



Bio-based magnetic Fe₃O₄/SiO₂@SA composite beads for efficient removal of methylene blue from water

Jia Li^{a,b}, Mohd Ridhwan Adam^c, Kydyr Askaruly^a, Alzhan Baimenov^a, Zhexenbek Toktarbay^a, Jechan Lee^{d,*}, Seitkhan Azat^{a,*}

^a Satbayev University, Almaty, Kazakhstan

^b Shandong Huayu University of Technology, Dezhou, China

^c School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia

^d Department of Global Smart City & School of Civil, Architectural Engineering, and Landscape Architecture, Sungkyunkwan University, Suwon 16419, Republic of Korea

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ABSTRACT

Dye wastewater pollution has become a significant environmental issue threatening aquatic ecosystems and human health. To achieve green and efficient removal of organic dye (e.g., methylene blue (MB)), bio-based magnetic composite beads (Fe₃O₄/SiO₂@SA) were prepared through HCl-assisted SiO₂ extraction, coprecipitation and ion-crosslinking under mild conditions, without high pressure, high reaction temperature or toxic chemicals. Batch adsorption studies of MB were used to explore the adsorption performance and mechanism of Fe₃O₄/SiO₂@SA. The experimental results demonstrate that the MB removal rate of Fe₃O₄/SiO₂@SA composite beads reaches 91.75% under optimised adsorption conditions (25 °C, pH 9, 100 mg/L initial MB concentration, 20 mL solution volume, and 10 mg adsorbent dosage). Compared to Fe₃O₄ and Fe₃O₄/SiO₂ powders, the adsorption capacity is much higher at 183.77 mg/g. Physisorption and monolayer adsorption were demonstrated. The optimal adsorption capacity of Fe₃O₄/SiO₂@SA on MB is 925.77 mg/g. In addition, Fe₃O₄/SiO₂@SA enabled rapid and efficient solid-liquid separation through an external magnetic field and exhibits excellent reusability. The removal efficiency stayed at 80.1% after six cycles of adsorption and desorption, and reached 81.1% in river water. The Fe₃O₄/SiO₂@SA composite beads possess excellent adsorption capability, rapid magnetic separability and good reusability, providing a sustainable solution for dye water treatment. This research provides novel viewpoints and experimental supports for the evolution of low-cost, recyclable, environmentally friendly adsorbents.

1. Introduction

Organic dyes, as a crucial chemical material resource in modern industrial production and civilian fields, have been extensively used in industries like papermaking, leather, textiles, printing, rubber, and plastics [1]. When dye effluents are discharged directly without treatment, they will cause very severe water pollution and ecological imbalance problems. Consequently, the treatment of dye wastewater has become an issue of high social concern [2]. Methylene Blue (MB) is a synthetic cationic dye with the molecular formula C₁₆H₁₈N₃S, which is widely used in industries such as paper, wool, silk, cotton, as well as food, cosmetics and pharmaceuticals. Due to its large usage and widespread discharge, MB has become one of the most common organic dye pollutants in industrial wastewater [3]. Studies have shown that MB

exhibits significant biotoxicity to humans and animals [4], which can cause various health problems such as long-term eye damage and burns, skin irritation, breathing difficulties, seizures, tachyarrhythmia, and neurotoxicity. Meanwhile, MB molecules in aqueous solutions mainly exist as a monovalent cation, which are prone to electrostatic interaction with negatively charged cell membranes and enter cells, thereby leading to bioaccumulation and potential ecological risks [5]. Therefore, water containing methylene blue must be effectively treated before being discharged. As one of the most widely used cationic dyes in industry, MB was selected as the model pollutant in this study to evaluate the adsorption performance and application potential of the prepared materials.

Researchers have developed a variety of treatment technologies for water containing MB. Traditional water treatment technologies include

* Corresponding authors.

E-mail addresses: jechanlee@skku.edu (J. Lee), s.azat@satbayev.university (S. Azat).

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coagulation, chemical precipitation, filtration, biodegradation, ozonation, photochemistry, advanced oxidation processes, and chemical oxidation. Although these methods have been widely applied in dye wastewater treatment, they still have limitations such as complex treatment processes, high energy consumption, reliance on chemical reagents, and limited removal efficiency for organic dyes [6]. In contrast, adsorption has become one of the most promising methods in the field of water treatment due to its simple operation, high treatment efficiency, low cost, environmental friendliness and no need for complex pretreatment. In recent years, traditional adsorbents such as activated carbon [7], alumina, zeolites and anatase titanium dioxide have been widely used in the research of organic pollutant removal and have demonstrated excellent adsorption performance. However, traditional adsorbents still have problems such as high preparation costs, difficult regeneration, low adsorption selectivity, complex preparation processes, limited adsorption capacity and the potential risk of secondary pollution, which restrict their large-scale applications. Therefore, the development of novel adsorption materials with high adsorption capacity, good cycling stability and environmental sustainability has become a current research focus [8]. Especially, bio-based adsorbents derived from abundant and renewable resources, which have received extensive attention in water treatment due to their rich surface functional groups, excellent biocompatibility and sustainability, and demonstrate considerable application potential.

In recent years, magnetic nanomaterials have attracted considerable attention due to their low cost, abundant resources, simplicity of separation, and high adsorption efficiency, making them a popular research focus [9]. Traditional separation methods usually employ filtration and centrifugation techniques, which lead to adsorbent loss and increase operational costs. Introducing magnetic nanoparticles into the adsorbent can easily overcome this problem. Fe_3O_4 magnetic nanoparticles possess abundant resources, low cost, simplicity in preparation, high oxidizability, high specific surface area, and strong magnetic responsiveness [10]. However, their tendency to aggregate and poor chemical stability limit the large-scale practical application of Fe_3O_4 nanoparticles.

