Amino-rich polymer-coated Fe–Fe₂O₃ nanoparticles with high adsorption capacity and rapid magnetic separation for anionic dye removal

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Abstract

The development of excellent dye adsorbent with high adsorption capacity and good separation function is imperative to clean the wastewater. Herein, an innovative magnetic Fe–Fe₂O₃@poly(cyclotriphosphazene-co-polyethyleneimine) (named as Fe–Fe₂O₃@PCP) composite was fabricated through a facile copolymerization between hexachlorocyclotriphosphazene and polyethyleneimine in the presence of Fe–Fe₂O₃ nanoparticles. With the help of scanning electron microscope, transmission electron microscope, Fourier transform infrared spectroscope and vibrating sample magnetometer, the microstructure of the resulting magnetic Fe–Fe₂O₃@PCP composite was characterized. Then, the adsorption performance of magnetic Fe–Fe₂O₃@PCP composite was evaluated by removing anionic dye acid chrome blue K (ACBK) from aqueous solution. The effects of contact time, initial solution pH and temperature on the adsorption of ACBK onto magnetic Fe–Fe₂O₃@PCP composite were systematically studied. The kinetics, isotherms and mechanism of the adsorption process were analyzed. Results show that the maximum adsorption capacity of the magnetic Fe–Fe₂O₃@PCP toward ACBK dye could be up to 260 mg g^{−1} at 25 °C in neutral solution. The adsorption kinetics follows both the pseudo-second-order kinetic model and the Weber's intraparticle diffusion model well. And the Freundlich isotherm model can nicely fit the adsorption equilibrium data. The electrostatic attraction between Fe–Fe₂O₃@PCP and ACBK plays a dominant role in the adsorption process. Moreover, the magnetic Fe–Fe₂O₃@PCP composite owns a high saturation magnetization of 30.1 emu g^{−1}, rendering it rapid magnetic separability and good reusability. After five adsorption–desorption cycles, the magnetic composite still kept 75% of removal efficiency with the adsorption capacity of 195 mg g^{−1}. The excellent adsorption capacity and good magnetic separability make the magnetic Fe–Fe₂O₃@PCP composite a promising adsorbent for efficient removal of anionic dyes including ACBK from contaminated wastewater.

Keywords Adsorption · Dye · Magnetic separation · Polymer · Composite

1 Introduction

With the decreasing availability of freshwater and increasing concern for ecosystem and human health, water pollution never fails to fascinate scholars and researchers [1–4]. In particular, dye pollutants in industrial wastewater caused by textiles, paper, leather and so on [5] have been highlighted owing to the tremendous effluents,

complicated compositions and dramatic toxicity. Therefore, it is quite imperative to carry off dye contamination on their way to the environment. To date, a great range of strategies including physical, chemical and biological methods have been put forward to treat with dye-containing wastewater [6–11]. Among these approaches, adsorption is considered to be the most promising way due to its easy preparation, high efficiency and low cost.

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Many porous materials, such as metal organic frameworks (MOFs) [10–13], activated carbon [14, 15] and layered double hydroxides (LDHs) [16, 17], have been used as adsorbents for the treatment of dye wastewater. Nevertheless, the most reported adsorbents still face the problem of poor adsorption capacity. To further improve the adsorption performance of adsorbents, more efforts should be made to synthesize materials with higher specific surface area, stronger selectivity and more functional groups.

