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Highly selective removal of organic dyes from aqueous solutions with recyclable Fe₃O₄@PDA-Ag magnetic microspheres

Rong Luo, Fei Yan, Zheng Zhu, Yu Zhao, Qing-dan Luo, Yu-hua Fan, Xia Zhang^{*} Cai-feng Bi^{*}

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Shandong 266100, China, email: luoronggirl@163.com (R. Luo), 18846036121@163.com (F. Yan), zhzhqqcool@163.com (Z. Zhu), 17865321938@163.com (Y. Zhao), lqd19860723@163.com (Q.-D. Luo), fanyuhua301@163.com (Y.-H. Fan), zxcindy@ouc.edu.cn (X. Zhang), Tel. +86 (0532-66781922), email: bicaifeng302@163.com (C.-F. Bi)

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ABSTRACT

Fe₃O₄@PDA-Ag microspheres with excellent paramagnetic nature have been successfully prepared by a fast and straightforward strategy. The easily recycled Fe₃O₄@PDA-Ag microspheres were employed in the adsorptive removal of various dyes from aqueous solution. The results indicate that Fe₃O₄@PDA-Ag microspheres show excellent selectivity for cationic dyes adsorption and separation, and the adsorption efficiency is 98.2%, 97.8% and 96.9% for AH, MB, and MG in this work, respectively. Meanwhile, various influencing factors on the dyes adsorption have been explored. The results indicate that the adsorption rate strongly depends on the type of surfactant in solution and the pH value of the dye solution. Moreover, Fe₃O₄@PDA-Ag microspheres can be rapidly regenerated in 3 min using the saturated solution of NaCl in DMF as eluent, and display excellent reversibility in the process of the dye adsorption-release for at least 29 cycles. Overall, the experimental results showed that the Fe₃O₄@PDA-Ag microspheres had a great adsorption ability to remove cationic dyes in wastewater and can be applied for the separation of dyes mixtures.

Keywords: Fe₃O₄@PDA-Ag; Polydopamine; Selective adsorption; Dye removal; Water treatment

1. Introduction

According to the Colour Index, over 10,000 types of dyes are being manufactured in recent years, and annual worldwide dye production is more than 700,000 tones [1]. Dyes are widely used in chemical industries, such as food, textile, plastic, leather, paper and pulp, cosmetics, printing and medicine [1,2]. Most synthetic dyes have complex structure and xenobiotic properties, so they cannot be efficiently degraded under natural conditions and cause serious environmental problems [3]. To remove toxic dyes from wastewater before discharging them into the environment, various techniques have been well developed, such as adsorption [3,4], membrane filtration [5], biological treatment [6], oxidation [7], ionic liquid [8], electrochemistry

In recent years, many noble metal nanoparticles are widely applied in energy, environment, and biology filed, such as Ag, Au, Pt, Pd [16]. In particular in environment filed, noble metal nanoparticles have displayed excellent performance in alkylation, C-C and C-H bond coupling, hydrogenation and oxidation-reduction [17]. However, because noble-metal nanoparticles have relatively small

treatment [9,10], coagulation-flocculation [11], combined techniques [12]. Unfortunately, these methods suffer from inherent limitations in various aspects, including formation of by-products (generally sludge, contaminated solids, or brine), not effective for all dyes, very expensive, safe operation, or unsatisfactory regeneration and cycling ability [13– 15]. Thus, it is essential for us to develop a safe, efficient, and environmental friendly process to remove dyes from aqueous solution.

^{*}Corresponding author.

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size and higher surface energy, they inevitably suffer from the limitations in aggregation and separation in practical applications [18].

Thus, keeping in view of the shortcomings in the previous studies, it is necessary to develop some supporting materials to stabilize noble metal nanoparticles, such as graphene oxide [19], metal oxide [20,21], metal-organic frameworks [22], silica [23] and magnetic material [24]. Due to its numerous advantages such as unique magnetic response, chemical stability, highly modifiable surface and low cost, magnetic Fe₃O₄ loaded materials could be a good candidate for practical applications in wastewater treatment technology [25]. However, pure Fe₃O₄ nanoparticles are limited by disadvantages including poor acid resistance, bad thermal stability and salt stability. In most cases, the surface of Fe_3O_4 nanoparticles can be functionalized to improve its chemical stability. Dopamine (DA), a mussel adhesive protein inspired molecule, has been widely used to modify diverse substances without surface pretreatment since it was reported by Lee et al. [26,27]. In addition, DA can undergo self-polymerization in alkaline or oxidants contained aqueous solutions, and the resultant polydopamine (PDA) with the coupling catechol and amine groups can be used as a convenient platform for secondary reactions [28]. These advantages endow DA with extensive applications in water treatment. For instance, Duan et al. reported a free-standing PDA-modified graphene hydrogel as reusable adsorbents for water purification [29]. Xu et al. fabricated microfiltration membranes by simple co-deposition of PDA and polyethyleneimine (PEI) [30]. The membranes were applied to separate oil-in-water emulsions under ultra-low pressure, which holds promise for the treatment of oily waste water through a microfiltration process. Recently, since it could incorporate the private advantages of PDA and Fe₃O₄ nanoparticles, Fe₃O₄@PDA core-shell nanostructure has been proposed to be as a novel, efficient substrate to immobilize noble metal nanoparticles. Up to now, significant efforts have already been dedicated for the preparation and application of Fe₃O₄@PDA core-shell nanohybrids. For example, Manna et al. reported a magnetically isolable Pd⁰/PDA-Fe₃O₄ catalyst for hydrolytic dehydrogenation of ammonia borne [31]. Liu and his coworkers designed a binary-metal centered magnetic metal-organic framework (Fe₃O₄@PDA@Zr-Ti-MOF) for phosphoproteome analysis [32]. Xie and coworkers reported a simplistic method to prepare Fe₃O₄@polydopamine-Ag microspheres, which exhibited a predictable catalytic performance toward the reduction of methylene blue by NaBH₄ [33]. Although Xie's method could produce magnetic core-shell composite, it necessitates long synthesis time. Therefore, to shorten the synthesis time of magnetic core-shell composites, development of an uncomplicated and forthright method is extremely essential. In addition, to our knowledge, there is no systematic report on the selective adsorption behaviors of dye pollutants using Fe₃O₄@PDA-Ag microspheres.

Herein, a fast and straightforward approach is established to synthesize Fe₃O₄@PDA-Ag nanohybrids with excellent paramagnetic nature by adding the appropriate amount of glucose. In addition, changing the reaction time can control the thickness of the shell and Fe₃O₄@PDA nanoparticles show excellent dispensability in the ethanol-water synthesis system. More importantly, we demonstrated that Fe₃O₄@PDA-Ag microspheres have an ability to rapidly and selectively remove cationic dye pollutants. The structure, adsorption and release behaviors, and the influence factors including the surfactants, solution pH and inorganic salt were explored to assess the suitability of their applications in the wastewater treatment domain. The results indicate that Fe₃O₄@PDA-Ag microspheres have easy separability, great reusability, good stability and rapid regeneration ability. These properties show that Fe₃O₄@ PDA-Ag nanohybrids can be selective for the removal of dye contaminants, which can be used to remove specific dye molecules in particular wastewater. The adsorbed toxic dye molecules or valuable dye molecules can be further treated or utilized by desorption and concentration. From the perspective of environmental protection and resource recovery, Fe₃O₄@PDA-Ag microspheres are more suitable for practical applications than non-selective adsorbents.