To improve their dispersion and structural stability, Fe_3O_4 magnetic nanoparticles are composited with mesoporous materials such as silica, clay, zeolite, graphene, and polymers [11]. Especially bio-based SiO_2 , which can be extracted from agricultural waste (such as rice husks, straw, rice straw ash), offers advantages including wide availability, low cost, green and renewability, high specific surface area [12], high structural stability, and abundant reactive silanol groups on the internal pore surfaces [13], and is often used as a composite material for magnetic nanoparticles [14]. The porous structure of SiO_2 [15] can effectively prevent the aggregation and oxidation of magnetic Fe_3O_4 nanoparticles over a wide pH range [16], in addition to affording numerous silanol functional groups (-Si-OH) as active sites, numerous pores, and a high specific surface area, thus improving the adsorption ability and chemical stability. Meanwhile, its ecological and economic benefits conform to the principles of sustainable development [17]. However, the adsorption capacity and recyclability of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites in water treatment still have limitations. Their small particle size makes recovery difficult and may lead to secondary pollution. Therefore, modification is necessary to facilitate the rapid separation of the adsorbent from aqueous solution.

To further enhance the adsorption performance and recyclability of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites [18], $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites can be embedded into a sodium alginate (SA) matrix to prepare magnetic beads with controllable structures. SA is a natural anionic polysaccharide polymer with abundant reserves, which is rich in -COOH and -OH groups [19], and can cross-link with divalent metal ions to form a three-dimensional gel network known as the "egg-box structure" [20]. SA beads possess properties such as gelation, hydrophilicity, non-toxicity, biodegradability, renewability, biocompatibility, stability, and flocculation. However, the size of the three-dimensional network structure adsorbent

is generally at a millimeter level, with a relatively small specific surface area. Moreover, during the cross-linking process, some carboxyl groups are occupied by metal ions, resulting in insufficient exposure of active groups, reduced adsorption sites, and diminished adsorption capacity. To overcome the limitations, introducing $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites into the SA matrix can achieve "magnetic separation, structural stability, high specific surface area, multiple active sites, a supportive three-dimensional network, and renewability." Therefore, the construction of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ can not only effectively utilise biomass resources but also achieve efficient adsorption and reusability of dye wastewater, providing new research perspectives and technical approaches for the green, economic and sustainable treatment of dye wastewater.

In summary, in view of the problems such as the easy agglomeration of Fe_3O_4 magnetic nanoparticles, the limited adsorption capacity and recyclability of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites, as well as the low specific surface area and utilization rate of active sites after the ionic crosslinking of sodium alginate (SA), a facile interface modification and multi-component synergistic enhancement strategy was proposed. The bio-based SiO_2 extracted from rice husks was introduced as the core-shell intermediate layer, which effectively inhibited the aggregation of Fe_3O_4 nanoparticles and increased the specific surface area due to its excellent dispersibility and chemical stability. Meanwhile, silanol functional groups (-Si-OH) enhanced the interfacial interaction with the SA matrix. The ternary composite constructed integrates the magnetic separation ability of Fe_3O_4 , the structural regulation function of SiO_2 , and the abundant oxygen-containing functional groups of SA, forming a bio-based adsorbent with rapid mass transfer, good mechanical stability and magnetic separation ability, thereby significantly improving the adsorption performance and reusability.

In this research, a novel bio-based magnetic composite bead ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$) was successfully prepared and applied for the removal of methylene blue (MB) from water. A systematic analysis was performed on the morphology, crystal structure, functional groups, and specific surface area of the materials using SEM-EDS, STEM, XRD, FTIR, and BET. Furthermore, research on adsorption kinetics, isotherm models, the impact of pH on adsorption performance, and comparison of characterization before and after adsorption changes clarified the adsorption mechanism and the adsorption performance of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ in removing MB from water, as well as evaluating the reusability of the composite beads.

Table 1
Specifications of chemical reagents and materials.

Chemical Name	Chemical Formula	Purity	Molecular Weight (g/mol)	Source
Rice Husk	/	/	/	Kazakhstan
Sodium Hydroxide	NaOH	99%	40.00	Meryer (China)
Hydrochloric Acid	HCl	37%	36.46	Meryer (China)
Ferric Chloride Hexahydrate	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	99%	270.30	Meryer (China)
Ferrous Chloride Tetrahydrate	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	99%	198.81	Meryer (China)
Calcium Chloride	CaCl_2	99%	110.98	Meryer (China)
Sodium Alginate	$(\text{C}_6\text{H}_9\text{O}_6\text{Na})_n$	98%	216.12 (monomer)	Meryer (China)
Methylene Blue	$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$	98%	319.85	Meryer (China)

2. Materials and methods

2.1. Materials

All chemical reagents and raw materials used in this study, along with their purity and sources, are summarized in Table 1. Except for the rice husk (RH) collected from a local site in Kazakhstan, all chemicals were used as received without further purification.

2.2. Preparation of bio-based SiO₂

Bio-based silica was extracted from rice husks (RH) produced in Kazakhstan, which was prepared after pretreatment with HCl [21]. The detailed procedure is as follows: (1) Obtain 50 g of RH. Rinse the rice husks with deionized water (DI water). Then, dry the RH in a benchtop oven at 120 °C. (2) HCl pretreatment: Mix the dried 50 g RH with 500 mL of 2 mol/L HCl solution (HCl can be reused) and maintain the dry reaction at 90 °C for 2 h. After the reaction, the mixture is filtered with a 12 µm filter paper. Then wash RH with DI water until the pH value reaches 6–7. Subsequently, dry the treated RH at 120 °C for 4 h [22]. (3) Calcination: The dried RH is placed in a muffle furnace for calcination at 600 °C for 4 h to obtain white rice husk ash (WRHA). (4) The WRHA was mixed with a 100 mL solution of 2 M NaOH and stirred at 90 °C for 2 h to produce Na₂SiO₃. Filter the Na₂SiO₃ solution with vacuum filtration using a microporous membrane (diameter 50 mm, pore size 0.22 µm) to remove insoluble impurities. Subsequently, 8–15 mL of concentrated HCl was added to the filtrate, and the process was allowed to continue for a further 30 min to convert Na₂SiO₃ into SiO₂ gel. Then, SiO₂ gel was rewashed with DI water (at 65 °C and 340 rpm) until the pH reached 6–7. (5) The gel was dried at 105 °C, then ground to produce a pure white powder of bio-based SiO₂.

