Coal-fly-ash magnetic sphere based magnetic adsorbent for multiple-dye adsorption

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Abstract
Owing to the synergetic characteristics of effective adsorption and magnetic separation, adsorption using magnetic adsorbents was regarded as one of the most promising methods for synthetic dye removal. Herein, a green, cheap, and efficient magnetic adsorbent was synthesized by a simple chemical oxidation in situ polymerization method. Processed coal-fly-ash magnetic spheres (CMS) were employed as the magnetic core material. A polyaniline (PANI) layer was covered on the CMS@SiO₂ surface to form a core–shell structural magnetic adsorbent, CMS@SiO₂@PANI. Careful investigations showed that the PANI layer was composed of nanorods of dozen nanometers in width and several microns in length, which forms an interconnected network and covers the overall surface of the core. The saturation magnetization of CMS@SiO₂@PANI is as high as 30.99 emu g⁻¹, enabling efficient magnetic separation. It showed high selective adsorption for various synthetic dyes. The highest adsorption capacity for cationic dyes Methyl Orange and Congo Red was tested as 216.72 and 413.49 mg g⁻¹ at pH 3, respectively, while that for anionic dyes Methylene Blue and Rhodamine B were 108.65 and 41.49 mg g⁻¹ at pH 11, respectively. Systematic adsorption studies suggest that the pH value of the water has a significant influence on the surface properties of PANI, as well as the molecular structure and functional groups of the dyes. This could affect the interaction between PANI and dye molecules significantly. Thus, the multiple-dye adsorption performance of CMS@SiO₂@PANI could be adjusted by adjusting the pH value. The adsorption kinetics and isothermal simulation results show that the dye adsorption is dominated by the monolayer chemical adsorption, and electrostatic attraction plays a vital role in the adsorption process. The multiple-dye adsorption of CMS@SiO₂@PANI could be explained as a two-step process.

1. Introduction
Synthetic dyes have been widely used in leather, textile, paper-making, printing, electroplating, paint, cosmetics, and food industries since the invention of the first dye [1–3]. However, researches showed that 12%–50% of the total dye consumption was wasted during the production process and was released into water [6]. Most synthetic dyes, such as Methylene Blue (MB) [7, 8], Rhodamine B (RhB) [9], Methyl Orange (MO) [10], and Congo Red (CR) [11, 12], are toxic and carcinogenic, posing a serious threat to human health and environment. Furthermore, most organic dyes have complex molecular structures, which are hard to degrade naturally. Therefore, the effective elimination of dyes from water becomes an urgent task for humankind. Many techniques, such as flocculating [13], biodegradable [14], catalytic oxidation [15–17], ion exchange [18], membrane separation [19], and adsorption [20–23], have been explored and used to remove dye molecules from water. Among them, adsorption technology is regarded as one of the most promising methods for its low cost, high efficiency, and simple operation. Dye adsorbents originated from various natural and artificial materials,
including activated clay [24], diatom mud [25], activated carbon [26], fiber series [27], fly ash [28], and cinder [29], fabricated and carefully studied. Porous structure, high specific surface area, and a wide variety of surface functional groups were the common features of these dye adsorbents. Since most adsorbents were only effective for one or two dyes, the adsorption efficiency was low in the application. The development of multiple-dye selective adsorbent was one of the most promising methods to improve the total adsorption efficiency. Recently, polyaniline (PANI) has been intensively studied as an efficient dye selective adsorbent [30, 31]. The PANI molecule contains many amino and imino groups, which has affinity for dye molecules with different structures and electrical properties. Besides, the molecular structure and chemical properties of PANI can be adjusted by changing the chemical environment. Therefore, PANI could be one of the best candidates for multiple-dye selective adsorbents.

The difficulty of solid-liquid separation is another challenge that hinders the application of the adsorption method. Most adsorbents have excellent particle size to pursue a high specific surface and better suspension. Thus, conventional reselection is hard to achieve efficient solid-liquid separation [32]. Magnetic separation technique has been introduced to improve the ability of solid-liquid separation [11, 32, 33]. Since making the magnetic adsorbent is the premise of magnetic separation, many magnetic composite adsorbents have been fabricated and studied. However, most magnetic adsorbents used chemically synthesized magnetic nanoparticles (e.g., nano-Fe₃O₄) as magnetic core [13, 34, 35]. Due to the complex synthesis process, high cost, potential environmental impact, and harsh preservation condition of nano-Fe₃O₄, the complete application of magnetic separation technology was limited. It is necessary to develop clean and cheap magnetic core materials.

Coal-fly ash magnetic sphere (CMS), derived from industrial solid waste coal fly ash, has strong magnetism, even diameter, and high porosity. Considering its low cost, abundant reserves, CMS could be ideal for the magnetic core material [36].