2. Experiment section

2.1. *Materials*

Dopamine hydrochloride was obtained from Shanghai Macklin Biochemical Co., Ltd., China. Ferrous chloride tetrahydrate (FeCl₂·4H₂O), sodium hydroxide (NaOH), Trisbase (tris(hydroxymethyl)aminomethane), silver nitrate (AgNO₃), D(+)-glucose monohydrate, tritonX-100 (TX-100) and sodium dodecyl sulfate (SDS) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Acriflavine hydrochloride (AH), methylene blue (MB), malachite green oxalate (MG), methyl orange (MO), Orange IV (OIV) and hexadecyltrimethyl ammonium bromide (CTAB) were obtained from Jinan Henghua Sci. & Tec. Co., Ltd., China. Total ethanol was purchased from Tianjin Fuyu Fine Chemical Reagent Co., Ltd., China. All chemicals were used without further purification. Ultrapure water was used in all experiments.

2.2. Synthesis of Fe_3O_4 nanoparticles

The Fe₃O₄ nanoparticles were prepared according to our earlier work [34]. Firstly, FeCl₂·4H₂O (0.3 mol) was dissolved into 300 mL of deoxygenated water and N₂ protection at 90°C, then a certain volume of NaOH solution (17 wt%) was added dropwise into the above solution at a rate of 6 mL·min⁻¹ under constant stirring, and the final pH was 6–7. Afterwards, the solution was stirred for 30 min to obtain milky Fe(OH)₂ suspension. Then the nitrogen gas was converted to air and the suspension began to oxidize. The milky Fe(OH)₂ suspension turned dark green and finally black suspension was obtained. Finally, the substances obtained were separated from solution by a powerful magnet and washed repeatedly with deionized water and ethanol. Then the product was dried at 80°C in vacuum for 8 h for further characterizations.

2.3. Preparation of Fe₃O₄@PDA microspheres

Polydopamine coated Fe_3O_4 (Fe $_3O_4$ @PDA) was synthesized according to previous paper with some modifications [31,33,35]. Typically, Fe $_3O_4$ nanoparticles (100 mg) were

dispersed in 40 mL tris-buffer solution (10 mM, pH = 8.5) consisting of water and ethanol. Then 100 mg of dopamine hydrochloride were added, and the mixture was sonicated for 30 min. Afterwards the reaction was allowed to proceed under stirring at ambient temperature for 12 h. The magnetic complexes were obtained and collected using magnet, washed with water and ethanol for three times, and then dried under vacuum at 60°C for 8 h.

2.4. Preparation of Ag modified Fe₃O₄@PDA core-shell microspheres

Silver nanoparticles supported on Fe₃O₄@PDA microspheres were prepared by in situ reduction of silver ions on the surface of Fe₃O₄@PDA at ambient temperature. First of all, Fe₃O₄@PDA (80 mg) was dispersed in ultrapure water (50 mL) by ultrasonic irradiation for 3 min. Then 10 mL 0.1 mol·L⁻¹ silver ammonia solution was added into the Fe₃O₄@PDA suspension and mechanically stirred for 4 h. Afterwards, 10 mL 5 g·L⁻¹ glucose solution was added dropwise into the solution mixture. After 1 h, the products (Fe₃O₄@PDA-Ag) were separated with a magnet and washed several times with water and ethanol, then dried under vacuum at 60°C overnight.

2.5. Characterization and measurements

Fourier transform infrared spectra were recorded from KBr pellet using Nicolet 170SX spectrometer with a range of 400-4000 cm⁻¹. X-ray powder diffraction (PXRD) patterns were collected using PANalytical X'Pert Pro diffractometer with Cu-Kα radiation from 5° to 80°. The chemical binding information was recorded by multifunctional imaging electron spectrometer (XPS, Thermo ESCALAB 250XI, US). The transmission electron microscopy (TEM) images were taken on a JEM-1200EX electron microscope (JEOL, Japan). And scanning electron microscopy (SEM) images were taken on a JEM-1200EX electron microscope (JEOL, Japan). Magnetic property was recorded on a Lakeshore 7410 vibrating sample magnetometer (VSM) and M-meter (PES laboratorium, EPPING) at room temperature. A zeta potential measurement of samples was also carried out using Zetasizer Nano ZS90 (Malvern, UK). Ultraviolet visible (UV-Vis) absorption spectra of dyes were recorded on UV-2550 spectrophotometer.

2.6. Dye adsorption

In a typical adsorption experiment, 10 mg $Fe_3O_4^{(0)}$ PDA-Ag was added into 10 mL of AH aqueous solution (5 mg·L⁻¹) under regular shaking at room temperature. At different time intervals, $Fe_3O_4^{(0)}$ PDA-Ag particles were collected with a magnet and samples were taken and further measured using an UV-Vis spectrophotometer at the maximum absorption peaks of the dyes (450 nm for AH).

To verify the pH effect on the dyes adsorption of Fe_3O_4 [@] PDA-Ag microspheres, the solution pH value was changed from 3.0 to 9.0 for AH.

The effects of inorganic salt in dye solution on the dyes adsorption were studied. The experiments were measured by the addition of $Na_{2}SO_{4}$ (or NaCl) to a 5 mg·L⁻¹ AH solu-

tion. The concentration of inorganic salt was changed from 1 to $10 \text{ g}\cdot\text{L}^{-1}$.

The effects of surfactants in dye solution on the dyes adsorption were also studied. The experiments were measured by the addition of different surfactants to a 5 mg·L⁻¹ AH solution. The surfactants, such as CTAB, SDS, and TX-100 were chosen.

The adsorption experiments of other model dyes, such as MG, MB, OIV and MO were calculated according to the identical methods as depicted.

2.7. Recycling test of the Fe_3O_4 @PDA-Ag microspheres

After the adsorption process was complete, the $Fe_3O_4@$ PDA-Ag particles were collected with a magnet. Then the microspheres were transferred into 8 mL saturated solution of NaCl in DMF with vigorous stirring for 3 min. And then the microspheres was washed with water for several times for another adsorption-desorption cycle. The recyclability of the sample was evaluate by repeating the process of adsorption and desorption. This procedure was repeated 29 times following the same procedure

For comparison, pure DMF solution (8 mL) was also used as desorption solution in place of saturated solution of NaCl in DMF following the same procedure.

3. Results and discussion

3.1. Characterizations of Fe₃O₄@PDA-Ag microspheres

 Fe_3O_4 @PDA-Ag microspheres were synthesized using a two-step process (Fig. 1): namely, pH-induced polymerization of dopamine hydrochloride and the deposition of Ag nanoparticles. Further details, the concentration of dopamine salt was 2.5 mg·mL⁻¹. And silver nanoparticles were located onto the Fe_3O_4 @PDA spheres by impregnation of as-prepared silver ammonia solution followed by their reduction with glucose. Fe_3O_4 @PDA-Ag microspheres were separated with a magnet and further were characterized.