2.3. Preparation of Fe₃O₄

Fe₃O₄ nanoparticle was synthesized by the co-precipitation method [23]. Firstly, 1.622 g of FeCl₃·6H₂O and 1 g of FeCl₂·4H₂O were dissolved in 50 mL DI water, heated to 90 °C and stirred continuously to ensure thorough dispersion. Under stirring conditions, 20 mL of 2 M NaOH solution was added to the mixture. During the reaction, black precipitates gradually formed (reaction time of 0.5–1 h at pH 10–12), which confirmed that Fe₃O₄ nanoparticles were prepared successfully. After the reaction, Fe₃O₄ nanoparticles are cooled to room temperature and static separation is performed to collect the black precipitate. Then the precipitate was repeatedly purified several times by washing with DI water until neutral. Finally, the samples were ultrasonically dispersed for 30 min and vacuum-dried (60 °C) to obtain Fe₃O₄ nanomaterials.

2.4. Preparation of Fe₃O₄/SiO₂

Except for the additional silica-loading step, the preparation procedure of Fe₃O₄/SiO₂ was basically the same as that of Fe₃O₄. First, 1.622 g of FeCl₃·6H₂O and 1 g of FeCl₂·4H₂O were dissolved in 50 mL of DI water. Then heated to 90 °C, and 1 g of bio-based silica was added, with stirring continued to ensure complete dispersion. Under stirring conditions, 20 mL of 2 M NaOH solution was added to the mixture. During the reaction, brown precipitates gradually formed (reaction time 0.5–1 h, pH 10–12), indicating Fe₃O₄ nanoparticles and bio-SiO₂ were successfully composited. After the reaction, Fe₃O₄/SiO₂ nanoparticles are cooled to room temperature. After washing the brown precipitate to neutrality with DI water, the sample was ultrasonically dispersed for 30 min and vacuum-dried (60 °C). The dried samples were ground to get Fe₃O₄/SiO₂ nanoparticles.

2.5. Preparation of Fe₃O₄/SiO₂@SA

Fe₃O₄/SiO₂@SA core-shell composite beads were synthesized by

ion-crosslinking [24]. Initially, 1.5 g of sodium alginate powder was mixed with 50 mL of DI water under stirring. Then, 1 g of Fe₃O₄/SiO₂ composite was added, followed by ultrasonic treatment for 30 min. 10 g of CaCl₂ dissolved in 200 mL of DI water. The Fe₃O₄/SiO₂@SA mixture was dropped into the CaCl₂ solution with a syringe while slowly stirring to form beads. After soaking for 0.5–1 h, the beads were freeze-dried (-60 °C) to obtain Fe₃O₄/SiO₂@SA core/shell composite beads (Scheme 1).

2.6. Characterization

FTIR spectroscopy was applied to identify the surface functional groups of the samples (Nicolet APEX, Thermo Scientific, UK). The surface morphology and elemental distribution were examined by SEM coupled with EDS (Quattro S, Thermo Fisher, USA). Crystallographic structures were obtained from XRD (Bruker D8 ADVANCE, Bruker, Germany) with Cu-Kα radiation. Porosity characteristics were evaluated through nitrogen adsorption-desorption measurements using a Nova 600 analyzer (Anton Paar, Austria), and the specific surface area and pore parameters were calculated by the BET and BJH models. The concentration of MB was determined using a UV-Vis spectrophotometer (Specord 50 plus, Analytic Jena, Germany).

2.7. Batch adsorption experiment

Taking MB as a representative pollutant, the adsorption performance of Fe₃O₄/SiO₂@SA (with Fe₃O₄ and Fe₃O₄/SiO₂ as reference samples) was evaluated through batch adsorption experiments (unless otherwise specified, all adsorption experiments were performed in parallel three times at 25 °C). In each experiment, 10 mg of Fe₃O₄/SiO₂@SA was dispersed into 20 mL of MB solution, with a concentration of 100 mg/L. The solution was shaken at a constant speed until the adsorption equilibrium was reached. The MB concentration was tested with a UV-vis spectrophotometer. A calibration curve was established using ten standard MB solutions in the concentration range of 0–10 mg L⁻¹, yielding R² of 0.9974. The adsorption capacities were calculated via Eq. (1).

$$q_e = V \times (C_0 - C_e) / m \quad (1)$$

The removal efficiency was calculated based on Eq. (2) as follows:

$$\%R = (C_0 - C_e) / C_0 \times 100 \quad (2)$$

where C₀ and C_e denote the initial and equilibrium concentrations of the MB solution (mg/L), V represents the solution volume (L), and m is the mass of the adsorbent (g) [25].

2.7.1. Adsorption kinetics

10 mg of Fe₃O₄, Fe₃O₄/SiO₂ and Fe₃O₄/SiO₂@SA samples were added into 20 mL of MB solution, respectively, with a concentration of 100 mg/L. The solutions were stirred constantly until the adsorption reached equilibrium.

Adsorption kinetic models were employed to examine the adsorption rate of MB onto the samples. The pseudo-first-order and pseudo-second-order models are typically given by Eqs. (3) and (4).

