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Metal ions crosslinked poly (arylene ether nitrile) adsorbent for removal of rhodamine B

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Abstract. A novel water soluble poly (Arlene ether nitrile) (PEN) containing pendent carboxyl and sulfonic acid groups was synthesized, which displayed high reactivity to different metal ions and Rhodamine B (ChB). After a crosslinking with certain metal ions, the PEN produced obvious precipitate in aqueous solution. Moreover, the precipitate was capable to adsorb ChB and the effect of operational parameters (contact time, dye concentration, temperature and pH) on RhB removal was studied. Results showed the adsorption capacity at 25°C could reach up to 112.5 mg/g.

1. Introduction
With the rapid development of modern industry, dyes are widely used in papermaking, textile, rubber, leather, plastics, cosmetics, printing and other fields [1-3]. For the dyes contain a large π conjugated structure, which endowed it various color and strong stability under light, heat and oxidants, the active groups on the side chains give them excellent solubility in water [4]. However, their structural features greatly increase the difficulty of dye processing, most organic dyes are bio accumulative and can cause various diseases such as cancer and human skin or respiratory organs allergies [5, 6]. At present, the dye wastewater treatment methods mainly include physical, chemical and biological schemes [7, 8]. But most of the methods show some limitations, such as high cost, complicated operation, low efficiency, and secondary pollution [9]. To our delight, adsorption process has been an effective technique and it was crucial to select more efficient and cheaper adsorbents with higher adsorption ability. Poly(Arlene ether nitrile) (PEN) has been a kind of high-performance thermoplastic special polymer material with benzene rings and aryl ether bonds in main chain and the strong polar canon in the side chain of polymer [10]. The benzene rings and the cyan groups assist PEN high mechanical strength, resistance to acid and alkali corrosion, etc., while the ether bonds endowed it certain hydrophobicity and processing flexibility. More importantly, the diverse source of raw materials and mature synthesis technology enables PEN various structures and excellent performance [11, 12].

In this work, we synthesized a kind of poly (Arlene ether nitrile) (PEN) containing pendent carboxyl and sulfonic acid groups, these active groups endow PEN enough reactive site to interact with positively charged materials. Moreover, the strong hydrophilic carboxyl and bibulous sulfonic acid groups make PEN soluble in water with blue fluorescence emission. After crosslinking with several certain metal ions, the PEN displayed obvious precipitate along with the varied fluorescence property, moreover, the metal ions cross-linked PEN was capable to adsorb Rhodamine B. The effect of contact...
time, dye concentration, temperature and pH on Rhoda mine B removal were studied with the metal ions cross-linked poly (Arlene ether nitrile) as adsorbent.

2. Experimental section

2.1. Synthesis of PEN (PPL-SHQ) and crosslinking of PEN (PPL-SHQ) with metal ions in aqueous solution

The PEN (PPL-SHQ) was synthesized from DFBN and biphenyl monomers of PPL and SHQ with a molar ratio of 3 to 7. The PEN (PPL-SHQ) aqueous solution with a concentration of 5 mg mL⁻¹ and different metal ions solutions with the same concentration of 0.1 M were prepared. Under a continuous magnetic stirring, 1 mL of certain metal ion solution was injected into the vial containing 10 mL PEN (PPL-SHQ) aqueous solution.

2.2. Batch adsorption experiment

The adsorption experiment was conducted with the Zr⁴⁺ cross-linked PEN (PPL-SHQ) (C-PEN). The initial concentrations of ChB used in the adsorption were 25 and 35 mg L⁻¹. The effect of temperature was performed by mixing 10 mg C-PEN into 20 mL ChB solution of 100 mg/L in the condition of pH=7. The initial temperature of ChB solution was adjusted to values in the range of 15-45 °C. The effect of pH was studied at 25 co. at different pH in the range of 2-11.

2.3. Characterization

The Fourier transform infrared spectra were obtained with a Shimadzu 8400S FTIR spectrometer. Thermal stability and transition analysis was measured by TA Instruments TGA-Q50 and differential scanning calorimetric (DSC-Q100), respectively. The absorption and fluorescence spectra were recorded using a UV–Vis spectrophotometer (TU 1901, Parsee) and an optical microscope (Motif, BA410E) coupled with a 405 nm laser spectrophotometer. Surface morphology was characterized by a scanning electron microscope (SEM) (JSM-6490LV, JEOL).