The combination of CMS and PANI may produce an expectable magnetic adsorbent for multiple-dye adsorption. In this study, CMS@SiO₂@PANI magnetic adsorbents were fabricated by a chemical oxidation in situ polymerization method with CMS particle as a magnetic core. The magnetic adsorbent is expected to be green and clean due to the recovery of magnetic core material from industrial waste, the simple synthesis process, and low chemical consumption, and it can be reused several times after efficient magnetic separation. The structure, magnetic property, and dye adsorption of the samples were systematically studied. The CMS@SiO₂@PANI adsorbent showed high adsorption capacity for multiple dyes, including MO, CR, MB, and RhB. The mechanism of the multiple-dye adsorption was discussed in detail.

2. Materials and methods

2.1. Materials

The CMS used in this work was magnetically separated from the coal fly ash obtained from the Luohe power plant in Huainan, China. The percentage of CMS in the coal fly ash was tested as 7.32%. The main CMS components are SiO₂, Al₂O₃, CaCO₃, CaO, Fe₂O₃, and MgO. Detailed information of the element components of the CMS is shown in table. S1 (available online at stacks.iop.org/MRX/8/015504/mmedia). Ammonium persulfate (APS, 98.5%), Aniline monomer (An, 99.5%), and Methylene blue (MB, C₂₉H₃₁CIN₂O₃, Mw 373.9) were bought from Shanghai Macklin Biochemical Co. Ltd. Methyl orange (MO, C₁₄H₁₄N₃NaO₃S, Mw 327.33) and Congo red (CR, C₁₂H₁₀N₄Na₂O₆S₂, Mw 696.66) were procured from Shanghai Aladdin Biochemical Technology Co. Ltd. Ethyl silicate (TEOS, 28%) and Rhodamine B (Rhb, C₂₈H₁₇ClN₂O₃S, Mw 479.02) was provided by Fuchen chemical reagent factory and Bodi chemical Co. Ltd., respectively. Hydrochloric acid (36%) was purchased from Jiangsu Yangzhou Lubao chemical reagent Co. Ltd. Ammonia water (25%) was acquired from Bengbu chemical reagent factory. Anhydrous ethanol was purchased from Wuxi Yasheng chemical Co. Ltd.

2.2. Preparation of CMS@SiO₂

The CMS particles were processed from the raw CMS by a two-step process [37]. Typically, a magnetic separation tube is used to process 100 mesh coal fly ash under a 300 mT strong magnetic field to obtain the raw CMS. Weak magnetic separation (100 mT) was performed to obtain the refined CMS. The refined CMS was ball-milled for 10 h at a rotation speed of 400 rpm to get the CMS particles. CMS particles–silicon dioxide (CMS@SiO₂) was synthesized using a sol-gel method. Briefly, CMS particles were added in a 100 ml mixture solution of 80 ml anhydrous ethanol and 20 ml deionized water into the beaker. A uniform sol solution was obtained with an ultrasonic cleaner. After ultrasonic oscillation, 4 ml ammonia water and 5 ml TEOS at 2 s per drop were added into the sol solution, which uses the agitator at a speed of 250 rpm for 6 h. The product was separated with a magnet and rinsed with deionized water, and then dried at 80 °C for 12 h.
2.3. Synthesis of CMS@SiO2@PANI
The composites of PANI and CMS@SiO2 were prepared by a chemical oxidation in situ polymerization method. Briefly, 1 g CMS@SiO2 was added to the beaker of 20 ml 1 mol l\(^{-1}\) HCl solution and 0.05 mol An, and ultrasonicated properly to get homogeneous dispersion. After that, APS (11.4 g APS dissolved in deionized water) was added to it at a rate of 3–5 s per drop. The beaker was left for 8 h under stirring for 300 rpm. The final precipitate was magnetically separated, washed several times with anhydrous ethanol and deionized water until colorless, and dried at 60 °C for 8 h. And two magnetic adsorbents with different mass ratios of polyaniline monomers and CMS@SiO2 were prepared. The samples obtained at different mass ratios of 5:1, 5:2, and 1:1 were named CN1, CN2, and CN3, respectively. The synthesis of CMS@SiO2@PANI is schematically illustrated in Scheme 1.

2.4. Characterization methods
The morphology of the CMS particles, CMS@SiO2, and CMS@SiO2@PANI was investigated by scanning electron microscopy (SEM, ZEISS SUPRA 40, Germany). The materials structure was analyzed using X-ray diffractometer (XRD, scanning angle range 10°–80°, scanning speed 1°·min\(^{-1}\)). Fourier transform infrared (FT-IR) spectra in the range of 4000–400 cm\(^{-1}\) were recorded to determine the functional group of materials. The Brunauer-Emmette-Teller (BET) specific surface areas of the samples were calculated by a multi-functional N2 adsorption instrument (V-Sorb 2800P, Beijing Jin Aipu Technology Co., Ltd). The sample magnetism was measured by the HH-20 vibration sample magnetometer (VSM, Nanjing University Instrument Factory). The PANI percentage in the samples was measured by thermogravimetry (TG, NETZSCH STA 449F3, Germany). The Zeta potential of the material at different pH values (3–11) was measured by a micro-electrophoresis instrument (JS94H, Shanghai Zhongchen Digital Technology Equipment Co., Ltd).