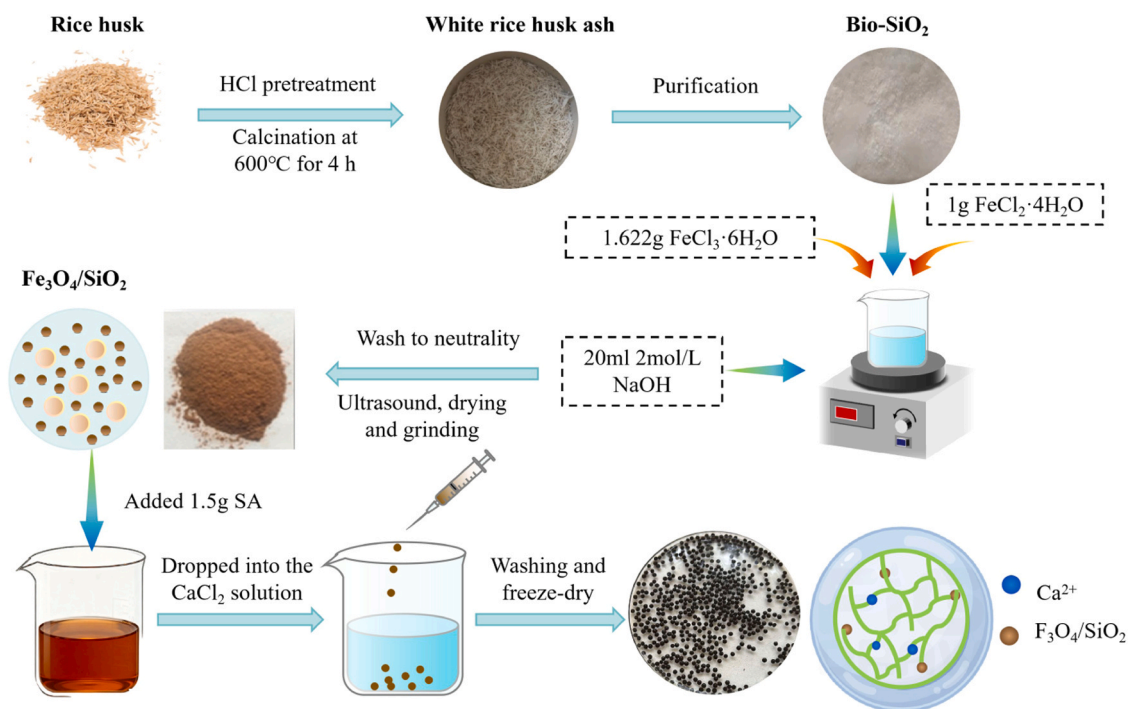
$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

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

where the adsorption capacity at equilibrium and time t (min) are q_e (mg/g) and q_t (mg/g). The kinetic parameters k₁ (min⁻¹) and k₂ (g mg⁻¹ min⁻¹) are the constants of the pseudo-first- and pseudo-second-order model [19].

2.7.2. Adsorption isotherms

Add 10 mg of Fe₃O₄/SiO₂@SA into 20 mL of MB solutions with varying initial concentrations (50, 100, 150, 200, 450 and 700 mg/L).



Scheme 1. Schematic illustration of the preparation of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$.

The Langmuir and the Freundlich isotherm models were applied to analyze the adsorption data, given in Eqs. (5) and (6) [26].

$$C_e/q_e = 1/q_{\max}K_L + C_e/q_{\max} \quad (5)$$

$$\log q_e = \log K_F + (1/n) \cdot \log C_e \quad (6)$$

In Eqs. (5) and (6), q_e (mg/g) and C_e (mg/L) denote the equilibrium adsorption capacity and equilibrium concentration. The parameter $q_{\max}$ (mg/g) is the maximum adsorption capacity. K_L (L/mg) is the constant of the Langmuir (It reflects the adsorbent–MB affinity and binding site energy). In the Freundlich model, K_F (mg/g) reflects the adsorption capacity and intensity, $1/n$ is a constant describing the adsorption nonlinearity.

2.7.3. Research on the influence of pH

The influence of pH (3–11) on MB adsorption by $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$ was investigated.

2.7.4. Evaluation of the point of zero charge (pHzpc)

To investigate the surface charge characteristics of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$, the point of zero charge pH (pHzpc) was determined. First, prepare a 0.1 M NaCl solution with pH values ranging from 3 to 11. Then add 10 mg of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$ to 20 mL of NaCl solution and shake at room temperature for 24 h. Subsequently, the final pH values of each sample were measured using a pH meter. A plot of $\text{pH}_f - \text{pH}_i$ (pH_i and pH_f representing the final pH and the initial pH) versus pH_i was constructed, and the intersection point of the curve with the horizontal axis is determined as the pHzpc.

2.7.5. Reusability test

After the adsorption experiment, initially rinsed with DI water. The washed beads were immersed in a 0.1 M solution of CaCl_2 and shaken to facilitate desorption, then washed with DI water. The adsorption experiment was repeated under the same conditions. To investigate the reusability of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$.

3. Results and discussion

3.1. Adsorbent characteristics

XRD is an essential analytical technique for identifying the crystal structure of synthetic nanomaterials. As shown in Fig. 1a, the XRD results of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA-MB}$ ($\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$ after adsorption of methylene blue) were compared, respectively. For Fe_3O_4 nanoparticles, diffraction peaks match well with the standard diffraction card (JCPDS 19-0629) [27], indicates that the Fe_3O_4 nanoparticles have a typical cubic spinel structure. After adding SiO_2 , the peaks of Fe_3O_4 were still retained, while the diffraction intensity decreased due to the presence of amorphous SiO_2 . Following the SA modification, the diffraction peaks further weakened, and the amorphous background increased, which could be attributed to the amorphous polymer structure of sodium alginate. After MB adsorption, no new crystalline peaks appeared, while the peak intensity slightly decreased further, indicating that MB was successfully adsorbed onto the material surface without altering the crystal structure of Fe_3O_4 . The results demonstrate that the Fe_3O_4 crystal phase remained stable during the coating, modification, and adsorption processes.

FTIR spectroscopy was employed in order to identify the surface functional groups and structures of the synthesized samples. As shown in Fig. 1b, distinct absorption peaks appear at approximately $540\text{--}560\text{ cm}^{-1}$ in the samples of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$, corresponding to the Fe–O stretching vibration, indicating that all samples contain Fe_3O_4 nanoparticles.

