Preparation and Catalysis of Pd Loaded PS/Fe₃O₄@PPy/Pb Magnetic Composite materials

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Abstract: Fe₃O₄ particles were prepared by chemical co-precipitation method. Then, the functionalized PS nanoparticles were mixed with the prepared Fe₃O₄ particles, the PS/Fe₃O₄ magnetic nanocomposite were obtained by electrostatic interaction; the pyrrole monomer was added, and the pyrrole monomer undergoes oxidative polymerization on the surface of the composite. The PS/Fe₃O₄@PPy composite coated with polypyrrole was obtained. Finally, the PS/Fe₃O₄@PPy/Pb magnetic composite was prepared by the depositionPrecipitation method. The morphology and structure of the composite particles were analyzed by scanning electron microscope, X-ray diffractometer, Fourier transform infrared spectrometer, and thermogravimetric analyzer. The concentration of organic dye molecules was determined by ultraviolet-visible spectrophotometer. The results showed that the dispersion of the PS/Fe₃O₄@PPy/Pb magnetic composite was excellent; the PS/Fe₃O₄@PPy/Pb magnetic composite showed excellent catalytic performance in the reduction of methylene blue with sodium borohydride as reducing agent. The composite could be recycled and reused many times.

1. Introduction

With the rapid development of the current industry, the problem of water pollution has attracted attention from all walks of life[1]. Especially with the vigorous development of textiles, papermaking, cosmetics and other industries[2]. It is a pollution problem that cannot be ignored of the dye wastewater generated. The water quality of dye wastewater is complex, deep in color, and large in discharge[3]. It is a kind of organic matter that is highly toxic, difficult to biodegrade, and easy to accumulate. It is very harmful to the human body. Direct discharge will cause great damage to the ecological environment and drinking water. harm. Therefore, its modification or functionalization to remove pollutants in water has become a research hotspot in recent years[4,5].

For sewage treatment, the traditional method is to use adsorbents. Traditional adsorbent materials mainly include montmorillonite, activated carbon, clay, silica, zeolite, etc. Their disadvantage is that they are easy to saturate and difficult to recycle[6,7]. Nanomaterials have always received widespread attention due to their excellent performance. Magnetic nanoparticles in nanomaterials have become a good separation and catalyst due to their large specific surface area, easy functionalization, and good separation performance. Used to treat wastewater and remove heavy metals. In recent decades, Fe₃O₄ magnetic nanocomposite materials have attracted attention in the field of environmental remediation as adsorbents[8,9]. Its advantage is that it can achieve the purpose of solid-liquid separation only under
the action of an external magnetic field, which provides a faster and more convenient way for the repeated use of adsorbent materials. Conditions, can save a lot of money in production. Therefore, Fe₃O₄ magnetic nanocomposite materials adsorb dyes in water as a new development direction that year[10].

Fe₃O₄ nanoparticles are easy to aggregate due to the dipole force between the particles, which reduces the intrinsic magnetic properties, resulting in weak magnetic response and reduced specific surface area[11-13]. Coating Fe₃O₄ nanoparticles in a dense shell layer to form magnetic composite microspheres with a core-shell structure is one of the effective methods to solve this problem. In this study, Fe₃O₄ particles were prepared by the chemical co-precipitation method, and PS/Fe₃O₄ nanocomposite particles were used as seeds[14-16]. The PPy nanocomposite was successfully deposited on the surface of the seed particles by the reaction of pyrrole polymerization. Finally, the deposition-precipitation method was used to obtain a multifunctional PS/Fe₃O₄@PPy/Pb magnetic composite. More importantly, due to the catalytic effect of PdNPs and the enrichment effect of PPy in the PS/Fe₃O₄@PPy/Pd nanocomposite, it exhibits excellent performance in the catalytic degradation of methylene blue (MB) and can be recycled and reused.

2. Materials and Methods

2.1 materials
Ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), polystyrene microspheres (PS), pyrrole monomer, palladium chloride, absolute ethanol. Methylene blue(MB): analytically pure, Sinopharm Chemical Reagent Co., Ltd.; all water used is ultrapure water.