The TEM images of Fe_3O_4 , Fe_3O_4 @PDA and Fe_3O_4 @PDA-Ag are shown in Fig. 2. The size of Fe_3O_4 core is approximately 200 nm (Fig. 2a). The TEM images show that: (1) the thickness of PDA layer on the surface of Fe_3O_4 nanoparticles



Fig. 1. Schematic demonstration of the preparation process of Fe₃O₄@PDA-Ag composites.

is about 16.3–17.5 nm (Fig. 2b), (2) highly dispersed silver particles are formed on the surface of Fe₃O₄@PDA spheres (Fig. 2c). The average size of silver particles is calculated to be 9–11 nm. Obviously, this phenomenon indicates that Fe₃O₄@PDA-Ag with core-shell structures has been shaped. Moreover, in the presence of glucose, the preparation process of silver nanoparticles supported on Fe₃O₄@PDA can be completed just in 5 h, faster than the method reported previously, which typically lasts more than 12 h [33]. It can be explained that glucose accelerates the reduction of silver ammonia ions.

Fig. 2e shows the growth process of the PDA shell onto Fe_3O_4 core as the reaction proceed. It can be seen that the thickness of PDA layer is about 34 nm after 24 h, but with further increasing of the reaction time (36 h), the thickness only increases about 5 nm. Thus, it can be conducted that



Fig. 2. TEM images of Fe_3O_4 (a), Fe_3O_4 @PDA (b) and Fe_3O_4 @PDA-Ag (c) showing PDA coating and Ag nanoparticles (Ag nanoparticles enclosed by the red rectangular area in (c)), respectively; and the inset in (c) contains photographs of the size distribution of Ag nanoparticles. And SEM image of Fe_3O_4 @PDA (d) showing the surface morphology; (e) The shell thickness of the PDA layer functioned with time during the coating process in the ethanol-water solution, and the inset in (e) contains photographs of the Fe_3O_4 @PDA in solution.

polydopamine can be deposited on the surface of Fe_3O_4 within 24 h. Furthermore, the obtained nanoparticles can be well dispersed in water to form a steady suspension, which shows much better water dispensability than the pristine Fe_3O_4 (Fig. 2e, inset).

The FTIR spectra can also confirms the successful modification of Fe₃O₄ with polydopamine and Ag nanoparticles (Fig. S1⁺). In the spectrum of bare Fe_3O_4 (Fig. S1a), the bands around 587 cm⁻¹ and 634 cm⁻¹ correspond to the Fe-O vibration [36,37]. The peaks at 1066 cm⁻¹ is assigned to the C-H vibrating. In the spectrum of PDA spheres, the main absorption bands in the range 1200-1600 cm⁻¹ and 3350 cm⁻¹ are due to the aromatic rings and catechol -OH groups, respectively [35]. In the spectrum of Fe₃O₄@PDA and Fe₃O₄@PDA-Ag, both the characteristic peaks of Fe₃O₄ and PDA can be observed, indicating PDA has been successfully attached to the surface of the magnetic particles as well. By contrast, the peak at 3350 cm⁻¹ for both Fe₃O₄@PDA and Fe₃O₄@PDA-Ag composites is broader than that of the Fe_3O_4 sphere, which results from the overlapping of hydroxyls groups, amines and water adsorbed in PDA polymer [38]. Overall, these FTIR spectra provided supportive evidence that Fe₃O₄@ PDA-Ag composites have been successfully prepared.

The XPS data of the Fe₃O₄@PDA-Ag elucidated the presence of Ag, C, O and N elements (Fig. 3). Fig. 3b describes the spectrum of the Ag3d transition of Fe₃O₄@PDA-Ag. Chemical binding energies of Ag3d_{5/2} and Ag3d_{3/2} are observed at 368.1 and 374.1 eV, respectively, illustrating the presence of metallic Ag nanoparticles on the complex. The C1s spectrum shows two peaks at 287.2 and 284.8 eV, which can be assigned to C=O and C-C/CH_x, respectively (Fig. 3c) [31]. The N1s spectrum of the XPS measurements can be curve-fitted into three peak components with binding energy at 406.4, 399.6 and 392.9 eV (Fig. 3d). The XPS peaks at 399.6 and 392.9 eV can ascribe to the pyridine-N and pyrrolic-N, respectively [39]. Meanwhile, the peak at 406.4 eV is caused by amine groups. The XPS results clearly further demonstrate that Fe₃O₄ core have been modified by PDA layer and metallic Ag.

Fig. 4 shows the magnetization curve of the Fe_3O_4 microspheres at room temperature. Because almost no hysteresis loops were found in the magnetization curve, the final product presented the paramagnetic nature at 300 K. The measured saturation magnetization values (Ms) were 87.13, 79.01 and 40.33 emu·g⁻¹ for Fe₃O₄, Fe₃O₄@PDA-Ag, respectively (Table 1). And the remnant magnetization (Mr) was about 1.8 emu·g⁻¹, while the coactivity (Hc) was about 74.4 Oe for Fe₃O₄@PDA-Ag microspheres. This value permits the adsorbent to be quickly collected from reaction system using an external magnet (inset of Fig. 4),



Fig. 3. X-ray photoelectron spectrum of Fe_3O_4 @PDA-Ag (a) and high-resolution XPS spectra of Ag 3d (b), C 1s (c), and N 1s (d) regions for the Fe_3O_4 @PDA-Ag microspheres.



Fig. 4 Magnetic hysteresis loop of Fe_3O_4 microspheres. Inset photographs: separation of Fe_3O_4 @PDA-Ag microspheres from aqueous dispersion using an external magnet.

which is satisfactory for their practical application. Ms of Fe_3O_4 particles is higher than those of Fe_3O_4 @PDA, Fe_3O_4 @PDA-Ag microspheres, which can be attributed to the PDA coating and Ag deposition on Fe_3O_4 core.

Fig. 5 shows the PXRD patterns of Fe₃O₄, Fe₃O₄@PDA and Fe₃O₄@PDA-Ag. In the three samples, the appeared diffraction peaks at 30.11, 35.41, 43.07, 53.44, 56.84 and 62.48° are indexed to the (220), (311), (400), (422), (511) and (440) diffractions of Fe₃O₄ nanoparticle respectively (JCPDS file 89-4319). For Fe₃ O_{47} similar PXRD results were reported in literature [40,41]. The PXRD peaks can match well with the characteristic peaks of inverse cubic spinel structure, and the characteristic peak is more obvious and sharper, which indicates that the crystalline structure of Fe₃O₄ nanoparticle can be preserved after the surface modification with PDA polymer and Ag nanoparticle. Compared with Fe₃O₄ and Fe₃O₄@PDA, the PXRD patterns of Fe₃O₄@PDA-Ag have four obvious absorption peaks. The peaks at 2θ values 38.06, 44.22, 64.44 and 77.35° can be assigned to (111), (200), (220) and (311) planes of silver [42], respectively. In combination with XPS results, it can be concluded that the magnetic particles loaded by Ag have high purity.

3.2. Adsorption performance

3.2.1. Selective adsorption dyes

We tried to explore the ability of Fe_3O_4 @PDA-Ag microsphere to adsorb different pollutant dyes from water. We selected AH, MB, MG, OIV and MO (Fig. 6) as model dye to test Fe_3O_4 @PDA-Ag microsphere adsorption and releasing abilities from their aqueous solution. Interestingly, when Fe_3O_4 @PDA-Ag microspheres were added in the different dye solution over a period of time, the extraordinary differences could be seen in different dye solution.