In the spectrum of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite, the absorption bands at 1077 and 795 cm^{-1} are the asymmetric and symmetric vibrations of Si–O–Si bonds. Confirming the presence of SiO_2 , consistent with the XRD results [28]. In the spectrum of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{@SA}$, the broad band around 3349 cm^{-1} corresponds to the –OH stretching vibrations. The absorption peak at 2921 cm^{-1} belongs to the stretching vibration of –CH₂, indicating that a small number of organic groups are on the material surface. In addition, absorption peaks at 1596 and 1425 cm^{-1} correspond to the antisymmetric and symmetric stretching vibrations of the –COO[−] group in sodium alginate, indicating that SA successfully participated in the

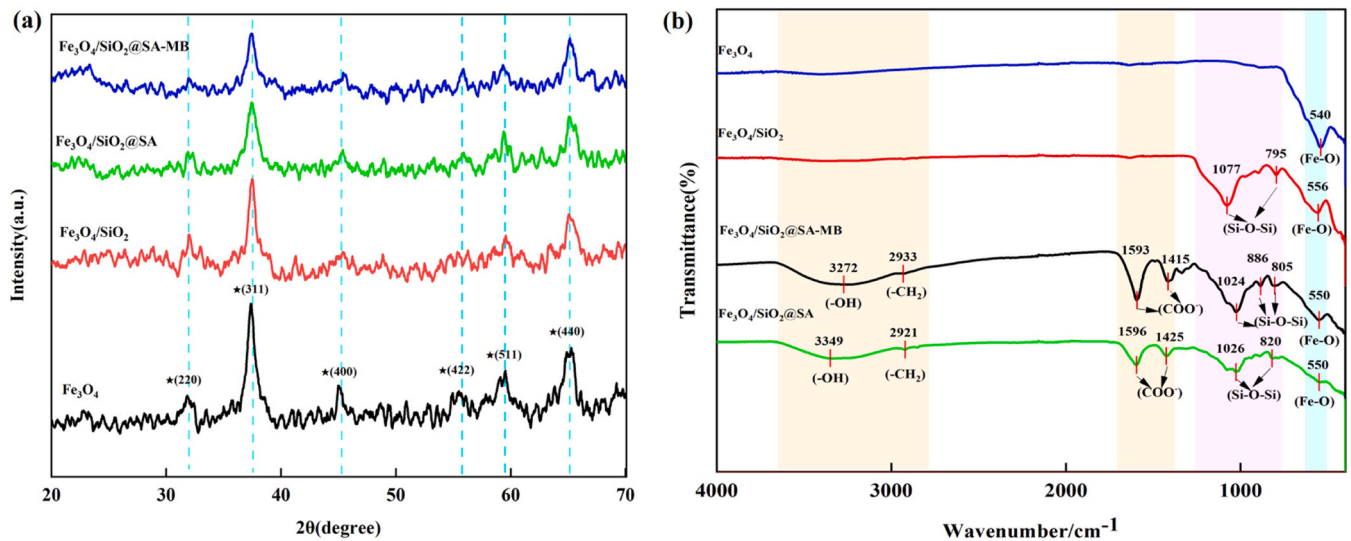


Fig. 1. (a) XRD diffraction patterns and (b) FTIR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA-MB}$.

composite structure. Overall, the characteristic peaks observed in the FTIR spectra are consistent with the samples' structure and demonstrate

that the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ core-shell structure has been successfully prepared [29].