2.5. Dyes adsorption experiments
Magnetic adsorbents (CN\(_2\)) in the range of 0.02–0.1 g were added in a beaker containing 100 ml of 20 mg l\(^{-1}\) dyes solution (MO, CR, RhB, and MB). After mechanical stirring for 180 min, the residual concentration of dyes was measured using a UV-visible spectrophotometer (UV-5100, Shanghai Yuanxi Instrument Co., Ltd) at different wavelengths (464, 497, 554, and 664 nm, respectively). Four dye solutions with various dye concentrations (MB and RhB solutions ranging from 10 to 100 mg l\(^{-1}\), MO, and CR solutions ranging from 80 to 500 mg l\(^{-1}\)) were prepared to study the adsorption capacity of the magnetic adsorbents at different dyes concentration. The contact time test was performed in the dye solution of the best concentration, and the samples were measured at selected time intervals. pH values ranging from 3–11 were prepared and analyze the pH effect. The following equations calculate the adsorption capacity:

\[
q = \frac{V(C_0 - C_t)}{m}
\]

where \(q\) (mg g\(^{-1}\)) is adsorption capacity, \(C_0\) and \(C_t\) are the initial and final concentration (mg l\(^{-1}\)) of the dye solution, respectively, \(V\) (L) is the volume of dye solution, and \(m\) (g) is the dosage of the adsorbent.

3. Results and discussion
3.1. Structural characterization
The SEM images of CMS, CMS@SiO2, and CMS@SiO2@PANI samples are illustrated in figure 1. It is seen that ball milling changed raw CMS both in particle size and morphology. The shape of CMS changed from spherical to irregular. After the first modification, the CMS particles surface became smooth, suggesting the uniform
growth of the silicon compound. The morphology changed a lot after the in situ polymerization. A porous layer was grown on the surface of CMS@SiO2@PANI samples. As shown in figures 1(d)–(f), this layer is composed of nano-sized rods, particles, and sheet morphologies. The morphology and microstructure of CN1, CN2, and CN3 are significantly different due to the different proportions of reactants. In comparison, the PANI layer of CN2 has a more uniform microstructure. It is mainly composed of nanorods dozens of nanometers in width and several microns in length. An interconnected network forms by the clusters of the nanorods and covers the overall surface of the core. According to the EDS mapping, there are four major elements in the CN2 sample, Fe, Si, C, and N. As the primary components in CMS particles, Fe and part of the Si element should come from the CMS core. The first modification further increased the Si element. The detailed element distribution of CMS@SiO2 is shown in figure S1. Since CMS@SiO2 has no C and N element, the C and N should come from the coating layer.

The XRD patterns (figure 2(a)) indicate that the CMS particles mainly contain magnetite, magneisoferrite, hematite, and maghemite. All these diffraction peaks present in the XRD spectra of CMS@SiO2 and CMS@SiO2@PANI. It suggests the Si modification process did not change the composition and structure of the CMS particles. A broad peak presents at \(2\theta = 22^\circ - 26^\circ\) in the CMS@SiO2 spectra. This peak corresponds to

![Figure 1. SEM of (a) raw CMS, (b) CMS particles, (c) CMS@SiO2, (d) CN1, (e) CN2, (f) CN3, (g)–(k) SEM and corresponding EDS surface scanning images of CN2.](image-url)
amorphous SiO$_2$. In the XRD pattern of CMS@SiO$_2$@PANI, a broad peak appears at 18° – 27°, corresponding to the characteristic diffraction peak of amorphous PANI [38]. To further prove the structure of the sample, FT-IR spectra were conducted. As shown in figure 2(b), a characteristic absorption peak at around 1078 cm$^{-1}$ is observed in addition to the CMS particles absorption peak. This peak is assigned to the stretching vibration of Si-O groups [39]. The peak at 794 cm$^{-1}$ could be ascribed to the C–H plane bending vibration in the benzene ring [30, 40]. The peaks at 1221 cm$^{-1}$ and 1293 cm$^{-1}$ correspond to the C–N stretching vibrations in the benzoquinone and the aromatic ring [30, 41], respectively. The peak at 1501 cm$^{-1}$ presents the C=C stretching vibration on the benzene ring skeleton [30, 42]. The peaks at 1599 cm$^{-1}$ and 1652 cm$^{-1}$ represent the C-N stretching vibration and the C = N stretching vibration in aromatic amines and quinone rings [40, 41], respectively. The detailed assignments of all the characteristic peaks are listed in table S2. According to the discussion, amorphous SiO$_2$ and PANI have been coated on the CMS core layer by layer, consistent with the SEM and EDS results.