As shown in Fig. 7, the UV-vis spectroscopy results showed that Fe_3O_4 @PDA-Ag microspheres exhibited an excellent capacity to adsorb AH (Fig. 7a), MB (Fig. 7b) and MG (Fig. 7c), while the samples in MO (Fig. 7d) and OIV (Fig. 7e) solution showed almost no adsorption ability. Such



Fig. 5. Powder XRD pattern of $\rm Fe_3O_4$ (a), $\rm Fe_3O_4$ @PDA (b) and $\rm Fe_3O_4$ @PDA-Ag (c).



Fig. 6. Structure of dyes in this work: Acriflavine Hydrochloride (AH), Malachite Green Oxalate (MG), Methylene Blue (MB), Orange IV (OIV) and Methyl Orange (MO).

adsorption results indicated that Fe₃O₄@PDA-Ag microspheres could selectively adsorb cationic dyes. Moreover, it is worthy to mention that Fe₃O₄@PDA-Ag can adsorb AH completely within 100 s, indicating the rapid adsorption of AH. Furthermore, Fe₃O₄@PDA-Ag can adsorb about 97.8% of MB within 6 min and 96.9% of MG within 12 min (Fig. S2⁺). This difference in the adsorption capacity could be explained that the structure and functional group of AH are different from those of MB and MG. In comparison with those reported adsorbents based on Table S1⁺, the adsorption capacity of Fe₃O₄@PDA-Ag microspheres is only higher than part of them [43–55].

To validate whether microsphere possesses the ability to selectively adsorb cationic dyes from mixture solution, the comparison experiments were measured in mixture solution comprising of MO and MB. As depicted in Fig. 8, the UV-Vis spectra clearly disclosed that the absorption



Fig. 7. UV-Vis spectra of aqueous solution of AH (a), MB (b), MG (c), MO (d) and OIV (e) in the presence of freshly prepared Fe_3O_4 @ PDA-Ag monitored with time. (Initial dye concentration = 5 mg·L⁻¹; Adsorbent dosage = 10 mg; Experimental temperature = 26°C; Dye volume = 10 mL).

intensity of MB (665 nm) decreases significantly, while the characteristic absorption wavelengths of MO (465 nm) did not change. It is also observed with the naked eye that the color of the mixed dyes gradually change from their initial green to orange, indicating that MO was left in the solution. Similar results had also been gained when we tested the selective adsorption properties of microsphere in mixture solution of MO-MG and MO-AH (Fig. S3⁺). This result confirmed that Fe₃O₄@PDA-Ag microspheres could effectively

and selectively adsorb cationic dye molecules, leaving anion dye molecules in the solution.

3.2.2. Effect of pH on dye adsorption

To study the effect of solution pH on cationic dyes removal from solution, the experiments were carried out at three different pH values (pH = 3.0, 6.5 and 9.0). Fig. 9a



Fig. 8. UV-Vis spectra of MO and MB mixture in the presence of freshly prepared Fe_3O_4 @PDA-Ag monitored with time (Insert: the color change of MO-MB solution with time after the addition of Fe_3O_4 @PDA-Ag microspheres); (Initial dye concentration = 5 mg·L⁻¹; Adsorbent dosage = 10 mg; Experimental temperature = 26°C; Dye volume = 10 mL).

Table 1 Summary of magnetism data

Sample name	Magnetization (Ms) (emu· g ⁻¹)	Remnant magnetization (Mr) (emu· g ⁻¹)	Coactivity (Hc) (Oe)
Fe ₃ O ₄	87.13	2.84	55.41
Fe ₃ O ₄ @PDA	79.01	3.64	75.21
Fe ₃ O ₄ @PDA-Ag	40.33	1.80	74.40

shows that the removal efficiency of AH is better at higher pH conditions. AH is a typical cationic dye containing amino functional groups. At the lower pH values, the poor adsorption performance of Fe₃O₄@PDA-Ag microspheres could ascribe to the strong competition of H⁺ and the cationic dye molecules on the active sites of the adsorbent. On the other hand, a significant change on the adsorption rate under different pH implies that surface charge may affect the electrostatic interaction between adsorbent and cationic dye molecules. In order to prove this conclusion, the zeta potentials of Fe₃O₄@PDA-Ag were ascertained in the range of pH from 2.0 to 10.0, and the result is shown in (Fig. S4^{\dagger}). The zeta potential of adsorbent at pH = 6.0 is about -36.8 mV, suggesting that there are many negative charges on the surface of adsorbent. Fe₃O₄@PDA-Ag microspheres are protonated at low pH, reducing the negative charge on the surface, which results in obvious reduction in adsorption performance. Whereas Fe₂O₄@PDA-Ag microspheres surface is deprotonated at high pH and negative charge enhance sharply, and strongly attract the positively charged dye molecules [56]. The strength of electrostatic interactions between adsorbent and cationic dye molecules provides a reasonable interpretation for variation of removal efficiencies of dye. Theoretically, Fe₃O₄@PDA-Ag microspheres could quantitatively adsorb cationic dye through electrostatic interaction in the whole pH range.



Fig. 9. Plots of C_i/C_0 at λ_{max} of AH versus time: (a) Using different pH values of AH solution; (b) In the absence and presence of different surfactants; (c) In the absence and presence of different concentrations of Na₂SO₄.

3.2.3. Influence of surfactants on dye adsorption

So as to evaluate the effects of surfactants on the dyes adsorption, CTAB, SDS and TX-100, as model surfactants, were considered. As shown in Fig. 9b, the presence of surfactants shows a strong influence on the adsorption rates of dye. As we all known, surfactants could move and accumulate on the surface of Fe₃O₄@PDA-Ag microspheres, thus hindering the approaching of the dye molecules to the Fe₃O₄@PDA-Ag microspheres and reducing adsorption performance [15]. The adsorption rate of AH is slower in the presence of SDS or CTAB than TX-100, as shown in Fig. 9b. Similar results were also obtained when we tested the effects of surfactants on MB (or MG) adsorption (Fig. S5⁺). This phenomenon could be explained by the following reason: on the one hand, SDS and cationic dye have different charges, which prevents the dye molecule from approaching Fe₃O₄@PDA-Ag microspheres due to electrostatic attraction between them. On the other hand, surfactants could interact with the surface of Fe₃O₄@PDA-Ag microspheres and gathering around them, and further neutralize or obstruct the adsorbent to interact with dye molecule.

