Fenton-like Prussian Blue Coated Magnetic Hollow Fe₃O₄ Nanocomposites for Dye Removal

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Abstract. In this work, Prussian blue (PB) coated magnetic hollow Fe₃O₄ nanoparticles (PB@Fe₃O₄NPs) were fabricated to degrade two modal dyes in wastewater via a typical peroxidation. Typically, the as-prepared PB@Fe₃O₄NPs were found to present intrinsic Fenton-like catalytic capacity and could catalyze the modal peroxidatic reaction for dyes degradation. Meanwhile, the obtained PB@Fe₃O₄NPs could be easily separated from the reaction solution by an external magnet since the magnetic Fe₃O₄ core for cyclic utilization. The relative removal efficiency of the PB@Fe₃O₄NPs was still above 80% after 10 cycles, which showing excellent recycling performance.

1. Introduction
Over the past several decades, due to the human industrial activities and the rapid developments in printing technologies, pigments and dyestuffs are widely used worldwide in various sorts of industrial applications such as papermaking, textile, garment manufacturing, petrochemical and chemical industry, etc[1]. Approximately 100 tons of different dyes are emitted in wastewater from factories each year, the effluents that not reaching the takeover standard would cause serious environmental problems like obstinate persistent color and high biological oxygen demand (BOD) existing[2]. The content of dyes in aquatic environment, even at very low doses, is extremely harmful and thoroughly unwanted. Therefore, many government organizations such as United States Environmental Protection Agency (US EPA), Environment Canada (EC) and European Environment Agency (EEA) have established environmental legislations regarding the quality of colored wastewater and have forced dye-adopting industries for decolorizing their sewage before discharge[3].

Many kinds of conventional treatment approaches for dye removal and/or degradation have been proposed such as physical filtration, chemical coagulation, activated sludge method, advance superoxidation, photo/electro-catalysis, nano-adsorption and so on[4]. Nevertheless, since most of the dyes are well solvable in aqueous system that make the traditional technologies ineffective for its removal from effluents. Meanwhile, some of these conventional treatments have the deficiencies of being costly, complex, inefficient and time-consuming[5]. It is noticeable, nano-adsorbents that based on nanomaterials, has been proved to be a high-efficiency strategy for water purification in terms of low cost, easy to design, easy to operation, high effectiveness and reusability[6]. Till now, various of nano-adsorbents have been already adopted for the expulsion of dyes like mesoporous silica, zeolites, kaoline, cycloexdrin-based adsorbent, activated carbon, graphene, fullerene, carbon nanotube, Prussian blue (PB), titanium oxide, zinc oxide and iron oxide nanoparticles[7-11]. Among these applied nano-adsorbents, magnetic iron oxide Fe₃O₄ nanomaterials have better adsorption properties and
excellence repeatability owing to their unique physical properties including magnetic performance and Fenton-like catalytic effect\cite{12}.

In this present study, we have synthesized the Prussian blue coated magnetic Fe$_3$O$_4$ nanoparticles (PB@Fe$_3$O$_4$NPs), which was efficiently used for dyes removal from aqueous medium via a typical Fenton-like reaction with the by the iron ions system (Fe$^{2+}$, Fe$^{3+}$). Scheme 1 showed the Fenton-like degradation process of dyes by PB@Fe$_3$O$_4$NPs with the assist of H$_2$O$_2$.

Scheme 1. Overview of dyes removal mechanism of PB@Fe$_3$O$_4$NPs nano-adsorbents.

2. Materials and Methods

2.1. Materials

Chemicals and Materials: sodium dodecyl sulfate (SDS, 99.5%), methacrylic acid (99%), potassium persulfate (KPS, 99%) and K$_4$[Fe(CN)$_6$] (99%) were purchased from Sigma-Aldrich (St. Louis, USA). FeCl$_2$ (99.5%), FeCl$_3$ (99%) were supplied by Aladdin Co., Ltd (Shanghai, China). Other common used chemical reagents were bought from Alfa Aesar Co., Ltd (Tianjin, China) without any further purification.