As far as we know, polymer-based composites and ligand-modified mesoporous silica monoliths have been regarded as promising adsorbent candidates for application in the field of adsorption due to their structure advantages including large specific surface area, plentiful functional groups, suitable pore structure, good chemical stability and so forth. So far, many efforts have been devoted to the structure design of the above two types of adsorbents. For example, Gonzalez et al. [18] developed a chitin/graphene oxide hybrid composite for the efficient removal of pollutant dyes. Yu et al. [19] have prepared bio-inspired polydopamine coated on natural zeolites to remove copper from wastewater. Awual et al. have done a series of work to anchor functional ligand in mesoporous silica for efficient detection and adsorption of metal ions in wastewater [20–25]. Hollow polymer microcapsules with high surface density of amino groups were also prepared by our group for selective adsorption of anionic dyes [26]. Nevertheless, like the porous adsorbents mentioned in the first paragraph, the polymer-based nanocomposites are also confronted with a great challenge on separation. Unless the adsorbents were separated or filtrated in time, it will bring about high cost, secondary pollution, and even decreasing the adsorption capacity because of the natural desorption. Therefore, it is of great significance to design adsorbents with an easy separation process. Normally, researchers suggest that endowing the adsorbent with magnetic functionality is very advisable to simplify the traditional separation procedures [27–32].

In our earlier study, Fe@Fe₂O₃ nanoscale stirring bars with ultrahigh saturation magnetization have been prepared in quantity [33]. Naturally, we expect to associate polymer-based nanocomposites with magnetic materials to purify the dye-containing wastewater. Herein, magnetic Fe–Fe₂O₃@poly (hexachlorocyclotriphosphazene-co-polyethyleneimine) composite (Fe–Fe₂O₃@PCP) with high adsorption capacity up to 260 mg g^{−1} has been successfully prepared via a facile polymerization means, which is regarded as one kind of potential adsorbents for the removal of anionic dye (ACBK). Besides, fast and operable magnetic separation rather than centrifugation is employed during the process of preparation and adsorption. Also, the adsorption process has been systematically studied, which covers a variety of influencing factors

including selective adsorption, equilibrium, kinetics as well as cycle stability. We think the magnetic Fe–Fe₂O₃@PCP composite might be a prospective adsorbent to remove anionic dyes from dye-containing wastewater selectively and efficiently.

2 Experimental

2.1 Materials

Hexachlorocyclotriphosphazene (HCCP), triethylamine (TEA) and sodium borohydride (NaBH₄) were purchased from Sinopharm Chemical Reagent Co., Ltd. Branched polyethyleneimine (PEI, MW = 600 g mol^{−1}, 99%) and ferric chloride hexahydrate (FeCl₃·6H₂O) were purchased from Aladdin Industrial Corporation. Acetonitrile, ethanol, methylene blue (MB) and acid chrome blue K (ACBK) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. These chemical reagents were analytical grade and used directly. The dye solutions were all prepared by dissolving the certain amounts of organic dye in deionized water.

2.2 Preparation of magnetic Fe–Fe₂O₃@PCP composite

2.2.1 Preparation of magnetic Fe–Fe₂O₃ nanoparticles

Fe–Fe₂O₃ nanoparticles with excellent magnetic performance were firstly prepared according to our previous report with small modification [33]. Fifty milliliters aqueous solution and 0.02 mol NaBH₄ were stirred mechanically in an ice bath. After stirring for 10 min, 0.1 mol L^{−1} FeCl₃ solution (50 mL) was added to the above solution within 1 min, and the black precipitations appeared immediately. After stirring for another 15 min, the final precipitates were collected with a magnet, washed with ethanol for six times and dried at 60 °C overnight.

2.2.2 Preparation of core@shell structural magnetic Fe–Fe₂O₃@PCP composite

In order to obtain magnetic Fe–Fe₂O₃@PCP composite, 100 mg as-prepared Fe–Fe₂O₃ and 80 mL acetonitrile were under ultrasonic treatment for 30 min. Then, 50 mg PEI dispersed into 10 mL acetonitrile was dropped into the above solution. After ultrasonic treatment for 10 min, another solution containing 50 mg HCCP and 10 mL acetonitrile was added dropwise. While the solution was well distributed, 2 mL TEA was injected into the solution mentioned above. After that, the reaction solution was sonicated for 3 h continuously. The final precipitates were collected with the help of an external magnetic field and

washed with deionized water and ethanol no less than three times, respectively. Ultimately, the resulting products were dried at 60 °C for 12 h to obtain magnetic Fe–Fe₂O₃@PCP composite.