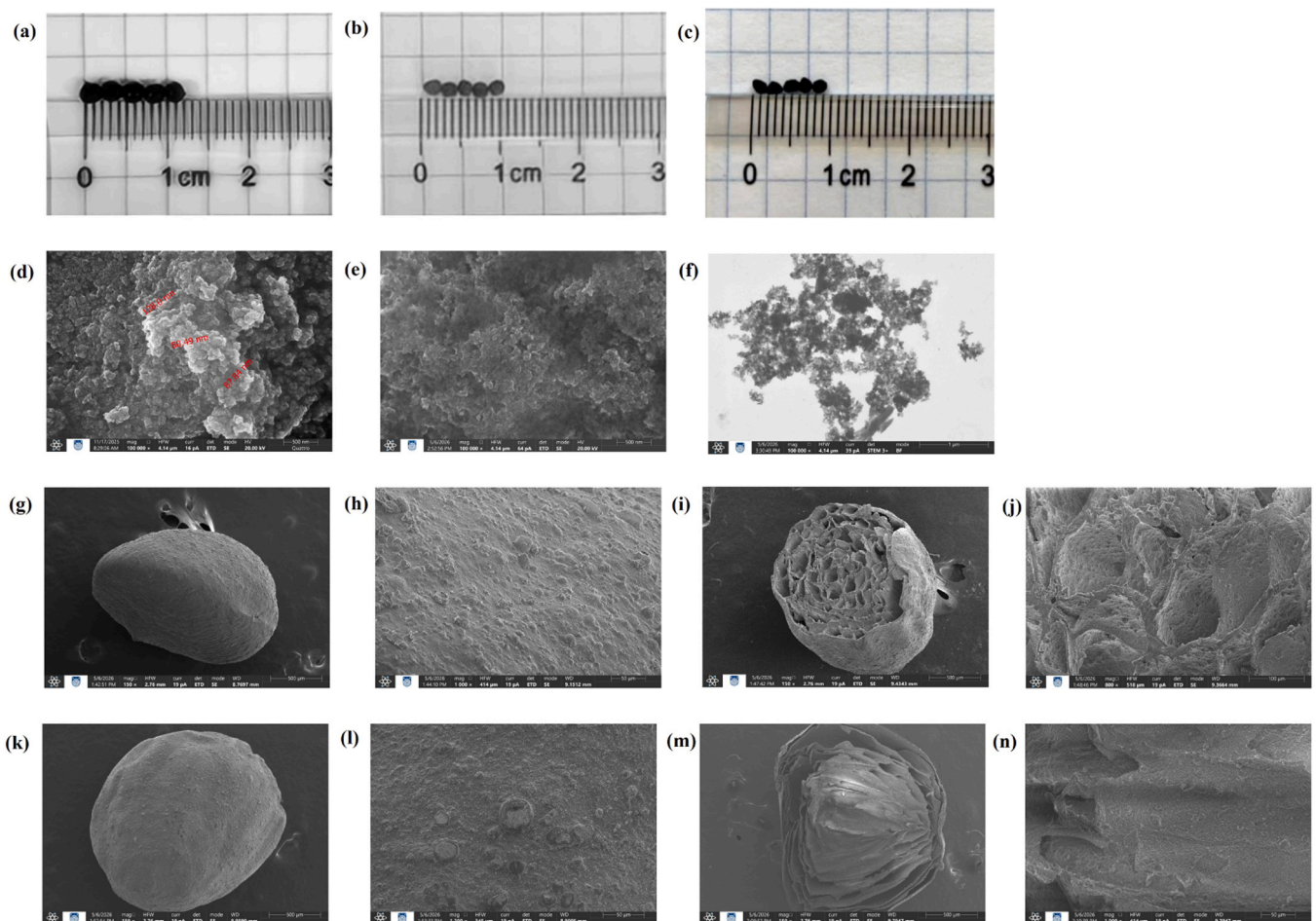


Fig. 2. Photographs of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ beads (a) wet beads, (b) freeze-dried $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ beads and (c) freeze-dried $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA-MB}$ beads; SEM image of (d) Fe_3O_4 nanoparticles and (e) $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites; (f) STEM image of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites; SEM image of (g) the external morphology of freeze-dried $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ bead; (h) the locally magnified surface morphology of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ bead; (i) the internal structure of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ bead; and (j) local magnified morphology of the internal structure of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ bead; SEM image of (k) the external morphology of freeze-dried $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA-MB}$ bead; (l) the locally magnified surface morphology of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA-MB}$ bead; (m) the internal structure of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA-MB}$ bead; and (n) local magnified morphology of the internal structure of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA-MB}$ bead.

After MB adsorption, the FTIR spectrum analysis results show that $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$ exhibits obvious Fe–O stretching vibration peaks at 550 cm^{-1} , and the absorption intensity slightly increases after adsorption, which confirms that the crystalline structure of the Fe_3O_4 magnetic core remains intact after adsorption. The Si–O–Si asymmetric stretching exhibited a slight shift from 1026 to 1024 cm^{-1} , while the symmetric stretching vibration band shifted from 820 to 805 cm^{-1} . Moreover, the absorption intensities of both significantly increased, indicating that the Si–O–Si functional groups located on the SiO_2 shell participated in the adsorption process. The broad –OH peak shifts from 3349 to 3272 cm^{-1} , indicating that –OH on the surface of the adsorbent acts as a hydrogen bond donor and form new hydrogen bonds with MB after adsorption. In addition, the antisymmetric (1593 cm^{-1}) and symmetric (1415 cm^{-1}) stretching vibrations of $-\text{COO}^-$ groups on the SA chains show slight shifts accompanied by an enhancement of their intensities after the adsorption. The changes shown by these peaks suggest the active involvement of the $-\text{COO}^-$ groups in the adsorption phenomenon and interact strongly with MB molecules. Notably, a novel weak absorption peak appeared at 886 cm^{-1} after adsorption. The above phenomenon suggests that the adsorption process has changed the local chemical environment on the surface.

Fig. 2a–c shows the images of wet $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ beads, freeze-dried $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ beads and freeze-dried $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$ beads. The wet beads appear as uniformly sized, smooth-surface, blackish-brown spheres with a diameter of approximately 2.4 mm . After freeze-drying, the shape of the beads remained spherical morphology, while the diameter decreased to about 2.0 mm . After adsorption and secondary freeze-drying, $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$ beads became more compact, and the diameter decreased to about 1.8 mm .

To obtain a more intuitive understanding of the microstructural features of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$, and $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$, SEM was performed. As depicted in Fig. 2d, Fe_3O_4 forms nanoscale magnetic particles during the synthesis process, which exhibit a nearly regular spherical morphology with particle sizes in the range of $50\text{--}200\text{ nm}$. However, due to their superparamagnetic nature, significant particle agglomeration is observed. After the incorporation of SiO_2 (Fig. 2e), the Fe_3O_4 nanoparticles were significantly dispersed and had a more uniform particle size. Combined with the STEM results (Fig. 2f), this further confirms that SiO_2 effectively improves the dispersion of Fe_3O_4 nanoparticles. Fig. 2g shows the external morphology of $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$, which is a dark brown sphere. After magnification (Fig. 2h), fine particles are observed attached to the bead surface. When cutting $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ (Fig. 2i), the interior presents a three-dimensional network structure and is attached with nanoparticles, which is conducive to enhancing the overall mechanical strength of the material [30]. After a 1000-fold magnification (Fig. 2j), the composite particles are uniformly distributed across the network structure. This three-dimensional network structure provides stable fixed sites for the nanoparticles, effectively preventing particle agglomeration. Meanwhile, the nanoparticles in reverse avoid the aggregation of the hydrogel matrix. The morphology of beads provides a high number of accessible active sites, facilitating rapid ion diffusion, a key factor in increasing adsorption rate and capacity.

In contrast, the microstructure of $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$ has undergone significant changes (Fig. 2k–n). The beads show varying degrees of shrinkage and collapse, further exposing the internal pore structure, making the surface rougher and presenting layered or sheet-like features. This change indicates that the introduction of MB molecules may weaken the three-dimensional crosslinked network constructed by SA, thereby leading to a looser overall structure. This process not only indicates the successful capture of the target pollutant but also reflects that the SA three-dimensional network has certain dynamic structural response characteristics during MB adsorption.