2.2 Characterizations
HD 2015W electric stirrer; KQ 5200E ultrasonic instrument; Fourier Transform Infrared Spectrometer: Model Cary630; The structures of nanoparticles and nanocomposites were investigated by Lambda7600 -FT-IR. A JEOL JSM-6700F scanning electron microscope (SEM) with primary electron energy of 3 keV employed to examine the surfacemorphologies of products. Inorganic content of the composite spheres was measured by DSC-404 F3 and TG-209 F3. X-ray diffraction (XRD) data was collected on a X'Pert PRO X-ray diffractometer . New century general T6 ultraviolet and visible (UV–Vis) spectrophotometer was employed for analysis of MB dye reduction.

2.3 Methods

2.3.1 Preparation of Fe₃O₄ nanoparticles
At room temperature, 12.2 g FeCl₃·6H₂O and 5.9 g FeCl₂·4H₂O were added to a 100 mL round bottom flask, and 50 mL water was added in the flask. Under mechanical stirring, 25 mL ammonia water was added in and maintained the reaction for 30 mins. After repeated washing and magnet decanting, the resulting sample was dried in an oven at 60 °C and stored as a solid for later use.

2.3.2 Preparation of polystyrene/ferroferric oxide nanocomposite particles(PS/Fe₃O₄)
A certain mass of PS particles and Fe₃O₄ nanoparticles were weighed in a 100 mL round bottom flask, the mass ratio of PS particles and Fe₃O₄ nanoparticles were 1:1.25, a certain volume of ultrapure water was added. The system was maintained 30 mL and the pH was adjusted to 3. After mechanical stirring for 5 hours, the supernatant was poured by magnet decanting and washed with ultrapure water repeatedly until the supernatant was clear. The sample was dried in an oven at 60 °C for later use.

2.3.3 Preparation of polystyrene/ferroferric oxide@polypyrrole nanocomposite particles (PS/Fe₃O₄@PPy)
the pyrrole monomer was polymerized on the surface of the composite to form PS/Fe₃O₄@PPy nanocomposites.
2.3.4 Preparation of polystyrene/ferroferric oxide/palladium@polypyrrole nanocomposite particles (PS/Fe₃O₄@PPy/Pd)

50 mg PS/Fe₃O₄@PPy nanocomposites were dispersed in 30 ml of water under 60°C water bath conditions, 20 mg of PdCl₂ was added in the system with mechanical stirring for 24 h. The precipitate was centrifuged and washed with water for three times. Then the precipitate was dried in oven under 60°C for 12 h.

3. Results and discussion

The whole procedure to prepare PS/Fe₃O₄@PPy/Pd composites is illustrated in Fig. 1.

![Fig.1 Synthesis route to PS/Fe₃O₄@PPy/Pd composites](image1.png)

3.1 Analysis of the surface morphology of the composites

It can be seen from the picture of SEM in Fig. 2(a), the micrographs of PS nanoparticles that the surface of the PS nanoparticles is smooth and uniformly spherical.

![Fig.2 SEM of PS nanoparticles(a), PS/Fe₃O₄ nanocomposites(b)](image2.png)

Compared with Fig.2(a), Fig.2(b) shows the PS/Fe₃O₄ nanocomposite particles loaded with Fe₃O₄ nanoparticles. The surface of the PS nanoparticles becomes rough and has obvious particles. This is because the surface of the PS nanoparticles is negatively charged, which provides conditions for the
positive and negative combination of Fe$_3$O$_4$ nanoparticles. Fe$_3$O$_4$ nanoparticles synthesized by co-precipitation method are deposited on the surface of PS nanoparticles by electrostatic self-assembly at pH=3. Then the pyrrole monomer undergoes oxidative polymerization on the surface of the PS.

3.2 XRD analysis of magnetic nanocomposites

In order to verify the prepared PS/Fe$_3$O$_4$@PPy/Pd nanocomposite particles, x-ray diffraction (XRD) was used to analyze them. XRD was an important method to characterize the prepared materials, the phase structure of nano-materials can be obtained by XRD. As shown in Fig. 3 is the XRD pattern of Fe$_3$O$_4$ nanoparticles. The (220), (311) and (400) crystal faces of Fe$_3$O$_4$ nanoparticles in 30º, 35.5º and 43.3º can be seen, respectively, showing the face-centered cubic structure of the prepared Fe$_3$O$_4$ nanoparticles. At the same time, there are new characteristic diffraction peaks, which belong to the (110), (200) and (311) crystal planes of PD nanoparticles in 39.8º, 46.4º and 67.6º, which also indicate the formation of PD nanoparticles in the process of PPy formation.