2.3 Adsorption and separation toward organic dyes

In order to evaluate the adsorption performance of magnetic Fe–Fe₂O₃@PCP composite for the removal of organic dyes, we resorted to the batch contact adsorption method via a constant shaking incubator at a shaking speed of 120 rpm. For the selective adsorption assessment, 5 mg magnetic Fe–Fe₂O₃@PCP composite was added to the binary dye (ACBK and MB) solution ($V = 20$ mL, $C_{ACBK} = C_{MB} = 10$ mg L^{−1}) for 5 h. Kinetic experiments were performed by adding 25 mg magnetic Fe–Fe₂O₃@PCP composite into 100 mL ACBK solution (100 mg L^{−1}) at 25 °C. The amount of adsorbed dye at time t (q_t (mg g^{−1})) and the removal efficiency (R , %) were calculated by Eqs. (1) and (2), respectively:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

$$R(\%) = \frac{(C_0 - C_t) \times 100}{C_0} \quad (2)$$

where C_0 and C_t (mg L^{−1}) are the initial and final concentrations of ACBK solution, respectively. m (g) is the mass of magnetic Fe–Fe₂O₃@PCP composite and V (L) is the volume of ACBK solution. To study the influence of temperature, a series of temperature gradient was set from 15 to 40 °C with an interval of 5 °C. To evaluate the influence of the initial solution pH, the initial pH of ACBK solution was regulated from 2 to 10 by adding 0.1 mol L^{−1} NaOH or 0.1 mol L^{−1} HCl dropwise. In the adsorption–desorption cycling, 5 mg magnetic Fe–Fe₂O₃@PCP composite was added into ACBK solution (20 mL, 100 mg L^{−1}) for 7–8 h. Subsequently, the equilibrated magnetic Fe–Fe₂O₃@PCP composite was immersed in NaOH solution (0.1 mol L^{−1}) for 5 min and rinsed sufficiently prior to the next cycling. In addition, control variable was employed to assure that other conditions were the same as the kinetic experiments.

2.4 Characterization

The morphology and size of magnetic Fe–Fe₂O₃@PCP composite were examined by scanning electron microscope (SEM, JSM-7401F, JEOL) with an acceleration voltage of 5.0 kV and transmission electron microscope (TEM, JEOL JEM-100CX) operated at 200 kV. The characteristic functional groups of HCCP, PEI and magnetic Fe–Fe₂O₃@

PCP composite were determined by Fourier transform infrared (FTIR) spectroscopy (PerkinElmer Paragon 1000 Fourier transform spectrometer) pressed with KBr pellet at the scanning wavenumber range of 4000–400 cm^{−1}. The pH meter (Mettler Toledo Co., Ltd., Shanghai, China) was used to measure the pH value of ACBK solutions. The concentration of residual ACBK supernatant solutions was monitored by UV–Vis spectrophotometer (Electrical and Instrument Analysis Instrument Co., Ltd., Shanghai, 752 N). The magnetic performance of Fe–Fe₂O₃@PCP composite was performed by a vibrating sample magnetometer (VSM, LDJ9600) at 25 °C between −1 T and 1 T.

3 Results and discussion

3.1 Formation mechanism of the PCP cover

The preparation of magnetic Fe–Fe₂O₃@PCP composite is illustrated in Fig. 1. To begin with, as-prepared magnetic Fe–Fe₂O₃ nanoparticles were distributed sufficiently in acetonitrile solution under ultrasonic irradiation. Simultaneously, branched PEI and HCCP dissolved in an appropriate amount of acetonitrile were dropped successively. Then, excess TEA as an acid acceptor was added into the above solution to trigger the polymerization. At the beginning of the reaction, branched PEI precipitated on the surface of Fe–Fe₂O₃, which was featured as the core for the formation of the PCP cover. Thereafter, HCCP and PEI reacted to produce hydrochloric acid and uneven nano-sized primary particles with partial cross-linked structures. During the process, the hydrochloric acid produced was absorbed by TEA to accelerate the polymerization. Finally, the further cross-linked reaction between primary particles occurred on the surface of Fe–Fe₂O₃ to obtain core@shell structural magnetic Fe–Fe₂O₃@PCP composite. Notably, the core materials Fe–Fe₂O₃ endowed the composite particles with magnetic response, and the shell materials amino-rich PCP could offer available adsorption active sites. Thus, the magnetic Fe–Fe₂O₃@PCP composite enjoyed ultrahigh separation effect and adsorption capacity for dye removal.