3.2.4. Effect of inorganic salt on dye adsorption

It is believed that inorganic salt ions, such as Na₂SO₄ and NaCl, could considerably contribute to improve dyeing effect. However, inorganic ions in industrial wastewater have a negative impact on the treatment of dye wastewater. Therefore, NaCl and Na2SO4 were selected to explore the effect on dye adsorption. The effect of Na₂SO₄ on the AH removal by Fe₃O₄@PDA-Ag microspheres is presented in Fig. 9c. As seen that the rate of adsorption slows down with the increasing of ionic strength in solution, which indicates that adsorption process is partly governed by electrostatic interactions. Similar results were gained when we tested adsorption rate curves of MB (or MG) by addition of inorganic salt (Fig. S6⁺). The addition of Na, SO₄ tends to undermine the electric double layers of the Fe₂O₄@PDA-Ag microspheres, weakening the electrostatic interactions between cationic dye molecules and the adsorbent. Meanwhile charges of the adsorbent binding sites are neutralized by the additional ions, which results in the decline in available sites for adsorption of dyes and further decline the adsorption performance [57,58]. While with higher Na₂SO₄

concentration (>5 g·L⁻¹), the adsorption rate is still weakening, but the decreasing rate is slowdown. It is considered that π - π stacking interactions between PDA layer and dye molecules might play an important role in promoting dye adsorption. The similar phenomenon was found in the effect of NaCl (Fig. S7⁺).

3.3. Selective adsorption mechanism

It is of great significance for practical adsorbent material to understand the selective adsorption mechanism. Based on the above adsorption experiment analysis, it can be concluded that this adsorption selectivity of Fe₃O₄@PDA-Ag microsphere towards different dyes is due to the electrostatic interactions and π - π stacking interactions (Fig. 10). Due to the rich phenolic groups and aromatic rings of PDA, there are electrostatic interactions and π - π stacking interacting interactions between PDA layer and dye molecules [27,50,56].

To further confirm the adsorption mechanism, comparison experiments were also measured. Intriguingly, the adsorption performance of Fe_3O_4 @PDA and Fe_3O_4 @ PDA-Ag is similar, whereas Fe_3O_4 shows much lower adsorption capability for AH (Fig. 11). The similar results were also found when we tested adsorption rate curves of MB (or MG) after the addition of different adsorbents (Fig. S8⁺). This phenomenon implies that PDA payer plays a dominant role in the adsorption process and the amount of Fe_3O_4 nanoparticles has no effect on adsorption capability, but Fe_3O_4 nanoparticles are conducive to separation and improving the recovery efficiency.

Compared with the Fe₃O₄@PDA spheres, the Fe₃O₄@PDA-Ag microsphere exhibits an enhanced adsorption performance, which implies that Ag nanoparticles could improve the adsorption efficiency of Fe₃O₄@PDA-Ag for cationic dyes. We suspect that there is synergistic effect between the Ag nanoparticles and PDA layers, which causes faster adsorption rate of Fe₃O₄@PDA-Ag than Fe₃O₄@PDA. Zeta potentials of the adsorbents could disclose the reason for the great changes. As shown in Fig. S4, the value of pH



Fig. 10. Schematic illustration of the adsorption mechanism.

at which the point of zero charge of $Fe_3O_4@PDA$ occurs is around 4.3, whereas that of $Fe_3O_4@PDA$ -Ag drastically decrease to about 2.2. The alteration of zero charge provides a reasonable interpretation for the improvement of adsorp-



Fig. 11. Adsorption rate curves of AH after the addition of different adsorbents.

tion performance. On the other hand, silver nanoparticles have larger specific surface area and higher surface free energy and binding energy, which encourages other molecules to approach and gather around it. The Ag particles located on the surface of Fe₃O₄@PDA microspheres could attract and encourage rapid movement of the cationic dye toward the surface of the negatively charged adsorbent, which increase the dye adsorption rate. In addition, earlier work also demonstrated that silver nanoparticles could adsorb dye molecules by electrostatic interactions between them [59].

3.4. Recycling test of the adsorbent

As is well known, the stability and recyclability of the adsorbent is one of the prerequisites for evaluating its practicability. In this work, the release experiment were also discussed, after the AH (MG or MB) fully loaded Fe₃O₄@PDA-Ag microspheres. The static desorption of adsorbents was carried out with the saturated solution of NaCl in DMF (NaCl-DMF) as eluent. As shown in Fig. 12a, the results show that approximately 100% of the dye molecules on Fe₃O₄@PDA spheres can be rapidly released into NaCl-DMF within 3 min. Whereas in pure DMF, the release rate of AH turned much slower and the release



Fig. 12. (a) The reversible trapping and releasing of AH in a full adsorption-release cycle; (b) UV-Vis adsorption spectra of AH solution in the presence of adsorbents regenerated with different desorption agents; (c) The recyclability of Fe_3O_4 @PDA-Ag microspheres for the adsorption of AH; (d) Powder XRD pattern of Fe_3O_4 @PDA-Ag microspheres before and after adsorption-release of AH for 29 cycles.

amount is only 30% in 3 min (Fig. 12b). The results show that the enhanced dyes desorption after addition of NaCl is consistent with the electrostatic interaction mechanism of cationic dyes adsorption on Fe₃O₄@PDA-Ag microspheres. In the presence of NaCl, the negatively charged adsorbent and positively charged dyes would be screened by the respective Na⁺ and Cl⁻ counter ions, breaking their electrostatic interaction and releasing dyes molecules [60].

Such an adsorption-release process was performed for 29 continuous cycles, and it is clear that after using the adsorbent for 29 successive runs, there is a small decrease in its adsorption capture (Fig. 12c). The decrease of adsorption capture of Fe₃O₄@PDA-Ag microspheres may be caused by the loss of adsorbent during magnetic recovery using a magnet. The PXRD date of the recycled adsorbent were obtained to investigate the stability of Fe₂O₄@ PDA-Ag microspheres, as shown in (Fig. 12d). The PXRD results reveal that the adsorbent are stable after 29 adsorption-release cycles. In addition, after the Fe₃O₄@PDA-Ag microspheres were shaken in water for two hours, silver species were not detected by ICP-OES. The results indicate that there is no significant leaching of the silver species, which further proves that the structure of the adsorbent is stable. It can be concluded that Fe₂O₄@PDA-Ag showed good recyclability for the treatment of dye from aqueous solution.

4. Conclusion

In conclusion, we demonstrated that Fe₂O₄@PDA-Ag microspheres can be synthesized by a fast and straightforward strategy in the presence of glucose. The addition of glucose accelerates the reduction of silver ions, which shortens the reaction time of silver nanoparticles deposited on Fe₃O₄@PDA. Five organic dyes were selected to investigate the adsorption selectivity of the as-prepared magnetic adsorbent. Results showed that Fe₃O₄@PDA-Ag microspheres exhibit outstanding selective adsorption ability towards cationic dyes and almost no adsorption ability for anionic dyes, and the adsorption efficiency is 98.2%, 97.8% and 96.9% for AH, MB and MG in this work, respectively. The strong electrostatic interaction, π - π stacking interactions and the synergistic effect existing between the Ag nanoparticles, PDA layer and Fe₃O₄ of the composite are the main driving forces for cationic dyes adsorption. Thus, it is believed that Fe₃O₄@PDA-Ag microspheres would play an important role in separating mixture of dyes. Furthermore, the adsorption rate can be affected by pH and the type of surfactant in solution. And the adsorbability of Fe₃O₄@PDA-Ag microspheres shows satisfactory tolerance against the variations in both inorganic salts environment. In addition, the adsorbent can be regenerated in 3 minutes using the saturated solution of NaCl in DMF as eluent and exhibits excellent reusability for at least 29 cycles. The magnetic core enables them to be easily isolated for reuse from the reaction solution with a magnet. From the above experiments, we not only can prove outstanding selective adsorption ability towards cationic dyes of Fe₃O₄@PDA-Ag microspheres, but also demonstrate their potential application in dye separation technologies.

