes and metal ions. Adsorption on PPU of two anionic dyes (RBBR and AF) in their aqueous solutions was done at 30°C with 0.25 wt% of PPU and at initial concentration of 100 mg/L for the dyes in test. To assure an equilibrated adsorption for the dye molecules, an adsorption time of 4 h was allowed for all the tests. The results showed that the pH of the aqueous dye solution imposed important effect on the adsorptions for the two dyes involved. With pH controlled between 2 and 4, an adsorption of about 38 mg/g was detected for AF; whereas this adsorption was slightly decreased at pH=1, and once pH shifted to above 4, this adsorption was sharply declined. A similar adsorption profile was seen for RBBR. At pH=2, a highest adsorption of 39.39 mg/g was obtained, and a steep decline in the adsorption was clearly seen once pH was increased to a value above 4.

For the adsorption of metal ions on PPU, the test was done for five ions, i.e. Cu$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, and Cr$^{3+}$. The highest selectivity combined with the high adsorption for Cu$^{2+}$ ions was observed, which was interpreted by the formation of multifunctional complexation of Cu$^{2+}$ ions, based on XPS analysis on the PPU absorbent before and after the adsorption of the metal ions. The multifunctional complexation assumes that a coordination complex was formed not only between Cu$^{2+}$ ions and the terminal amine of PPU, it occurred also between Cu$^{2+}$ ions and the oxygen and nitrogen atoms of the carbamido units of PPU. Simulations of the adsorption kinetics showed that this adsorption followed the pseudo-second-order model; the simulation of the adsorption process demonstrated that a better fitting was found for the experimental data with Freundlich isothermal adsorption in comparison to Langmuir isothermal adsorption.

4. Conclusions

Optimization of the preparation of PU uniform microspheres was done with regard to different experimental conditions. In comparison with what achieved in the mixed solvent of H$_2$O-acetone, higher yield of the uniform PU microspheres was indeed obtained in the binary solvent of H$_2$O-AN, because of higher IPDI solubility in H$_2$O-AN than in binary solvent of H$_2$O-acetone. A highest productivity of 95.12% was obtained for the uniform microspheres with monomer concentration of 23 wt% and polymerization at 50 °C. Using these PU microspheres as support, enzyme laccase was immobilized on their surface using GA as the coupling agent in order to chemically attach aldehyde groups. Laccase was then immobilized through the reaction of the attached aldehyde groups with the amine groups of laccase. The highest activity was observed at 50 °C for the immobilized laccase, instead of 40 °C for the free enzyme. At pH 5.5 or below, the immobilized laccase manifested a lower activity than the free enzyme; and a higher activity than the free laccase was detected for the immobilized enzyme once pH increased to above 5.5. A distinctly higher thermal stability was also observed for the immobilized enzyme, owing to most likely a more restricted conformational mobility when enzyme was immobilized. Employed as the biocatalyst in RBBR degradation, 64.1% of RBBR was degraded within 300 min using the immobilized laccase, a better performance than the free laccase. Porous PU (PPU) was also prepared by precipitation polymerization using TDI as the monomer, and used as adsorbent in adsorption separation for two anionic dyes, RBBR and AF. For AF, an adsorption of up to 38 mg/g was achieved with pH controlled between 2 and 4. For RBBR, a high adsorption of 39.39 mg/g was achieved at pH=3, and a slight decrease was detected with pH shifted to either direction (pH<3 or pH>3). PPU was also directly used as adsorbent for metal ions. Among 5 ions tested, PPU was found to have a higher adsorption with better selectivity for Cu$^{2+}$ ions. Based on XPS analysis, the higher performance for Cu$^{2+}$ adsorption was explained by the formation of
multifunctional complexations of the ions with the nitrogen atoms of its carbamido units and the terminal amine of PPU, as well as with the oxygen atoms of the carbamido units.

5. References
[1] Taskin O S, Ersoy N, Aksu A, Kiskan B, Balkis N and Yageci Y 2016 Polym. Int. 65 439
[2] Karim Z, Claudpierre S, Grahn M, Oksman K and Mathew A P 2016 J. Membrane Sci. 514 418
[3] Hase H, Nishiuchi T, Sato T, Otake T, Yaita T, Kobayashi T and Yoneda T 2017 J. Hazard. Mater. 329 49
[4] Li S, Kong X Z, Jiang X and Zhu X 2013 Chinese Chem. Lett. 24 287
[5] Azarova Y A, Pestov A V and Bratskaya S Y 2016 Cellulose 23 2273
[6] Guo N, Su S J, Liao B, Ding S L and Sun W Y 2017 Carbohydr. Polym. 165 376
[7] Hasanzadeh R, Moghadam P N, Bahri-Laleh N and Sillanpää M 2017 J. Colloid Interface Sci. 490 727
[8] Jiang X, Zhu X and Kong X Z 2012 Chem. Eng. J. 213 214
[9] Jiang X, Kong X Z and Zhu X 2011 J. Polym. Sci. Part A: Polym. Chem. 49, 4492