3.2 Characterization of magnetic Fe–Fe₂O₃@PCP composite

To explore the microstructure of magnetic Fe–Fe₂O₃@PCP composite, SEM and TEM characterizations were employed. SEM image (Fig. 2a) shows that the as-prepared magnetic Fe–Fe₂O₃@PCP composite exhibits spherical morphology with the size of about 200–600 nm. TEM image presented in Fig. 2b reveals that the polymer PCP has been coated on the surface of Fe–Fe₂O₃ particles

Fig. 1 Schematic illustration of the preparation process of magnetic Fe-Fe₂O₃@PCP composite

Fig. 2 **a** SEM and **b** TEM images of magnetic Fe-Fe₂O₃@PCP composite. **c** The magnified TEM image of the core@shell structure of magnetic Fe-Fe₂O₃@PCP composite. **d** FTIR spectra of HCCP, branched PEI and magnetic Fe-Fe₂O₃@PCP composite. **e** The magnetization hysteresis loops of magnetic Fe-Fe₂O₃@PCP composite

successfully. What is more, the size of the core@shell structural composite is in agreement with the result of SEM characterization. Of note, these magnetic composite particles prefer to gather together slightly due to the magnetic character of the Fe-Fe₂O₃ core. Figure 2c is a magnified TEM image, and we can further observe the clear core@shell structure of as-prepared products with 60–100 nm thickness of PCP shell. To confirm the successful preparation of magnetic Fe-Fe₂O₃@PCP composite, the FTIR spectra of HCCP, branched PEI, as well as magnetic Fe-Fe₂O₃@PCP, were measured and are shown in Fig. 2d. The characteristic peaks at 1220 cm⁻¹ and 873 cm⁻¹ are attributed

to the P=N and P-N stretching vibrations, respectively [34, 35], and the peaks at 609 cm⁻¹ and 527 cm⁻¹ correspond to P-Cl bond in the precursor (PNCl₂)₃. The peak at 1640 cm⁻¹ is related to N-H bending vibration peaks, and the peaks at 2951 cm⁻¹ and 2840 cm⁻¹ belong to the symmetric and antisymmetric stretching vibrations of -CH₂ of the PEI chain, respectively [36, 37]. Besides, the strong peak at 3434 cm⁻¹ is assigned to the rich amino and imino groups [26]. Of note, the disappearance of P-Cl bond, the presence of P=N bond at 1180 cm⁻¹ and the generation of new peak at 1109 cm⁻¹ assigned to the P-N-C band in FTIR spectrum of magnetic Fe-Fe₂O₃@PCP indicated

the occurrence of chemical reaction between HCCP and PEI [38–40]. Figure 2e shows the typical hysteresis loops of the magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite. Clearly, the saturation magnetization of the magnetic composite is up to 30.1 emu g^{-1} , far higher than that the reported magnetic adsorbent [41, 42], indicating that the magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite owns excellent magnetic separability which has been proved by the following separation test (Fig. 4b).