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Conflict of Interest

The authors declare that they have no conflict of interest.

References

- A. Ahmad, S.H. Mohd-Setapar, C.S. Chuong, A. Khatoona, W.A. Wanic, R. Kumard, M. Rafatullah, Recent advances in new generation dye removal technologies: novel search for approaches to reprocess wastewater, RSC Adv., 5 (2015) 30801–30818.
- [2] M.T. Yagub, T.K. Sen, S. Afroze, H.M. Ang, Dye and its removal from aqueous solution by adsorption: A review, Adv. Colloid Interfac., 209 (2014) 172–184.
- [3] Z. Yang, F. Wang, C. Zhang, G. Zeng, X. Tan, Z. Yu, Y. Zhong, H. Wang, F. Cui, Utilization of LDH-based materials as potential adsorbents and photocatalysts for the decontamination of dyes wastewater: a review, RSC Adv., 6 (2016) 79415–79436.
- [4] L. Pan, K. Jia, Y. Huang, X. Liu, Formation of organometallic microstructures via self-assembling of carboxylated zinc phthalocyanines with selective adsorption and visible lightdriven photodegradation of cationic dyes, J. Mater. Sci., 53 (2018) 492–505.
- [5] L. Yao, L. Zhang, R. Wang, S. Chou, Z.L. Dong, A new integrated approach for dye removal from wastewater by polyoxometalates functionalized membranes, J. Hazard Mater., 301 (2016) 462–470.
- [6] J. Paul, A.A. Kadam, S.P. Govindwar, P. Kumar, L. Varshney, An insight into the influence of low dose irradiation pretreatment on the microbial decolouration and degradation of reactive red-120 dye, Chemosphere, 90 (2013) 1348–1358.
- [7] C. Yang, Q. Li, L. Tang, A. Bai, H. Song, Y. Yu, Monodispersed colloidal zinc oxide nanospheres with various size scales: synthesis, formation mechanism, and enhanced photocatalytic activity, J. Mater. Sci., 51 (2016) 5445–5459.
- [8] J. Lin, Y. Teng, Y. Lu, S. Lu, X. Hao, D. Cheng, Usage of hydrophobic ionic liquid [BMIM][PF6] for recovery of acid dye from wastewater and sequential application in Tussah silk dyeing, CLEAN-Soil, Air, Water, 42 (2014) 799–803.
- [9] M.C. Gutiérrez, M. Pepió, M. Crespi, Electrochemical oxidation of reactive dyes: method validation and application, Color. Technol., 118 (2002) 1–5.
- [10] P.A. Soloman, C.A. Basha, M. Velan, V. Ramamurthi, K. Koteeswaran, N. Balasubramanian, Electrochemical degradation of Remazol Black B dye effluent, CLEAN-Soil, Air, Water, 37 (2009) 889–900.
- [11] K. Okaiyeto, U.U. Nwodo, S.A. Okoli, L.V. Mabinya, A.I. Okoh, Implications for public health demands alternatives to inorganic and synthetic flocculants: bioflocculants as important candidates, Microbiologyopen, 5 (2016) 177–211.
- [12] A.M. El-Dein, J. Libra, U. Wiesmann, Cost analysis for the degradation of highly concentrated textile dye wastewater with chemical oxidation H₂O₂/UV and biological treatment, J. Chem. Technol. Biot., 81 (2006) 1239–1245.
- [13] G.A. Grande, G. Rovero, S. Sicardi, M. Giansetti, Degradation of residual dyes in textile wastewater by ozone: Comparison between mixed and bubble column reactors, Can. J. Chem. Eng., 95 (2017) 297–306.
- [14] M.T. Yagub, T.K. Sen, S. Afroze, H.M. Ang, Dye and its removal from aqueous solution by adsorption: a review, Adv. Colloid Interface, 209 (2014) 172–184.
- [15] L. Sun, J. He, S. An, J. Zhang, J. Zheng, D. Ren, Recyclable Fe₃O₄@ SiO₂-Ag magnetic nanospheres for the rapid decolorizing of dye pollutants, Chinese J. Catal., 34 (2013) 1378–1385.

- [16] A. Mathew, T. Pradeep, Noble metal clusters: applications in energy, environment, and biology, Part Part Syst. Char., 31 (2104) 1017–1053.
- [17] J. Li, L. Tan, G. Wang, M. Yang, Synthesis of double-shelled sea urchin-like yolk-shell Fe₃O₄/TiO₂/Au microspheres and their catalytic applications, Nanotechnology, 26 (2015) 095601.
- [18] Z.-Z. Wang, S.-R. Zhai, F. Zhang, Z.-Y. Xiao, B. Zhai, Q.-D. An, "Green" synthesis of magnetic core-shell Fe₃O₄@SN-Ag towards efficient reduction of 4-nitrophenol, J. Sol-Gel. Sci. Techn., 73 (2015) 299–305.
- [19] F. Yang, C. Wang, L. Wang, C. Liu, A. Feng, X. Liu, C. Chi, X. Jia, L. Zhang, Y. Li, Au/graphene oxide/carbon nanotube flexible catalyst film: synthesis, characterization and its application for catalytic reduction of 4-nitrophenol, RSC Adv., 5 (2015) 37710–37715.
- [20] Z. Cheng, S. Zhao, Z. Han, Y. Zhang, X. Zhao, L. Kang, A novel preparation of Ag@TiO₂ tubes and their potent photocatalytic degradation efficiency, Cryst. Eng. Comm., 18 (2016) 8756–8761.
- [21] S. Zhao, Z. Cheng, L. Kang, M. Li, Z. Gao, The facile preparation of Ag decorated TiO₂/ZnO nanotubes and their potent photocatalytic degradation efficiency, RSC Adv., 7 (2017) 50064–50071.
- [22] Y. Liu, X. Chen, M. Zhu, U. Jameel, Recent progress of synthesis and application in Au@MOFs hybrid materials, Catal. Surv. Asia., 21 (2017) 130–142.
- [23] S.M. El-Sheikh, A.A. Ismail, J.F. Al-Sharab, Catalytic reduction of p-nitrophenol over precious metals/highly ordered mesoporous silica, New J. Chem., 37 (2013) 2399–2407.
- [24] Z.-Z. Wang, S.-R. Zhai, B. Zhai, Q.-D. An, S.-W. Li, In situ reduction and stabilization of Ag NPs onto magnetic composites for rapid hydrogenation catalysis, J. Sol-Gel. Sci. Techn., 75 (2015) 680–692.
- [25] J. Zhang, S. Zhai, S. Li, Z. Xiao, Y. Song, Q. An, G. Tian, Pb(II) removal of Fe₃O₄@SiO₂-NH₂ core-shell nanomaterials prepared via a controllable sol-gel process, Chem. Eng. J, 215 (2013) 461–471.
- [26] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-inspired surface chemistry for multifunctional coatings, Science, 318 (2007) 426–430.
- [27] H. Sun, X. Yang, Y. Zhang, X. Cheng, Y. Xu, Y. Bai, L. Shao, Segregation-induced in situ hydrophilic modification of poly(vinylidene fluoride) ultrafiltration membranes via sticky poly(ethylene glycol) blending, J. Membrane Sci., 563 (2018) 22–30.
- [28] J. Fu, Z. Chen, M. Wang, S. Liu, J. Zhang, J. Zhang, R. Han, Q. Xu, Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): kinetics, isotherm, thermodynamics and mechanism analysis, Chem. Eng. J., 259 (2015) 53–61.
- [29] H. Gao, Y. Sun, J. Zhou, R. Xu, H. Duan, Mussel-inspired synthesis of polydopamine-functionalized graphene hydrogel as reusable adsorbents for water purification, ACS Appl. Mater. Interfaces, 5 (2013) 425–432.
- [30] H.-C. Yang, K.-J. Liao, H. Huang, Q.-Y. Wu, L.-S. Wan, Z.-K. Xu, Mussel-inspired modification of a polymer membrane for ultra-high water permeability and oil-in-water emulsion separation, J. Mater. Chem. A, 2 (2014) 10225–10230.
- [31] J. Manna, S. Akbayrak, S. Özkar, Palladium(0) nanoparticles supported on polydopamine coated Fe₃O₄ as magnetically isolable, highly active and reusable catalysts for hydrolytic dehydrogenation of ammonia borane, RSC Adv., 6 (2016) 102035–102042.
- [32] Q. Liu, N. Sun, M. Gao, C. Deng, Magnetic binary metal-organic framework as a novel affinity probe for highly selective capture of endogenous phosphopeptides, ACS Sustainable Chem. Eng., 6 (2018) 4382–4389.
- [33] Y. Xie, B. Yan, H. Xu, J. Chen, Q. Liu, Y. Deng, H. Zeng, Highly regenerable mussel-inspired Fe₃O₄@polydopamine-Ag coreshell microspheres as catalyst and adsorbent for methylene blue removal, ACS Appl. Mater. Interfaces, 6 (2014) 8845– 8852.