Fig. 3a–f shows the EDS spectra, element contents, and element mapping results of $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$, respectively. As demonstrated in Fig. 3a, the energy spectrum of

$\text{Fe}_3\text{O}_4/\text{SiO}_2$ exhibits distinct characteristic peaks for Fe, Si, and O, with mass percentages of 30.1% , 12.8% , and 32.6% , respectively (The carbon peak observed for the element C in the spectrum emanated from the conductive carbon tape employed for fixing the sample during SEM/EDS analysis). The elemental mappings further indicate Fe, Si and O are uniformly distributed within the nanocomposites, showing good compositional uniformity of the synthesized $\text{Fe}_3\text{O}_4/\text{SiO}_2$. In Fig. 3e, the distribution of the five elements C, O, Si, Fe, and Ca is relatively uniform, indicating that the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles are successfully embedded in the three-dimensional network structure of $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$, further verifying the homogeneity of the composite system. This proves that $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ alginate microbeads have been successfully synthesized with high purity and no significant impurities. The appearance of the S element in Fig. 3f serves as characteristic evidence of the successful capture of methylene blue, indicating that MB molecules have permeated and been loaded into the pore network.

Fig. 4a shows that Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$ have N_2 adsorption-desorption isotherms of typical type IV isotherms with H3 hysteresis loops, indicating all four samples have mesoporous structures. The differential pore size distribution curves ($dV/d\log(D)$) shown in Fig. 4b demonstrate the differences in the textural characteristics of the four samples in the mesoporous and macroporous ranges. Pure Fe_3O_4 is characterized by a pronounced mesoporous distribution with a dominant maximum in the region between $22\text{--}50\text{ nm}$, with a maximum value ($dV/d\log(D)$) of about $0.60\text{ cm}^3/\text{g}$. The low contribution of small ($<10\text{ nm}$) and large ($>70\text{ nm}$) pores indicates that a relatively narrow range of mesopore sizes is formed due to magnetite particle aggregation. After modification with silica ($\text{Fe}_3\text{O}_4/\text{SiO}_2$), an expansion of the pore distribution and a shift of the main maximum to the $40\text{--}90\text{ nm}$ region was observed, with an intensity decrease to $0.25\text{ cm}^3/\text{g}$. The silica shell prevents dense agglomeration of Fe_3O_4 nanoparticles and promotes the development of a more open pore. For the $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$, further smoothing of the distribution curves and a decrease in the absolute values ($dV/d\log(D)$) are observed after surface functionalization. The main contribution shifts to the $50\text{--}100\text{ nm}$ region, with a maximum of approximately $0.18\text{ cm}^3/\text{g}$, while the proportion of small mesopores ($<20\text{ nm}$) decreases noticeably. This indicates partial pore blocking by organic groups and compaction of the pore structure. For $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$, after adsorbing MB, the distribution curve becomes flatter, and the absolute values ($dV/d\log(d)$) decrease significantly. The pore distribution is at a relatively low level with a maximum value of only approximately $0.08\text{ cm}^3/\text{g}$, indicating that MB molecules effectively occupy the material's pores and induce the densification of the pore structure.

As shown in Table 2, the specific surface area of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was increased compared to that of pure Fe_3O_4 , indicating that the introduction of SiO_2 could prevent the agglomeration of Fe_3O_4 nanoparticles and enhance the dispersion of the material. However, during the process of co-precipitation and composite formation, some pores were occupied or blocked, resulting in a slight decrease in the average pore size and total pore volume. When $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was further incorporated into SA beads, the specific surface area and pore volume decreased further, indicating that the SA coating occluded some pores. However, the average pore size increases because the three-dimensional gel network formed after SA cross-linking contains numerous pores. In contrast, some of the original small pores are filled, thereby increasing the average pore size.

After adsorption of MB, the specific surface area of $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA-MB}$ decreased from $26.9\text{ m}^2/\text{g}$ to $13.67\text{ m}^2/\text{g}$, and the total pore volume decreased from 0.17 cc/g to 0.077 cc/g . The data strongly prove that MB molecules have successfully penetrated the three-dimensional gel network and effectively occupied the internal active sites and pores. Meanwhile, the average pore size decreased from 14.41 nm to 9.20 nm , indicating that the larger mesopores in the SA matrix were filled with MB molecules, and the electrostatic interaction between cationic dyes and sodium SA chains also led to structural compaction and local pore