3.3 Selective adsorption toward organic dyes

Selective adsorption toward diverse organic dyes is indispensable to recycle the valuable dye. Herein, the selective adsorption behavior of magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ toward anionic dye from binary mixed dye solution (using anionic

dye ACBK and cationic dye MB as mixed dye model) was investigated preliminarily, and the digital photographs of mixed dye solution before and after adsorption were taken and are exhibited in Fig. 3. Obviously, after adsorption the color of mixed dye solution changes from mauve to cerulean, which is almost the same as the color of individual MB solution. It can be deduced that the MB and ACBK mixed dyes were separated successfully by adsorbent magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ and almost all the ACBK dye was removed from the mixed solution. Thus, we concluded that magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite could selectively and efficiently adsorb anionic dye (such as ACBK) in the binary mixed solutions. In the next section, we discuss the adsorption behavior of magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite toward ACBK dye in detail.

3.4 Influence of various experimental conditions on adsorption

3.4.1 Influence of contact time

Figure 4a displays the influence of contact time on the ACBK uptake amount of magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite. Generally, prolonging the contact time is helpful to the sufficient contact between adsorbent and adsorbate. From Fig. 4a, the ACBK uptake amount of magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite fast increases in the initial 85 min, then performs a lower speed and finally reaches adsorption equilibrium within about 480 min. At the beginning stage, there are numerous available adsorption sites on the magnetic

Fig. 3 Digital photographs of selective adsorption of magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite to anionic dyes

Fig. 4 **a** Influence of contact time on adsorption capacity of ACBK onto magnetic $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite. **b** The digital photographs of excellent magnetic response toward external magnetic field of $\text{Fe-Fe}_2\text{O}_3\text{@PCP}$ composite. The relation curves of equilibrium adsorption capacity and efficiency via the initial solution pH (**c**) and experimental temperature (**d**). The optimum pH is 7.0 and the optimum temperature is 25°C

Fe-Fe₂O₃@PCP adsorbent. Meanwhile, there are sufficient ACBK adsorbate molecules in dye solution, which can provide a powerful driving force to promote the diffusion of dye molecules from solution to the surface of adsorbent. The two reasons lead to a rapid adsorption of ACBK onto magnetic Fe-Fe₂O₃@PCP composite in the initial adsorption stage. As the adsorption process goes, there are fewer and fewer vacant sites on magnetic Fe-Fe₂O₃@PCP composite and free ACBK molecules in solution, leading to the reduction in the driving force. Thus, the adsorption rate slows down gradually and reaches adsorption equilibrium after about 480 min. Additionally, the digital photographs (Fig. 4b) show that the magnetic Fe-Fe₂O₃@PCP adsorbent after adsorption could be separated within 15 s, indicating that magnetic Fe-Fe₂O₃@PCP composite owns quick magnetic response toward external magnetic field.

3.4.2 Influence of the initial solution pH

The solution pH is the most important factor to affect the adsorption efficiency as well as nature of adsorbent and adsorbate [43–45]. Figure 4c depicts the influence of the initial solution pH on the adsorption capacity of ACBK onto magnetic Fe-Fe₂O₃@PCP composite. It can be observed that along with the initial solution pH increases from 2 to 10 and the adsorption amount of magnetic Fe-Fe₂O₃@PCP composite toward ACBK dye decreases from 385 to 230 mg g⁻¹. The PCP is a typical polymer with abundant imino and amino groups. According to the previous report, the PCP is positively charged when the solution pH < 10, and the intensity and density of protons in PCP increase with the decrease in solution pH [26]. Similarly, we think that in the magnetic Fe-Fe₂O₃@PCP composite, the PCP as shell materials can behave like pure PCP in different solution pHs. Thus, the electrostatic attraction between anionic dyes (ACBK) and magnetic Fe-Fe₂O₃@PCP composite could be enhanced in low pH and declined in high pH, leading to an obvious decrease in the adsorption amount of magnetic Fe-Fe₂O₃@PCP composite toward ACBK along with the increase in solution pH (Fig. 4c).