- [34] Q. Dong, C. Bi, L. Chang, Controllable preparation and study of Fe₃O₄, Guangdong Chemical Industry, 42 (2015) 4–6.
- [35] Q. Yue, M. Wang, Z. Sun, C. Wang, C. Wang, Y. Deng, D. Zhao, A versatile ethanol-mediated polymerization of dopamine for efficient surface modification and the construction of functional core-shell nanostructures, J. Mater. Chem. B, 1 (2013) 6085–6093.
- [36] B.-Q. Mao, Q.-D. An, Z.-Y. Xiao, S.-R. Zhai, Hydrophilic, hollow Fe₃O₄@PDA spheres with a storage cavity for efficient removal of polycyclic structured tetracycline, New J. Chem., 41 (2017) 1235–1244.
- [37] Y. Wei, B. Han, X. Hua, Y. Lin, X. Wang, X. Deng, Synthesis of Fe₃O₄ nanoparticles and their magnetic properties, Procedia Engineering, 27 (2012) 632–637.
- [38] Y. Wang, S. Wang, H. Niu, Y. Ma, T. Zeng, Y. Cai, Z. Meng, Preparation of polydopamine coated Fe₃O₄ nanoparticles and their application for enrichment of polycyclic aromatic hydrocarbons from environmental water samples, J. Chromatogr. A, 1283 (2013) 20–26.
- [39] B. Zheng, T.-W. Chen, F.-N. Xiao, W.-J. Bao, X.-H. Xia, KOH-activated nitrogen-doped graphene by means of thermal annealing for supercapacitor, J. Solid State Electr., 17 (2013) 1809–1814.
- [40] O. Duman, S. Tunç, T.G. Polat, B.K. Bozoğlan, Synthesis of magnetic oxidized multiwalled carbon nanotube-κ-carrageenan-Fe₃O₄ nanocomposite adsorbent and its application in cationic Methylene Blue dye adsorption, Carbohyd. Polym., 147 (2016) 79–88.
- [41] O. Duman, S. Tunç, B.K. Bozoğlan, T.G. Polat, Removal of triphenylmethane and reactive azo dyes from aqueous solution by magnetic carbon nanotube-κ-carrageenan-Fe₃O₄ nanocomposite, J. Alloy. Compd., 687 (2016) 370–383.
- [42] T. Solaiyammal, S. Muniyappan, B.G.T. Keerthana, S.S. Nemala, P. Bhargava, P. Murugakoothan. Green synthesis of Ag and the effect of Ag on the efficiency of TiO₂ based dye sensitized solar cell, J. Mater. Sci: Mater. Electron., 28 (2017) 15423–15434.
- [43] Z. Wang, J. Guo, J. Ma, L. Shao, Highly regenerable alkali-resistant magnetic nanoparticles inspired by mussels for rapid selective dye removal offer high-efficiency environmental remediation, J. Mater. Chem. A, 3 (2015) 19960–19968.
- [44] Y.Q. Zhang, X.B. Yang, Z.X. Wang, J. Long, L. Shao, Designing multifunctional 3D magnetic foam for effective insoluble oil separation and rapid selective dye removal for use in wastewater remediation, J. Mater. Chem. A, 5 (2017) 7316–7325.
 [45] W. Fan, W. Gao, C. Zhang, W.W. Tjiu, J. Pan, T. Liu, Hybridiza-
- [45] W. Fan, W. Gao, C. Zhang, W.W. Tjiu, J. Pan, T. Liu, Hybridization of graphene sheets and carbon-coated Fe_3O_4 nanoparticles as a synergistic adsorbent of organic dyes, J. Mater. Chem., 22 (2012) 25108–25115.
- [46] W. Wang, Z. Ding, M. Cai, H. Jian, Z. Zeng, F. Li, J.P. Liu, Synthesis and high-efficiency methylene blue adsorption of magnetic PAA/MnFe₂O₄ nanocomposites, Appl. Surf. Sci., 346 (2015) 348–353.
- [47] S. Kant, D. Pathania, P. Singh, P. Dhiman, A. Kumar, Removal of malachite green and methylene blue by Fe_{0.01}N_{10.01}Zn_{0.98}O/ polyacrylamide nanocomposite using coupled adsorption and photocatalysis, Appl. Catal. B-Environ., 147 (2014) 340–352.
- [48] L. Cui, Y. Wang, L. Hu, L. Gao, B. Du, Q. Wei, Mechanism of Pb (II) and methylene blue adsorption onto magnetic carbonate hydroxyapatite/graphene oxide, RSC Adv., 5 (2015) 9759–9770.
- [49] W. Zou, H. Bai, S. Gao, K. Li, Characterization of modified sawdust, kinetic and equilibrium study about methylene blue adsorption in batch mode, Korean J. Chem. Eng., 30 (2013) 111– 122.
- [50] J. Fu, Q. Xin, X. Wu, Z. Chen, Y. Yan, S. Liu, M. Wang, Q. Xu, Selective adsorption and separation of organic dyes from aqueous solution on polydopamine microspheres, J. Colloid Interf. Sc., 461 (2016) 292–304.
- [51] L. Sun, S. Hu, H. Sun, H. Guo, H. Zhu, M. Liu and H. Sun, Malachite green adsorption onto Fe₂O₄@SiO₂-NH₂: isotherms, kinetic and process optimization, RSC Adv., 5 (2015) 11837– 11844.