The specific surface area and porous structure of all the samples were measured by N$_2$ adsorption-desorption isotherms. As shown in figures 3(a)–(e), all the curves are consistent with type-III adsorption/desorption isotherms, suggesting the weak interaction between the material surface and the N$_2$ molecules. The BET specific surface area values of CMS particles, CMS@SiO$_2$, CN$_1$, CN$_2$, and CN$_3$ are 3.30, 0.21, 9.57, 13.86, and 11.82 m$^2$ g$^{-1}$, respectively. Interestingly, the specific surface area of CMS@SiO$_2$ is much less than that of CMS particles, which indicates that the uniform growth of solid SiO$_2$ covered the overall CMS magnetic core surface and the porosity in the SiO$_2$ is very low. The BET surface area of the CMS@SiO$_2$@PANI samples is much higher than that of CMS@SiO$_2$, as shown in table 1. Thus, the increase of surface area should mainly come from the PANI layer. According to the insert of figure 3, all CMS@SiO$_2$@PANI samples have a porous structure with pore sizes from 20 to 200 nm. The mesoporous and macroporous structure significantly enlarges the surface area. Interestingly, the BET surface area and pore volume of CN$_2$ and CN$_3$ are significantly higher than those of CN$_1$. This may be because the PANI layers in CN$_2$ and CN$_3$ have a relatively uniform nanostructure and overall porous frame structures. As shown in the inset of figure 3, the N$_2$ adsorption of CN$_2$ and CN$_3$ at macroporous scale (80–90 nm and 170–180 nm around) increases significantly, compared with that of CN$_1$. The formation of different structural PANI of the three samples could be attributed to the different polymerization conditions.

3.2. Magnetic investigation
According to the VSM hysteresis loops, as shown in figure 4, all the samples have strong magnetism, smaller remanence, and coercivity. The specific saturation magnetization of CMS particles, CMS@SiO$_2$, CN$_1$, CN$_2$, and CN$_3$ composites is tested as 50.17, 49.66, 31.73, 30.99, and 38.98 emu·g$^{-1}$, respectively. The magnetism decrease of CMS@SiO$_2$@PANI was mainly owing to the coating of non-magnetic SiO$_2$ and PANI. Since the modification and polymerization didn’t affect the CMS core structure, the amount of non-magnetic SiO$_2$ and PANI cladding could be estimated according to the magnetic variation. The mass ratio of PANI was measured by TG investigation, as shown in the figure S2, the PANI percentage in CN$_2$ composite was calculated around 38.21 wt%.

Figure 2. (a) XRD patterns and (b) FT-IR results of CMS particles, CMS@SiO$_2$, and CN$_2$ (Mn: magnetite (JCPDS card. No.19-0629), Mg: magnesioferrite (JCPDS card. No.36-0398), H: hematite (JCPDS card. No.33-0664), Mn: maghemite (JCPDS card. No.39-1346)).

Although the magnetism of CMS@SiO$_2$@PANI is lower than CMS particles, it is also strong enough for effective magnetic separation. As shown in the inset of figure 4, the magnetic adsorbent could be magnetically separated by a magnet set 2 cm away from the container.
Figure 3. N$_2$ adsorption/desorption isotherms and the pore size distribution curves of (a) CMS particles, (b) CMS@SiO$_2$, (c) CN$_1$, (d) CN$_2$, and (e) CN$_3$.

Table 1. $S_{BET}$, Pore volume, and average pore size for different samples.

| Samples       | $S_{BET}$ (m$^2$ g$^{-1}$) | Pore volume (cm$^3$ g$^{-1}$) | Average pore size (nm) |
|---------------|-----------------------------|-------------------------------|------------------------|
| CMS particles | 3.30                        | 0.52                          | 75.54                  |
| CMS@SiO$_2$   | 0.21                        | 0.44                          | 124.10                 |
| CN$_1$        | 9.57                        | 0.43                          | 72.25                  |
| CN$_2$        | 13.86                       | 0.78                          | 174.90                 |
| CN$_3$        | 11.82                       | 0.80                          | 181.63                 |
3.3. Adsorption performances