3. Results and Discussion

To clarify the structure characters of PEN (PPL-SHQ), the FTIR spectrum was measured and the results displayed in Figure 1(A). Specifically, the absorption band at 2234 and 1716 cm⁻¹ belonged to the symmetric stretching vibration of nitrile and carboxyl groups, respectively. The characteristic absorption bands at 1598 and 1455 cm⁻¹ were assigned to the stretching vibration of the benzene rings. The symmetric and asymmetry stretching vibration of the aromatic ether were observed at 1243 and 1022 cm⁻¹, respectively. As for the absorption band at 1076 cm⁻¹, it corresponded to the stretching vibration of aromatic sulfocate. The TGA spectra in Figure 1(B) certificated that the PEN (PPL-SHQ) possessed high thermal stability under nitrogen atmosphere with the 5% weight loss temperature at 304 o C. Moreover, the DSC spectra in Figure 1 (C) indicated the thermally induced phase-transition behavior of PEN (PPL-SHQ) with glass transition temperatures (Tg) at 169.5 co. These results indicated that the PEN (PPL-SHQ) was successfully synthesized. Furthermore, the absorption spectra showed that PEN (PPL-SHQ) aqueous solution indifferent concentration possessed good solubility and strong absorption around ultraviolet band, as shown in Figure 1(D).

With an intense absorption band around ultraviolet band, the PEN (PPL-SHQ) aqueous solution gave the blue emission around 454 nm under 405 nm light excitation, and the fluorescence intensity gave good linear relativity with its concentration, as shown in Figure 2 (A). To explore its sensitivity to metal ions, various metal ions were involved to interact with PEN (PPL-SHQ) and induced different fluorescence intensity variation, as displayed in Figure 2 (B). And the concrete intensity variation in Figure 2 (C) also demonstrated the Cr³⁺, Ni²⁺, Fe³⁺ and Co²⁺ would lead to a decreased fluorescence intensity, while the Zr⁴⁺ and Al³⁺ induced an increased fluorescence intensity. Moreover, the Zr⁴⁺, Al³⁺, Zn²⁺, Fe³⁺ and Pb²⁺ were capable to form the apparent precipitation after
interact with PEN (PPL-SHQ) in aqueous solution, which would attributed to the active carboxyl and aromatic suffocate have been cross-linked with these metal ions, respectively.

![Figure 1](image1.png)

**Figure 1.** The FTIR (A), TGA (B), DSC (C) of PEN (PPL-SHQ) and UV-vies adsorption spectra (D) of PEN (PPL-SHQ) in aqueous solution at different concentrations.

![Figure 2](image2.png)

**Figure 2.** The fluorescence emission spectra of PEN (PPL-SHQ) in aqueous solution at different concentration (A). The fluorescence spectra (B) and the corresponding histogram (C) of PEN (PPL-SHQ) aqueous solution after interacted with different metal ions, respectively.

On the basis of the former results, the ZrCl4 was chosen for further exploration on the PEN (PPL-SHQ) completing behavior. As displayed in Figure 3 (A), the Zr4+ with various concentrations exhibited stable fluorescence properties. Specifically, the obvious precipitation was observed, the supernatant gave no fluorescence emission while the precipitation almost kept the equal fluorescence emission intensity under 405 nm light excitation, as the spectra and image shown in Figure 3 (B). The phenomenon that the PEN (PPL-SHQ) was qualified for completing with specific metal ions, and was potential in disposing wastewater containing heavy metal ion. The SEM image of Zr4+ interacted with PEN (PPL-SHQ) demonstrated in Figure 3 (C) and certificated that the Zr4+ indeed cross-linked with PEN (PPL-SHQ) leading in an barbarization microstructure.
Figure 3. The fluorescence emission spectra of PEN (PPL-SHQ) aqueous solution after crosslinking with Zr4+ at different concentrations (A), and the supernatant and precipitation of PEN (PPL-SHQ) in the presence of 0.1 M Zr4+ (B). The SME image of Zr4+ induced PEN (PPL-SHQ) precipitation (C).

The ChB was involved in the Zr4+ induced PEN (PPL-SHQ) (C-PEN) aqueous solution, which certificated that the ChB aggregated in the PEN (PPL-SHQ) precipitation and an intense red emission emerged in the fluorescence emission spectra, as displayed in the image and spectra of Figure 4 (A). Figure 4(B) clearly exhibited that the adsorption capacity of ChB increased rapidly at the initial stage and then slowed down until a state of equilibrium. Moreover, the effect of ambient pH and temperature of ChB adsorption capacity on C-PEN were also explored, as displayed in Figure 4 (C) and (D), respectively. It suggested that the adsorption capacity of Zr4+ cross-linked PEN (PPL-SHQ) at 25°C and pH=7 condition can reach up to 112.5 mg/g, and a certain high temperature and pH would contribute to a higher adsorption capacity. Therefore, it was believed that the adsorption was an endothermic process and the alkaline environment was beneficial to improve the reactivity of PEN (PPL-SHQ) with ChB.