3.3 Analysis of membrane structure

The temperature stability of the PS/Fe$_3$O$_4$@PPy/Pd nanocomposites in the system can be analyzed by infrared spectroscopy. Fig. 4 shows the infrared spectra of magnetic composite materials with different heating temperatures. As shown in Fig. 4(a) is the characteristic curve of PS. The characteristic peaks appear at 2980, 2830, 1495 and 750 cm$^{-1}$. The Fig. 4(b) is the PS/Fe$_3$O$_4$ nanocomposite particle at peaks appear at the same position, indicating that PS is contained therein, and the structure of PS is not damaged by loading Fe$_3$O$_4$ nanoparticles. The characteristic peaks of Fe$_3$O$_4$ are not obvious, mainly because: 1) The detection of inorganic substances by FTIR is not as good as that of organic functional groups; 2) The absorption peak of Fe$_3$O$_4$ nanoparticles is covered by the absorption peak of PS nanoparticles. In Fig. 4(c), the absorption peaks at 1568 and 1450 cm$^{-1}$ are attributed to the C-C asymmetric and symmetric stretching vibration peaks in the pyrrole ring, respectively. The absorption peak at 1360 cm$^{-1}$ is the C-N stretching vibration peak. The characteristic peak at 1050 cm$^{-1}$ is the C-H bending vibration peak on the pyrrole ring. These vibration peaks can indicate that PPy is formed on the PS/Fe$_3$O$_4$ nanocomposite particles.
3.4 Catalytic analysis of magnetic materials

MB is a typical industrial pollutant. Because of its stability in water, it is more complicated to handle. Therefore, MB is selected as the characteristic dye, and NaBH\textsubscript{4} is used as a reducing agent to catalyze the degradation of MB to explore the PS/Fe\textsubscript{3}O\textsubscript{4}@PPy/Pd nanocomposites. The catalytic performance of the particles as a catalyst. The degradation process of MB can be monitored by its absorbance change at the maximum wavelength of 665 nm. Fig. 5 shows the UV spectra of (a) the initial MB solution, (b) the MB solution after adding the reducing agent NaBH\textsubscript{4} and reacting for 30 minutes, and (c) the UV spectrum of the MB solution after adding the reducing agent NaBH\textsubscript{4} and the magnetic catalyst for 30 minutes.

Fig. 5 Vis spectra of the initial MB solution(a); the MB solution after adding the reducing agent NaBH\textsubscript{4} after reaction for 30 mins(b); the UV spectrum of the MB solution after adding the reducing agent NaBH\textsubscript{4} and the magnetic catalyst for 30 mins(c)
We prepared (0.2 mg/mL) aqueous solution of MB 3.5 mL. The reaction process was monitored by Vis spectra, as illustrated in Fig. 5a. The original aqueous MB dye solution is dark blue in color and the kmax appears at 665 nm (curve a). 2 mL NaBH4 (10 mg/mL) was added to the system. Upon the addition of NaBH4 without PS/Fe3O4@PPy/Pd catalysts, the absorbance intensity at kmax of MB decreases, but does not completely vanish after reaction for 30 minutes (curve b). The solution color only becomes light blue. After 10.0 mg of the PS/Fe3O4@PPy/Pd composites were added, the absorbance at kmax completely disappears within 30 minutes (curve c). The solution color turns colorless as seen. It could be concluded that the PS/Fe3O4@PPy/Pd composites had excellent catalytic performance in reduction of MB dye with NaBH4 as a reducing agent.

4. Conclusions

(1) Using PS/Fe3O4 nanocomposite particles as the carrier, based on the principle of "swelling-diffusion-interfacial polymerization", based on the redox effect between palladium chloride and pyrrole monomer, PPy coating on the surface of PS/Fe3O4 nanocomposite particles is formed, and loaded with palladium on the surface.

(2) Considering the harm caused by methylene blue dye to the water system, using the enrichment effect of PPy and the catalytic performance of PdNPs, we carried out catalytic degradation of methylene blue dye. The results showed that PS/Fe3O4@PPy/Pd nanoparticles with different shell thicknesses can be effective degrade methylene blue.

(3) This method not only simplifies the process conditions of the conventional method, but also solves the problem of poor adhesion between metal and polymer. The biggest advantage of this method is that the doped nano-palladium can be distributed in the polymer system with the original particles, so as to best reflect or maintain the unique properties of the nano-palladium. Therefore it is anticipated that this kind of catalysts will have great potential for further practical applications.

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