- [52] D. Wang, L. Liu, X. Jiang, J. Yu, X. Chen, Adsorption and removal of malachite green from aqueous solution using magnetic β-cyclodextrin-graphene oxide nanocomposites as adsorbents, Colloid. Surface. A, 466 (2015) 166–173.
 [53] M. Rajabi, B. Mirza, K. Mahanpoor, M. Mirjalili, F. Najafi,
- [53] M. Rajabi, B. Mirza, K. Mahanpoor, M. Mirjalili, F. Najafi, O. Moradi, H. Sadegh, R. Shahryari-ghoshekand, M. Asif, I. Tyagi, S. Agarwal, V.K. Gupta, Adsorption of malachite green from aqueous solution by carboxylate group functionalized multi-walled carbon nanotubes: determination of equilibrium and kinetics parameters, J. Ind. Eng. Chem., 34 (2016) 130–138.
- [54] Y. Han, S. Sheng, F. Yang, Y. Xie, M. Zhao, J.-R. Li, Size-exclusive and coordination-induced selective dye adsorption in a nanotubular metal-organic framework, J. Mater. Chem. A, 3 (2015) 12804–12809.
- [55] X. Meng, L. Cui, X. Wang, X. Zhang, X. Zhang, S. Bi, Syntheses, structural diversity, magnetic properties and dye absorption of various Co(ii) MOFs based on a semi-flexible 4-(3,5-dicarboxylatobenzyloxy)benzoic acid, Cryst. Eng. Comm., 19 (2017) 6630–6643.
- [56] S. Zhang, Y. Zhang, G. Bi, J. Liu, Z. Wang, Q. Xu, H. Xu, X. Li, Mussel-inspired polydopamine biopolymer decorated with magnetic nanoparticles for multiple pollutants removal, J. Hazard Mate., 270 (2014) 27–34.
 [57] J. Liu, H. Yu, Q. Liang, Y. Liu, J. Shen, Q. Bai, Preparation of
- [57] J. Liu, H. Yu, Q. Liang, Y. Liu, J. Shen, Q. Bai, Preparation of polyhedral oligomeric silsesquioxane based cross-linked inorganic-organic nanohybrid as adsorbent for selective removal of acidic dyes from aqueous solution, J. Colloid Interf. Sci., 497 (2017) 402–412.
- [58] J.-W. Liu, T. Yang, S. Chen, X.-W. Chen, J.-H. Wang, Nickel chelating functionalization of graphene composite for metal affinity membrane isolation of lysozyme, J. Mater. Chem. B, 1 (2013) 810–818.
- [59] N.R. Jana, T.K. Sau, T. Pal, Growing small silver particle as redox catalyst, J. Phys. Chem. B, 103 (1999) 115–121.
- [60] F. Jiang, D.M. Dinh, Y.-L. Hsieh, Adsorption and desorption of cationic malachite green dye on cellulose nanofibril aerogels, Carbohyd. Polymers., 173 (2017) 286–294.

Supplementary material

1. Experimental

1.1. Preparation of ultrapure water

Ultrapure water prepared with a Millipore Milli-Q water purification system (MA, USA) was used for all experiments. And water resistivity is about $18.2 \text{ M}\Omega \cdot \text{cm}$.

1.2. Preparation of silver ammonia solution

Silver ammonia solution was prepared by adding ammonia aqueous solution (2 wt%) into $AgNO_3$ solution until brown precipitation was just dissolved. The concentration of silver ammonia solution is 0.1 mol·L⁻¹.



Fig. S1. FTIR spectra of Fe_3O_4 nanoparticles (a), PDA spheres (b), core-shell Fe_3O_4 @PDA particles (c) and Fe_3O_4 @PDA-Ag microspheres (d).



Fig. S2. The effect of different organic dyes on the adsorption efficiency of Fe_3O_4 @PDA-Ag. (Initial dye concentration = 5 mg·L⁻¹; Adsorbent dosage = 10 mg; Experimental temperature = 26°C; Dye volume = 10 mL).



Fig. S3. (a) UV-Vis spectra of MO and MG mixture in the presence of freshly prepared Fe_3O_4 @PDA-Ag monitored with time; (b) UV-Vis spectra of MO and AH mixture in the presence of freshly prepared Fe_3O_4 @PDA-Ag monitored with time. (Initial dye concentration = 5 mg·L⁻¹; Adsorbent dosage = 10 mg; Experimental temperature = 26°C; Dye volume = 10 mL).



Fig. S4. Zeta potentials of $\mathrm{Fe_3O_4@PDA-Ag}$ under different pH values.

Table S1

Comparison of adsorption capacities of different adsorbents for dye removal

Adsorbent	Adsorption capacity	Adsorption time	References
Fe ₃ O ₄ @PDA/PEI	>95% for MB	5 min	[43]
Magnetic MF@Fe ₃ O ₄ @PDA/PSBMA	>96% for MB	2 min	[44]
Magnetic grapheme-Fe ₃ O ₄ @carbon hybrids	80% for MB	20 min	[45]
PAA/MnFe ₂ O ₄ nanocomposites	96.3% for MB	50 min	[46]
$Fe_{_{0.01}}Ni_{_{0.01}}Zn_{_{0.98}}O/polyacrylamide\ nanocomposite$	97.56% for MB 96.13% for MG	2 h 2 h	[47]
Magnetic carbonate hydroxyapatite/graphene oxide	96.43% for MB	3 h	[48]
Modified sawdust	96.6% for MB	480 min	[49]
Fe ₃ O ₄ @PDA-Ag microspheres	97.2% for MB	6 min	this work
Polydopamine microspheres	98.44% for MB	15 min	[50]
Fe ₃ O ₄ @SiO ₂ -NH ₂	>91% for MG	2 h	[51]
Fe ₃ O ₄ /β-CD/GO	98.97% for MG	120 min	[52]
Carboxylate group functionalized multi-walled carbon nanotubes	91.36% for MG	10 min	[53]
Fe ₃ O ₄ @PDA-Ag microspheres	96.9% for MG	12 min	this work
{[(CH ₃) ₂ NH ₂][Co ₂ NaL ₂ (CH ₃ COO) ₂]·xS}n	85% for AH	180 min	[54]
${[Co1.5(HL)(4,4'-bidpe)_2(H_2O)]\cdot 3H_2O}n$	92.8% for AH	480 min	[55]
Fe ₃ O ₄ @PDA-Ag microspheres	98.2%for AH	100 s	this work



Fig. S5. Plots of C_t/C_0 at λ_{max} of MB (a) and MG (b) versus time: In the absence and presence of different surfactant.



Fig. S6. Plots of C_t/C_0 at λ_{max} of MB (a) and MG (b) versus time: In the absence and presence of different concentrations of Na₂SO₄.

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Fig. S7. Plots of C_t/C_0 at λ_{max} of AH versus time: In the absence and presence of different concentrations of NaCl.



0.0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 Time (min))

Fig. S8. (a) Adsorption rate curves of MB after the addition of different adsorbents; (b) Adsorption rate curves of MG after the addition of different adsorbents.