3.3.1. Dye adsorption

The CMS@SiO2@PANI samples have good adsorption for various dyes, as shown in figure 5(a). Since CMS particles and CMS@SiO2 only have minimal adsorption, the dye adsorption should majorly come from the PANI layer. The dye adsorption capacity of CMS particles, CMS@SiO2, and CN2 is shown in figure S4. The highest adsorption of CN2 for MO, CR, MB, and RhB is 180.21, 91.20, 51.50, and 33.95 mg g\(^{-1}\), respectively. Obviously, under the same condition, the MO and CR adsorption capacity are much higher than those of MB and RhB. Since the charged nature of MO and CR in water is opposite to that of MB and RhB, the different adsorption capacities could be closely related to the different molecular structures, surface property, and surface charge nature of the dye molecules. The adsorption rate for all four dyes was very fast at the initial 16 min and gradually decreased with time the prolonged time until reaching an adsorption equilibrium. The fast dye adsorption at the initial stage could be due to two aspects, (1) rapid physical adsorption for the high specific surface area. (2) strong chemical adsorption for the availability of active chemical sites on the PANI surface. With the adsorption increase, the available surface dangling bonds and active sites decreased, and the adsorption became less effective and slowed down. When the amount of dye molecular being adsorbed equaled the amount of being desorbed, a dynamic equilibrium state was reached. This time is termed as equilibrium time, and the corresponding dye adsorption capacity is regarded as the maximum adsorption capacity \[31\]. It is evident from figure 5(a) that the equilibrium time for MO, CR, MB, and RhB is about 180, 90, 60, and 60 min, respectively.

3.3.2. Effect of adsorbent dosage

Single-factor adsorption experiments were carried out to verify the influence of experimental conditions on the multiple-dye adsorption performance of CMS@SiO2@PANI. The multiple-dye adsorption performance of CN1, CN2, and CN3 was tested under the optimal conditions, as shown in figure 5(e). It was found that the adsorption capacity of CN2 for the four dyes was significantly higher than the other two samples. It may be closely related to the microstructure of the PANI layer. As seen from the SEM images, the CN2 has the highest specific surface area and uniform network, and the overall PANI layer is composed of uniform nanorods. The high specific surface area and consistent morphology are conducive to the physical and chemical adsorption of dye molecules.

The adsorbent dosage also influences the dye adsorption. As shown in figure 5(b), the multiple-dye adsorption changed a lot with the increase of the amount of CN2. The best adsorbent dosages for MO, CR, MB, and RhB were tested as 0.4, 0.4, 0.2, and 0.2 g l\(^{-1}\), respectively, and the corresponding specific adsorption capacities were 42.38, 29.11, 13.5, and 8.99 mg g\(^{-1}\). The optimal adsorbent dosages were used in the following experiments. The effect of the initial dye concentration on the removal efficiency of CN2 was shown in figures 5(c) and (d). With the increase of dye concentration, the dye adsorption of CN2 increases while it keeps stable at a certain concentration. It could be related to the changing of the adsorption type. The optimal concentration of MO, CR, MB, and RhB was 350, 300, 70, 50 mg l\(^{-1}\), and the dye adsorption capacity was 166.91, 96.96, 50.22, and 35.15 mg g\(^{-1}\).
3.3.3. Effect of pH

pH is an essential factor influencing dye adsorption since it can affect the surface properties of adsorbents [43]. It can be seen from figure 6(a), the adsorption of four dyes changed very little at pH 6.0–9.0. The adsorption of MO and CR increased sharply when pH < 4 but decreased significantly when pH > 10. While MB adsorption increased sharply when pH > 9 but decreased slightly when pH < 6. The maximum adsorption of MO, CR, MB, and RhB was tested as 216.72 mg g\(^{-1}\) at pH 3, 413.49 mg g\(^{-1}\) at pH 3, 108.65 mg g\(^{-1}\) at pH 11, and 41.49 mg g\(^{-1}\) at pH 11, respectively. As discussed above, the different selective adsorption for various dyes may be closely related to the electrical properties of dye molecules after hydrolysis. As shown in figure 6(b), the zero point of charge of CN\(_2\) is 6.47. Thus, the surface potential of CN\(_2\) is positively charged in weakly acidic conditions. Because MO and CR are sulfonic acid-based dyes, they are negatively charged when dissolved in
water. While MB and RhB are positively charged. Therefore, the high adsorption capacity of anionic dyes under low pH may be partly due to the electrostatic attraction. Similarly, the same theory could be used to explain the adsorption increase of the other two dyes at high pH.

3.3.4. Adsorption kinetics
The quasi-first-order and quasi-second-order kinetic models were applied to gain a better understanding of the adsorption processes onto the CMS@SiO$_2$@PANI adsorbent, as shown in figure 7, and were expressed as follows:

$$\ln (q_e - q_t) = \ln q_e - kt$$  \hspace{1cm} (2)
and

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (3)

where $k_1$ and $k_2$ are constants of the adsorption rate, and $q_e$ is the adsorption capacity at time $t$. Adsorption rate constants and their regression correlation coefficients were summarized in table 2. The validity of the model is checked by the regression correlation coefficient ($R^2$). It is clear that the $q_e$ value was close to $q_e$ calculated by the quasi-second-order mechanism, and is quite different from the quasi-first-order mechanism [8, 31]. In other words, the adsorption of four dyes favorably follows the quasi-second-order model, and the rate of the reaction appeared to be controlled by the chemical process.