2.2. Synthesis of PB@Fe$_3$O$_4$NPs

The PB@Fe$_3$O$_4$NPs were fabricated through a simple soft template method\cite{13} as follows: Typically, polystyrene nanoparticles as prodromal template were firstly fabricated by the microemulsion polymerization method. Briefly, 0.1 g SDS, 0.2 g KPS and 10.0 mL methacrylic acid were dissolved into 25% ethanol solution (100.0 ml, 70 °C) under continuous magnetic stirring in a three-neck flask under nitrogen protection for 10 min. Then 5.0 mL styrene was dropwise added at the rate of roughly 1.0 mL per min. After 6 h of polymerization reaction, 0.13 g FeCl$_3$, 0.05 g FeCl$_2$ and 15 ml ethylene glycol were added into the above solution under a sonic bath for 10 min and heated to 85 °C. Then 2.0 mL ammonium hydroxide (28 wt %) was added into the above solution for another 4 h stirring to form the magnetic Fe$_3$O$_4$ nanoclusters. Next, 0.32 g K$_4$[Fe(CN)$_6$] was added into the mixture and the pH of the mixture was adjusted to 3.0 with acetic acid (0.1 M) to produce Prussian blue (PB) nanoshell. Finally, the precipitates were collected with a magnet and washed with dimethyl formamide (DMF) to eliminate the polystyrene template. The obtained nanoparticles were washed with alcohol and distilled water each for ten times and noted as PB@Fe$_3$O$_4$NPs.
2.3. Characterization of PB@Fe₃O₄ NPs

Herein, the morphology of the as-synthesized PB@Fe₃O₄ NPs was recorded by a transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) and a scanning electron microscopy (SEM, JSM-5600, JEOL, Japan). The XRD pattern of the PB@Fe₃O₄ NPs was observed by an X-ray diffractometer (XRD, Brux D8-X, BRUX, Germany). Next, the magnetic properties of the gotten PB@Fe₃O₄ NPs were investigated with a vibrating sample magnetometer (VSM, VSM-7410, Lake Shore, America).

2.4. Dyes removal by PB@Fe₃O₄ NPs

Subsequently, the dyes removal capacity of the as-synthesized PB@Fe₃O₄ NPs were evaluated. In our study, two modal dyes with different character, Rhodamine B (RhB) and Methylene blue (MB) were measured to estimate the degradation efficiency of the obtained nano-adsorbents. Typically, 100 mg PB@Fe₃O₄ NPs were dispersed in the modal dye (RhB and MB) solutions (10.0 mL, 0.25 mg/mL). Then by means of a UV-vis spectrophotometer, the solutions were by monitoring the absorbance changes at 441 nm and 554 nm, respectively.

3. Results and discussion

The morphology of the as-prepared PB@Fe₃O₄ NPs nano-adsorbents was observed by TEM and SEM. As shown in Figure 1 and Figure 2, the results show that the PB@Fe₃O₄ NPs nano-adsorbents are well mono-dispersive with distinguished uniform morphology. Meanwhile, the average diameter of the obtained PB@Fe₃O₄ NPs was about 142.6 ± 13.4 nm (Figure 3, n = 300). Then the crystal structure of the PB@Fe₃O₄ NPs was further monitored, the XRD pattern of PB@Fe₃O₄ NPs possessed characteristic peaks appear at 2θ = 30.1°, 35.5°, 43.1°, 53.4°, and 57.0°, which matched to the spinel Fe₃O₄ (JCPDS no. 19-0629), then the peaks appear at 2θ = 17.4°, 24.7°, 35.2°, 39.5°, 43.5°, 50.6°, 53.9°, and 57.1° were consistently corresponded to the characteristic peaks of PB (JCPDS No. 73-0687).

Figure 1. TEM image of the obtained PB@Fe₃O₄ NPs.
Figure 2. SEM image of the obtained PB@Fe₃O₄ NPs.
Figure 3. Particle size of the obtained PB@Fe₃O₄ NPs.
Figure 4. XRD pattern of the obtained PB@Fe₃O₄ NPs. PCNFs, PCNF, PCNFs.

The dye removal ability of the as-synthesized nano-adsorbents was further investigated via the Fenton reaction occurred in the reaction process[14]. Typically, the Fe²⁺ and Fe³⁺ iron system played an important role in dyes (RhB and MB) degradation reaction by generating reactive oxygen species (ROS) substances. Generally, the ROS activation process induced by the PB@Fe₃O₄ NPs takes place...
as follows. Firstly, Fe$^{3+}$ reacts with H2O2 to produce ROS by a redox reaction, accompanied with the Fe$^{2+}$ release (Equation 1). Subsequently, the released Fe$^{2+}$ also reacts with H2O2 to produce •OH via an oxygen activation pathway (Equation 2). Then the in-situ produced •OH reacts with Fe$^{2+}$ to renewedly produce Fe$^{3+}$ (Equation 3).