3.4.3 Influence of experimental temperature

Temperature is one of the vital parameters for understanding the adsorption process. As shown in Fig. 4d, the adsorption capacity ascends to the maximum value of 282 mg g⁻¹ when the temperature rises from 15 to 40 °C at an interval of 5 °C, which manifests that the adsorption process is endothermic between ACBK molecular and magnetic Fe-Fe₂O₃@PCP composite. The reason is that under the relatively higher temperature, the solution has a lower viscosity. Thus, the ACBK molecules diffuse more intensely and get

more chances to be absorbed by magnetic Fe-Fe₂O₃@PCP composite.

3.5 Kinetic studies and adsorption mechanism

To explore the diffusion process and adsorption mechanism, we studied the adsorption kinetics of ACBK onto magnetic Fe-Fe₂O₃@PCP composite via the pseudo-first-order and pseudo-second-order kinetic models, which are listed in linear form as follows [46, 47]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where q_e and q_t represent the amounts of adsorbed ACBK at adsorption equilibrium and at time t (min), respectively. k_1 (min⁻¹) is the rate constant of the pseudo-first-order model and k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant. The correlation coefficient (R^2) and kinetic parameters determined by linear regression are given in Table 1. As shown in Fig. 5a, the correlation coefficient of the pseudo-second-order model ($R^2 = 0.9969$) is higher than that of the pseudo-first-order model ($R^2 = 0.9754$). In addition, the $q_{e,cal}$ (271.74 mg g⁻¹) of the pseudo-second-order model is more close to the experimental q_e (259.73 mg g⁻¹) compared with that (164.68 mg g⁻¹) of the pseudo-first-order model, as given in Table 1. Based on the results above, we reasoned that the adsorption of ACBK by magnetic Fe-Fe₂O₃@PCP composite follows the pseudo-second-order model rather than the pseudo-first-order model.

To further understand the diffusion process, Weber's intraparticle diffusion model was employed to analyze the kinetic results. The model can be described as follows [48, 49]:

$$q_t = k_i t^{1/2} + c \quad (5)$$

where k_i (mg g⁻¹ min^{1/2}) represents the intraparticle diffusion rate constant and c is a constant referring to the

Table 1 Adsorption kinetic parameters of ACBK onto magnetic Fe-Fe₂O₃@PCP composite

Models	Model parameters	R^2
Pseudo-first-order	$q_{e,cal} = 164.68 \text{ mg g}^{-1}$ $k_1 = 0.00898 \text{ min}^{-1}$	0.9754
Pseudo-second-order	$q_{e,cal} = 271.74 \text{ mg g}^{-1}$ $k_2 = 0.00368 \text{ g mg}^{-1} \text{ min}^{-1}$	0.9969
Intraparticle diffusion	$k_{i1} = 14.362 \text{ mg g}^{-1} \text{ min}^{-1/2}$ $c_1 = 61.9 \text{ mg g}^{-1}$ $k_{i2} = 5.030 \text{ mg g}^{-1} \text{ min}^{-1/2}$ $c_2 = 156.6 \text{ mg g}^{-1}$	0.9871 0.9734

Fig. 5 **a** The linear regression of the pseudo-first-order model and the pseudo-second-order model. **b** Weber's intraparticle diffusion model for the adsorption of ACBK onto magnetic Fe-Fe₂O₃@PCP composite. **c** Langmuir and **d** Freundlich isotherms for the adsorption

boundary layer effect of the adsorption. As shown in Fig. 5b, the diffusion process of ACBK adsorption onto magnetic Fe-Fe₂O₃@PCP composite presents multilinear characteristic, which declares two steps—film diffusion and intraparticle diffusion. The first linear region is related to the diffusion of dye molecules from the bulk solution to the near surface of adsorbents. And the second linear region is ascribed to the intraparticle diffusion which resulted from the abundant available adsorption sites on PCP, which is rich in amino and imino groups. Meanwhile, k_{11} is larger than k_{12} obviously, indicating that the intraparticle diffusion is a lower-rate process. And both the intercepts do not equal to zero, which also means the joint contribution of film diffusion and intraparticle diffusion to the adsorption rate. Furthermore, the high R^2 value shows the great suitability of Weber's intraparticle diffusion model in elucidating the diffusion mechanism.