3.3.5. Adsorption isotherms

The adsorption isotherm reflects the distribution law of adsorption molecules between liquid and solid phases. The Langmuir isotherm is useful for monolayer adsorption because there are a finite number of homogeneous surfaces with similar sites [44, 45]. The linear form of the Langmuir equation is

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}}$$  \hspace{1cm} (4)

where $q_{max}$ is the Langmuir constant (mg g$^{-1}$), representing the monolayer adsorption capacity, and $K_L$ is the Langmuir equilibrium constant related to the heat of adsorption (l mg$^{-1}$). On the other hand, the Freundlich isotherm assumes that dye molecules adsorption is carried out by multilayer adsorption on heterogeneous surfaces [46]. The linear form of the Freundlich model is

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$  \hspace{1cm} (5)

where $K_f$ (mg g$^{-1}$) and $n$ are Freundlich constants related to the capacity of sorption and adsorption intensity, respectively [35]. The adsorption isotherms obtained by the Langmuir equation and Freundlich equation were shown in figure 8, respectively. The calculation results of isotherm constants were also shown in table 3. The

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**Figure 8.** Adsorption isotherms of CN2, (a), (b) Langmuir model (c), (d) Freundlich model.
correlation parameters obtained for CN₂ indicated that the Langmuir isotherm was in good agreement with the experimental data, and the correlation coefficient $R^2$ was high within the concentration range studied \[35\]. Moreover, the Langmuir model equilibrium data is closer to the experimental data than the Freundlich model. Therefore, the adsorption of CN₂ is more suitable for the Langmuir model, which indicates that four dyes are homogeneous adsorption in the single-molecule layer at the surface of CN₂ adsorbent.

3.3.6. Adsorption mechanism

Adsorption results indicate the CMS@SiO₂@PANI adsorbents have different dye selectivity. Even in near-neutral conditions, the adsorption properties of the four dyes were significantly different. This phenomenon could be partly owing to the different electrical properties of dye molecules after hydrolysis. Interestingly, the adsorption of the four dyes has different changing trends with the changing of pH. The adsorption capacity of MO and CR increases significantly at low pH conditions, while MB adsorption increases at high pH. How to understand this may be closely related to the adsorption mechanism. As discussed above, the dye adsorption of CMS@SiO₂@PANI is dominated by the monomolecular chemical adsorption, and electrostatic attraction also plays an important role. Therefore, the adsorption process could be described as a two-step procedure. Firstly, dye molecules were adsorbed onto the surface of CMS@SiO₂@PANI by electrostatic attraction. Secondly, the dye molecules chemically bonded with the functional groups on the PANI surface.

Table 3. Isotherm parameters for MO, CR, MB, and RhB adsorption on CMS@SiO₂@PANI composite.

| Parameters           | MO       | CR       | MB       | RhB      |
|----------------------|----------|----------|----------|----------|
| Langmuir isotherm    |          |          |          |          |
| $q_{max}$ (mg g⁻¹)   | 178.25   | 105.04   | 58.58    | 38.75    |
| $K_L$ (l mg⁻¹)       | 0.0369   | 0.0328   | 0.0742   | 0.1421   |
| $R^2$                | 0.9992   | 0.9990   | 0.9979   | 0.9981   |
| Freundlich isotherm  |          |          |          |          |
| $n$                  | 9.31     | 8.52     | 3.03     | 4.62     |
| $K_f$ (mg g⁻¹(mg l⁻¹)⁻¹/ₙ) | 88.07 | 48.52    | 12.38    | 14.30    |
| $R^2$                | 0.8705   | 0.8839   | 0.9326   | 0.9100   |

Scheme 2. Chemical structure of CR molecule: (a) Under near-neutral condition, (b) Under acidic condition.
At high or low pH conditions, the charge nature and surface properties of CMS@SiO₂@PANI and dye molecules were significantly affected. Thus, the interaction between them was different from that under near-neutral condition. The dramatic increase of CR adsorption at pH < 4 could be due to the protonation of CN₂ under acidic conditions. The amino (–NH₂) and imino (–NH) on the surface are easily protonated to form -NH₃⁺ and -NH₂⁺ in an acidic medium. This change is consistent with the results of the Zeta potential in figure 7(b). This phenomenon is beneficial for the adsorption of negative charge dyes, such as CR (Scheme 2) and MO (Scheme S2) [45]. The possible adsorption mechanism of CR is depicted in Scheme 3. At near-neutral conditions, hydrogen bonding and π–π stacking interaction are the main attraction force between CMS@SiO₂@PANI and CR molecules. Under the acidic condition, the structure of CR molecules changed. The sulfonic acid group was converted to -SO₃⁻ after hydrolysis [47]. The -SO₃⁻ could connect with -NH₂⁺ of PANI molecule by electrostatic attraction. Therefore, the overall interaction between CMS@SiO₂@PANI and CR...
molecules increased. The electrostatic attraction between CMS@SiO$_2$@PANI and CR molecules became stronger with the decreasing of pH. This could well explain the rapid increase of CR adsorption with decreased pH at the acid condition [44]. The increase of MO adsorption at low pH and MB adsorption at high pH could also be understood by a similar theory, as illustrated in Scheme S4 [41, 48, 49] and Scheme S5 [8, 44, 50, 51].