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2$$  \quad (1)

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}$$  \quad (2)

$$\text{Fe}^{2+} + \cdot\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$$  \quad (3)

The quantitative degradation performance of the PB@Fe$_3$O$_4$NPs to RhB and MB was examined by a UV-Vis spectrophotometry (Figure 5 and Figure 6). Different concentrations of PB@Fe$_3$O$_4$NPs reveal splendid dyes (RhB and MB) removal capacity in the reaction processes (Figure 7, Figure 8 and Figure 9). Thereafter, the PB@Fe$_3$O$_4$NPs nano-adsorbents could maintain above 80% of its initial catalytic property after being reused for 10 cycles (Figure 10).

4. Conclusion
In conclusion, a new protocol was advanced for dyes degradation from colored effluents based on the as-synthesized PB@Fe$_3$O$_4$NPs. Eventually, the Fenton-like nanoagents PB@Fe$_3$O$_4$NPs showed good recycling performance for dyes degradation even after a sustained 10-times reuse. To sum up, the easy-preparation, high catalytic capacity, excellent reusability of the as-prepared PB@Fe$_3$O$_4$NPs give its great potential for dyes removal from industrial colored effluents and other environmental aspects like potable water filtration, medical wastewater purification, etc.
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References
[1] Lu, B., Lu, J., Yan, Z., Liu, Z. Liu, Y. (2018) Plasma-etched electrospun nanofiber membrane as adsorbent for dye removal. Chem. Eng. Ees. Des., 132: 445-451.
[2] Kim, T., Jo, S., Ahmad, D., Lee, H. Kim, D. (2018) Fast adsorption kinetics of highly dispersed ultrafine nickel/carbon nanoparticles for organic dye removal. Appl. Surf. Sci., 439: 364-370.
[3] Chao, C., Guan, H., Zhang, J., Liu, Y., Zhao, Y., Zhang, B. (2018) Immobilization of laccase onto porous polyvinyl alcohol/halloysite hybrid beads for dye removal. Water Sci. Technol., 77(3-4): 809-818.
[4] Zohreh K and Hassan Z (2019) Phase selective amphiphilic supergelators for oil spill solidification and dye removal. Soft Mater., 17: 150-158.
[5] Kim, H., Saito, N. (2018) One-pot synthesis of purple benzene-derived MnO2-carbon hybrids and synergistic enhancement for the removal of cationic dyes. Sci. Rep., 8(1):4342.
[6] Katheresan, V., kansedo, J., Lau, S. (2018) Efficiency of Various Recent Wastewater Dye Removal Methods: A Review. J. Environ. Chem. Eng., 6(4): 4676-4697.
[7] Abdi, G., Alizadeh, A., Zinadini, S., Moradi, G. (2018) Removal of dye and heavy metal ion using a novel synthetic polyethersulfone nanofiltration membrane modified by magnetic graphene oxide/metformin hybrid. J. Membrane Sci., 552: 326-335.
[8] Li, J., Chen, Y., Wang, Z., Liu, Z. (2018) Self-templating synthesis of hollow copper tungstate spheres as adsorbents for dye removal. J. Colloid Interf. Sci., 526 459-469.
[9] Navneet, B., kamlesh, K., Dhiraj, S. (2018) A biopolymer-based composite hydrogel for rhodamine 6G dye removal: its synthesis, adsorption isotherms and kinetics. Iran. Polym. J., 27(7): 527-535.
[10] Tavangar, T., Hemmati, A., Karimi, M., Ashtiani, F. (2019) Layer-by-layer assembly of graphene oxide (GO) on sulfonated polyethersulfone (SPES) substrate for effective dye removal. Polym. Bull., 76(1): 35-52.
[11] Song, W., Qian, L., Gao, B., Zhu, Y., Zhu, M., Zhao, Y. (2019) Ionic liquid-based amphiphilic comonetwork with mechanical toughness: a promising candidate for dye removal. J. Mater. Sci., 54(8): 6212-6226.
[12] Gui-Bing, H., Chun-Jie, J., (2018) Biosynthesis of SnO2 Nanoparticles Based on Response Surface Methodology and the Study of Their Dye Removal. J. Nanosci. Nanotechnol., 18: 5020-5025.
[13] Li, J., Zhang, F., Hu, Z., Song, W., Li, G., Liang, G., Zhou, J., Li, K., Cao, Y., Luo, Z., Cai, K. (2017) Drug "Pent-Up" in Hollow Magnetic Prussian Blue Nanoparticles for NIR-Induced Chemo-Photothermal Tumor Therapy with Trimodal Imaging. Adv. Healthc. Mater., 6(14): 201700005
[14] Wang J., Yao, Z, Wang, Y., Xia, Q., Chu, H., Jiang Z. (2017) Preparation of immobilized coating Fenton-like catalyst for high efficient degradation of phenol. Environ. Pollut., 224: 552-558.