3.6 Adsorption isotherm

The equilibrium adsorption isotherm can be used to reflect the essence of the interaction between adsorbent and adsorbate. Herein, the adsorption data were successfully simulated using Langmuir and Freundlich isotherm models, which are given as follows [50, 51]:

$$C_e/q_e = 1/(q_0 K_L) + C_e/q_0 \quad (6)$$

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (7)$$

where C_e and q_e represent the equilibrium concentration of the adsorbate (mg L^{-1}) and the adsorption capacity (mg g^{-1}) at adsorption equilibrium, respectively. K_L is Langmuir constant (L mg^{-1}) and q_0 is the monolayer adsorption capacity (mg g^{-1}). K_F is Freundlich constant related to the maximum adsorption capacity and n is a constant which represents the adsorption intensity. Figure 5c, d illustrates the Langmuir and Freundlich isotherms for adsorption of ACBK onto magnetic Fe-Fe₂O₃@PCP composite, respectively, and the relative parameters are calculated and presented in Table 2. The correlation coefficient of Freundlich isotherm model ($R^2 = 0.9713$) is much larger than that of Langmuir isothermal model ($R^2 = 0.8186$). It indicates that Freundlich model is more suitable for describing the adsorption equilibrium between ACBK and magnetic Fe-Fe₂O₃@PCP composite. Noticeably, in our previous work, hollow PCP microcapsules fits the Langmuir isotherm model well rather than the Freundlich isotherm model [26]. Reasons may be as follows. First, to obtain

Table 2 Parameters for the Langmuir and Freundlich isotherm models at room temperature

Isotherms	Parameters	R^2
Langmuir	$q_0 = 1111.8 (\text{mg g}^{-1})$	0.8186
	$K_L = 0.077 (\text{L mg}^{-1})$	
Freundlich	$K_F = 144.95 (\text{L mg}^{-1})$	0.9713
	$n = 2.043$	

the hollow PCP microcapsules, the composite was dealt with acetone solution for 60 min; while the erratic imino and amino groups would react with carbonyl, the surface would become more uniform and the adsorption sites would distribute better, which is similar to the hypothesis of Langmuir isotherm model. But as discussed before, the microstructure morphology of magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite is un-uniform, which may cause the incompatibility with Langmuir isotherm model. Second, hollow PCP microcapsules enjoy an ultrahigh specific surface area and thus abundant adsorption sites. Therefore, dye molecules tend to associate with the active sites on monolayer first, which is suitable to the Langmuir isotherm model. However, in order to develop a kind of adsorbent capable of rapid magnetic separation, we have to give up the hollow structure. Meanwhile, the nanocomposites will gather closer and thus the specific surface area will be sacrificed a lot. Consequently, only the adsorption sites exposed on the external surface of magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite can really work, so it may lead to multilayer adsorption and deviate from the Langmuir isotherm model as a result. Although the adsorption capacity of magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite decreases compared with hollow PCP microcapsules, it is still high enough to remove anionic dye (ACBK) compared with the related reports [52, 53], and we think it more prospective in reality. And the smaller the value of $1/n$ in Freundlich isotherm model, the better the adsorption performance (easy ($1/n = 0.1 - 0.5$), difficult ($1/n > 2$)) [54]. In this work, the $1/n$ value was smaller than 0.5, indicating relatively easy adsorption.