4. Conclusion

In this work, three CMS@SiO$_2$@PANI magnetic adsorbents were fabricated by a chemical oxidation \textit{in situ} polymerization method. BET investigation suggests that all the samples have a highly porous structure. The morphology and structure of the PANI shell layer could be adjusted by tuning the reactant ratio. Among the three samples, CN$_2$ has the highest specific surface area. It has a uniform structural PANI layer composed of nanorods. The CMS@SiO$_2$@PANI has a saturation magnetization larger than 30.99 emu g$^{-1}$, enabling efficient magnetic separation. Adsorption results indicate the CMS@SiO$_2$@PANI composites have high adsorption for multiple-dye, especially for anionic dyes. The pH value of the water has a critical effect on the dye adsorption. The highest adsorption of CR was tested as 413.49 mg g$^{-1}$ at pH = 3. Adsorption kinetics and adsorption isotherms simulation show that the multiple-dye adsorption of CMS@SiO$_2$@PANI is dominated by the monomolecular chemical adsorption. Electrostatic adsorption also plays a vital role in dye adsorption. The structure, functional groups, and the surface property of the PANI and the dye molecules could be modified by tuning the pH value. In this way, the selective dye adsorption performance of CMS@SiO$_2$@PANI could be adjusted.

This work explored a green, cheap, and efficient magnetic adsorbent for multiple-dye adsorption. And the magnetic adsorbent could be effective for magnetic separation. This research would improve the broad application of magnetic adsorption techniques in the water treatment industry.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Data Availability Statement

Some or all data, models, or codes that support the findings of this study are available from the corresponding author upon reasonable request.