Figure 4. The fluorescence emission spectra of C-PEN before and after adsorbing ChB (A). Effects of contact time on the adsorption capacity of ChB onto the C-PEN at different initial concentrations (B). Effects of temperature (C) and pH (D) on the adsorption of MB onto the Zr4+ cross-linked PEN (PPL-SHQ).
4. Conclusion

In this study, a water soluble poly (Arlene ether nitrile) was synthesized with active functional groups, which were capable to interact with certain metal ions and form specific precipitation with blue fluorescence emission. Among these metal ions, the high valence state Zr$^4+$ not only cross-linked PEN (PPL-SHQ) but also preserved fluorescence property. Moreover, the Zr$^4+$ cross-linked PEN (PPL-SHQ) was capable to adsorb cationic Rhodamine B and the adsorption capacity at 25 o C could reach up to 112.5 mg/g. It is expected that the poly (Arlene ether nitrile) could be of great potential as a new class of adsorbent for organic dye removal from sewage.

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References

[1] P. Luo, Y.F. Zhao, B. Zhang, J.D. Liu, Y. Yang, J.F. Liu, Study on the adsorption of neutral red from aqueous solution onto halloysite nanotubes, Water Res. 44 (2010) 1489-1497.
[2] T.T. Ma, P.R. Chang, P.W. Zheng, F. Zhao, X.F. Ma, Fabrication of ultra-light graphene-based gels and their adsorption of methylene blue, Chem. Eng. J. 240 (2014) 595-600.
[3] G.S. Xu, J.F. Yao, K. Wang, L. He, P.A. Webley, C.S. Chen, H.T. Wang, Preparation of ZIF-8 membranes supported on ceramic hollow fibers from a concentrated synthesis gel, J. Membr. Sci. 385 (2011) 187-193.
[4] Z. Aksu, Biosorption of reactive dyes by dried activated sludge: equilibrium and kinetic modelling, Biochem. Eng. J. 7 (2001) 79-84.
[5] H. Wang, X. Yuan, Y. Wu, G. Zeng, X. Chen, L. Leng, H. Li, Synthesis and applications of novel graphitic carbon nitride/metal-organic frameworks mesoporous photocatalyst for dyes removal, Appl. Catal. B 174 (2015) 445-454.
[6] Acemioglu, B., Adsorption of Congo red from aqueous solution onto calciumrich fly ash. J. Colloid Interface Sci. 274(2004) 371-379.
[7] M.S. Sajab, C.H. Chia, S. Zakaria, P.S. Khiew, Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions, Bioresour. Technol. 128 (2013) 571-577.
[8] X. Zhou, X. He, S. Wei, K. Jia, X. Liu, Au nanorods modulated NIR fluorescence and singlet oxygen generation of water soluble dendritic zinc phthalocyanine, Journal of Colloid and Interface Science 482(Supplement C) (2016) 252-259.
[9] K.L. Ai, Y.L. Liu, C.P. Ruan, L.H. Lu, G.Q. Lu, Sp2 C-dominant N-doped carbon submicrometer spheres with a tunable size: a versatile platform for highly efficient oxygen-reduction catalysts, Adv. Mater. 25 (2013) 998-1003.
[10] K. Jia, L. Pan, Z. Wang, L. Yuan, X. Zhou, Y. Huang, C. Wu, X. Liu, Morphology and photophysical properties of dual-emissive hyperbranched zinc phthalocyanines and their self-assembling superstructures, Journal of Materials Science 51(6) (2015) 3191-3199.
[11] Xuefei Zhou, Kun Jia, Xiaohong He, Shiliang Wei, Pan Wang, Xiaobo Liu. Microemulsion self-assembling of novel amphiphilic block copolyarylene ether nitriles and photosensitizer ZnPc towards hybrid superparticles for photocatalytic degradation of Rhodamine B, Materials Chemistry and Physics 207 (2018) 212e220.
[12] H. Tang, Z. Pu, X. Huang, J. Wei, X. Liu, Z. Lin, Novel blue-emitting carboxyl-functionalized poly(arylene ether nitrile)s with excellent thermal and mechanical properties, Polym. Chem. 5 (2014) 3673-3679.