Based on the above discussion, we proposed the adsorption process and mechanism of ACBK onto magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite as shown in Fig. 6a. In this study, ACBK is an anionic dye with $-\text{SO}_3^-$ anions, and the $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite presents a positively charged surface because of the protonation of the amino and imino groups in the acid environment. Thus, the electrostatic attraction could easily happen between the positively charged active sites on the adsorbent and the anionic dye molecules. Under the shaking condition, the ACBK molecules diffuse across the range of liquid film of

magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite quickly on account of the existence of driving force from the initial ACBK concentration. Subsequently, the anionic ACBK molecules gradually get closer to the external surface of magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite with plenty of positively charged sites. With the help of electrostatic attraction, a large number of ACBK molecules were quickly adsorbed onto the magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite. But in the last stage of adsorption, the adsorption rate slows down to a constant due to the resistant force resulting from the great many ACBK molecules on magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite. To further confirm our guess about interaction mechanism between adsorbate and adsorbent, herein, the FTIR spectra of magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite before and after ACBK adsorption were tested and are shown in Fig. 6b. Comparing the two FTIR spectra, we find that the skeleton peaks of P=N and P-N-C have no obvious change, indicating the good stability of the as-prepared magnetic composite during the adsorption process. Noticeably, after ACBK adsorption, an obvious new peak appeared at 1041 cm^{-1} , which is related to S=O stretching vibration of the dye ACBK, suggesting that the magnetic adsorbent captured anionic dye ACBK from aqueous solution successfully. Moreover, the peak position of amino/imino groups has an obvious shift from 3434 to 3445 cm^{-1} after adsorption, demonstrating the strong electrostatic interaction between amino-rich magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite and ACBK dye.

3.7 Desorption

To evaluate the reusable performance of magnetic adsorbent $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite, we investigated its adsorption and desorption behavior toward ACBK dye, which also did a favor to identify the adsorption mechanism. To investigate the desorption property, the freshly prepared ACBK-filled magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite was added into the neutral deionized water and let stand for 3 h. We could observe that the solution just became slight red, indicating less desorption of ACBK. However, the solution turned crimson immediately after

Fig. 6 **a** Schematic illustration of the adsorption mechanism for anionic dye (ACBK) on magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite. **b** FTIR spectra of magnetic $\text{Fe-Fe}_2\text{O}_3@\text{PCP}$ composite before and after ACBK adsorption

Fig. 7 **a** Occupation percentage of adsorption sites during the adsorption/desorption cycles. **b** Five cycles of adsorption/desorption and magnetic separation performance

0.1 mol L⁻¹ of NaOH was added dropwise. It could be deduced that the imino and amino groups are deprotonated under high pH value condition [8], resulting in the desorption of ACBK. Thus, the attachment between ACBK and magnetic Fe-Fe₂O₃@PCP composite is owing to the electrostatic interaction, which is consistent with the proposed adsorption mechanism above.

Furthermore, we carried out adsorption/desorption tests repeatedly (Fig. 7a, b). The adsorption and desorption ACBK molecules were quantified by UV-Vis spectrophotometer, which revealed that about 94% of ACBK was released in each cycle and it still kept 75% of removal efficiency with the adsorption capacity of 195 mg g⁻¹ after five cycles.

4 Conclusions

In summary, a selective and highly efficient magnetic adsorbent (Fe-Fe₂O₃@PCP) for the removal of anionic dye (ACBK) was successfully prepared via the copolymerization of HCCP and PEI in the presence of Fe-Fe₂O₃ nanoparticles. The prepared magnetic Fe-Fe₂O₃@PCP composite exhibited high adsorption capacity toward ACBK at room temperature in neutral solution. Besides, the magnetic composite did well in separation thanks to its high saturation magnetization. The adsorption kinetic followed the pseudo-second-order model, and the diffusion mechanism was described well by Weber's intraparticle diffusion model. The Freundlich isotherm model was more appropriate to describe the adsorption equilibrium data of ACBK onto magnetic Fe-Fe₂O₃@PCP composite compared with the Langmuir model. Additionally, the magnetic Fe-Fe₂O₃@PCP composite performed well in adsorption and desorption cycles. Prospectively, the magnetic Fe-Fe₂O₃@PCP composite could be applied as an effective and selective adsorbent for the removal of anionic dyes from wastewater system.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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