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References

[1] Bergfeld W F, Belsito D V, Marks J G and Andersen F A 2005 \textit{J. Am. Acad. Dermatol.} 52 125–32
[2] Milby P and Kay K 1978 \textit{J. Toxicol. Env. Heal.} 4 31–6
[3] Ramalingam S and Rao J R 2017 \textit{Acc. Sustain. Chem. Eng.} 5 5537–49
[4] Tuzen M, Sarı A and Saleh T A 2017 \textit{J. Environ. Manage.} 206 170–7
[5] Yamjala K, Nairn M S and Ramisetti N R 2016 \textit{Food. Chem.} 192 813–24
[6] Adegoke K A and Bello O S 2015 \textit{Water. Resour. Ind.} 12 8–24
[7] Vargas A M M, Cazetta A L, Kunita M H, Silva T L and Almeida V C 2011 \textit{Chem. Hem. Eng. J.} 168 722–30
[8] Wang N, Chen J, Wang J, Feng J and Yan W 2019 \textit{Powder. Technol.} 347 93–102
[9] Liang H, Jia Z, Zhang H, Wang X and Wang J 2017 \textit{Appl. Surf. Sci.} 422 1–10
[10] Bhowmik K L, Deb K, Bera A, Deb Nath A and Saha B 2018 \textit{J. Mol. Liq.} 289–98
[11] Olusegun S J, Rodrigues G L S, Freitas E T F, Lara L R S, Rocha W R and Mohallem N D S 2019 \textit{J. Hazard. Mater.} 380 120872
[12] Chanzu H A, Onyari J M and Shiundu P M 2019 \textit{J. Hazard. Mater.} 380 120897
Feng X, Wang J, Deng J, Qin W, Zhao N, Luo X, He M and Chen X 2020 Int. J. Biol. Macromol. 155 1142–56
Nadaroglu H, Mosher G, Gungor A A, Adiguzel G and Adiguzel A 2019 J. Water. Process. Eng. 31 100886
Zeng Y, Song W, Wang Y, Meng Y, Song F, Zhang S and Zhong Q 2019 Chemosphere. 235 1146–53
Karthik K V, Reddy C V, Reddy K R, Ravishankar R, Sanjeev G, Kulakarni R V, Shetti N P and Raghu A V 2019 J. Mater. Sci-Mater. El. 30 20646–53
Srinivas M, Venkata R C, Kakarla R R, Shetti N P, Reddy M S and Anjanapura V R 2019 Mater. Res. Express. 6 125302
Kiseleva M G, Radchenko I V and Nesterenko P N 2001 J. Chromatogr. A. 920 79–85
Zhou L, He Y, Shi H, Xiao G, Wang S, Li Z and Chen J 2019 J. Hazard. Mater. 380 120865
Vall M, Stromme M and Cheung O 2019 Acs. Omega. 4 2973–9
Chen F et al 2017 Acs. Appl. Mater. Inter. 9 15566–76
Massey A T, Gusain R, Kumari S and Khatri O P 2016 Ind. Eng. Chem. Res. 55 7124–31
Jinendra U, Kumar J, Nagabhushana B M, Raghu A V and Bilehal D 2019 Green. Mater. 7 137–42
Unuabonah E I, Guenter C, Weber J, Lubahn S and Taubert A 2013 Acs. Sustain. Chem. Eng. 1 966–73
Aguedal H, Iddou A, Aziz A, Shishkin A, Locs J and Juhna T 2019 Int. J. Environ. Sci. Te. 16 113–24
Wu J, Zhang L, Long C and Zhang Q 2012 J. Chem. Eng. Data. 57 3426–33
Chen J, Hong X, Xie Q, Li D and Zhang Q 2014 J. Chem. Eng. Data. 59 2275–82
Chatterjee D, Patnam V R, Sikdar A and Moulik S K 2010 Acs. Sustain. Chem. Eng. 8 15566–74
M, Yaraki M T, Karami M, Karimi S, Kiadehi A D, Karimipour K and Wang S 2018 J. Alloy. Compd. 775 227–36
Li H, Xiao T, Chen Y, Long J, Zhang G, Zhang P, Li C, Zhuang L and Li K 2018 Chem. Eng. J. 353 867–77
Mahto T K, Chowdhuri A R and Sahu S K 2014 J. Appl. Polym. Sci. 131 04840
Muhammad A, Shah A-u-H A, Bilal S and Rahman G 2019 Materials. 12 1764
Chen T, Wang Q, Liu J, Bai P and Guo X 2020 Sep. Purif. Technol. 231 115930
Yuan D, Zhang S, Xiang Z, Liu Y, Wang Y, Zhou H, He Y, Huang W and Zhang Q 2018 Acs. Sustain. Chem. Eng. 6 9619–27
You N, Wang X-F, Li J-Y, Fan H-T, Shen H and Zhang Q 2019 J. Ind. Eng. Chem. 70 346–54
Li J, Lu W, Ding D, Dai Z, Cao C, Liu L and Chen T 2019 J. Solid. State. Chem. 270 666–73
Li J, Dan H-B, Xie W, Nazril F, Yang L-M, Ye X-K and Zhu J-B 2018 Chinese J. Inorg. Chem. 34 1455–62
Li J, Zhu J, Qiao S, Yu Z, Wang X, Liu Y and Meng X 2017 Int. J. Miner. Process. 169 162–7
Gabal M A, Al-Ijaid A A, El-Rashed S, Hussein M A and Al Angari Y M 2018 J. Alloy. Compd. 747 83–90
Zhang J, Han D, Ye X, Wu X, Wu Y, Wang Y and Zhang L 2018 Polymer 135 200–10
Yue X, Liu Z, Zhang Q, Li X, Hao F, Wei J and Guo W 2016 Desalin. Water. Treat. 57 15190–9
Dhanavel S, Nivetha E A K, Dhanapal K, Gupta V K and Arumainathan S 2016 Rsc. Adv. 6 28871–86
Reddy K R, Karthik K V, Prasad S B B, Soni S K, Jeong H M and Raghu A V 2016 Polyhedron 120 169–74
Ozer A, Akkaya G and Yurabik M 2006 J. Hazard. Mater. 135 335–64
Chen Y, Long W and Xu H 2019 J. Mol. Liq. 287 110888
Sharma V, Rekha P and Mohanty P 2016 J. Mol. Liq. 222 1091–100
Jinendra U, Bilehal D, Nagabhushana B M, Reddy K R and Reddy C V 2019 Mater. Sci. for. Energy. Techn. 2 657–66
Ansari M O, Kumar R, Ansari S A, Ansari S P, Barakat M A, Alshahrir E and Cho M H 2017 J. Colloid. Interf. Sci. 496 407–15
Aussavasukhi A, Kampoosan C and Kengknekorn O 2016 J. Clean. Prod. 134 506–14
Tanzifi M, Yaraki M T, Karami M, Karimi S, Kiadehi A D, Karimipour K and Wang S 2018 J. Colloid. Interf. Sci. 519 154–73
Nasar A and Maslihoo F 2019 Environ. Sci. Pollut. R. 26 5333–56
Minisy I M, Salauuddin N A and Ayad M M 2019 J. Appl. Polym. Sci. 136 47056