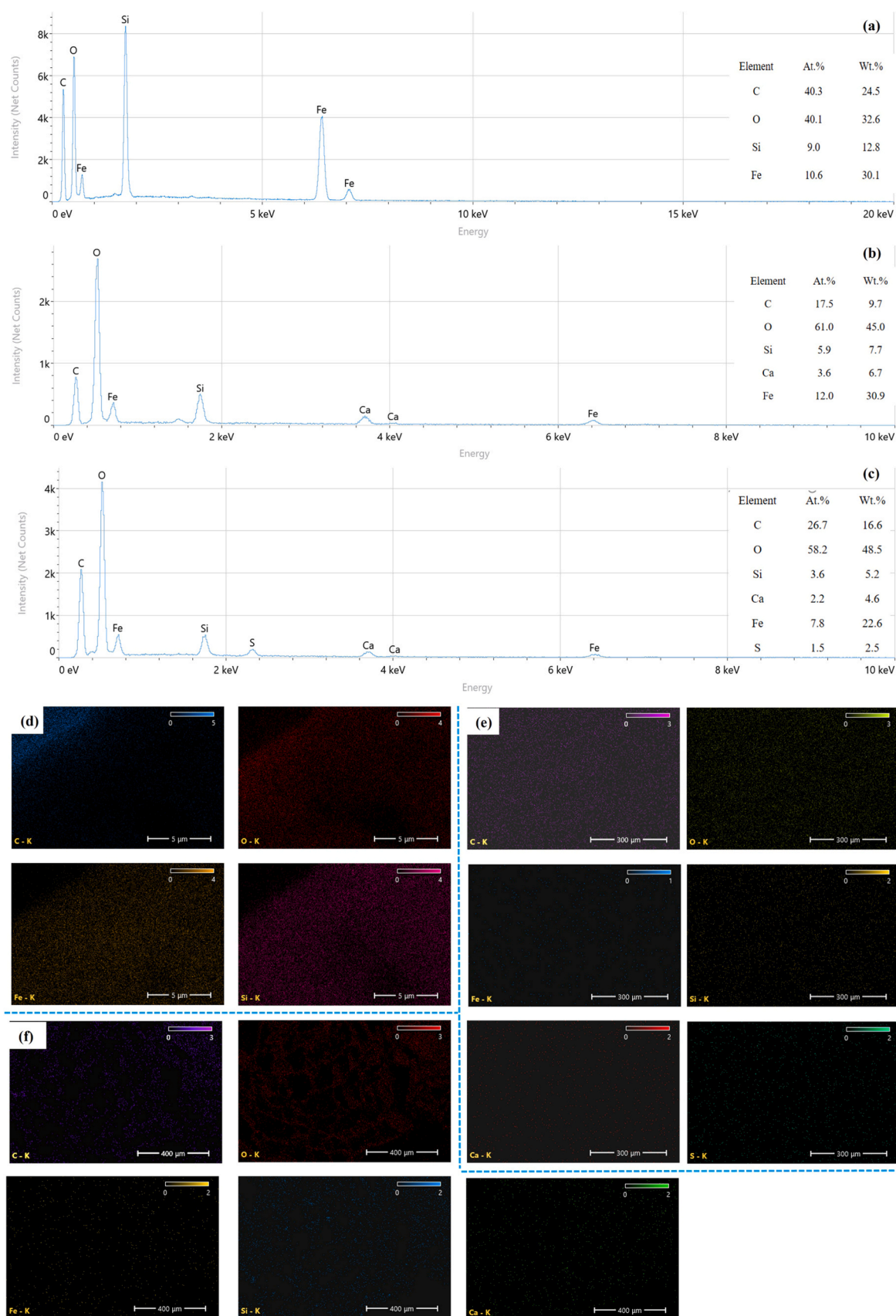


Fig. 3. EDS results of (a) $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites; (b) $\text{Fe}_3\text{O}_4/\text{SiO}_2@SA$; (c) $\text{Fe}_3\text{O}_4/\text{SiO}_2@SA-MB$; elemental mapping images of (d) $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites; (e) $\text{Fe}_3\text{O}_4/\text{SiO}_2@SA$ and (f) $\text{Fe}_3\text{O}_4/\text{SiO}_2@SA-MB$.

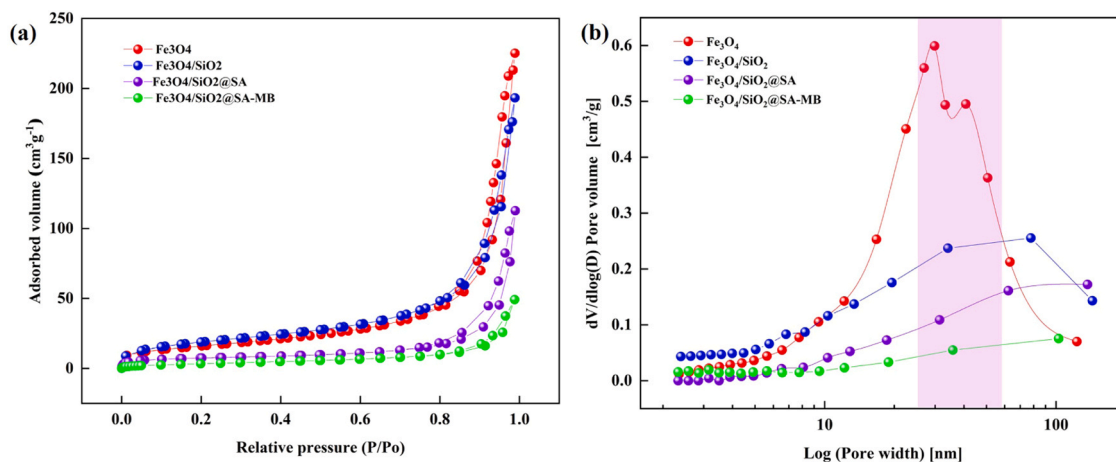


Fig. 4. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution curves of Fe_3O_4 , Fe_3O_4/SiO_2 , $Fe_3O_4/SiO_2@SA$ and $Fe_3O_4/SiO_2@SA-MB$.

Table 2

Surface area, pore size, and pore volume of Fe_3O_4 , Fe_3O_4/SiO_2 , $Fe_3O_4/SiO_2@SA$ and $Fe_3O_4/SiO_2@SA-MB$.

Sample	Surface area (m²/g)	Pore size (Radius) (nm)	Pore volume (cc/g)
Fe_3O_4	58.03	10.57	0.35
Fe_3O_4/SiO_2	69.19	8.61	0.30
$Fe_3O_4/SiO_2@SA$	26.96	14.41	0.17
$Fe_3O_4/SiO_2@SA-MB$	13.67	9.20	0.077

collapse.

3.2. Batch adsorption experiments

MB has been chosen to systematically evaluate the adsorption capacity of $Fe_3O_4/SiO_2@SA$ composite bead. Meanwhile, Fe_3O_4 and Fe_3O_4/SiO_2 powders were tested as reference materials. Under the conditions of 25 °C, pH 9, 100 mg/L MB solution (20 mL), and an adsorbent dosage of 10 mg, the impact of contact time on adsorption was studied (Fig. 5a). For Fe_3O_4 powder, adsorption equilibrium was achieved within the first 20 min, with a lower adsorption capacity of 5.18 mg/g. However, Fe_3O_4/SiO_2 displayed an outstanding adsorption ability within 10 min and an adsorption capacity of 33.99 mg g⁻¹, which is 6 times higher than that of Fe_3O_4 . This indicates that the composite effectively increases the specific surface area and sites for MB adsorption, thereby enhancing the rapid adsorption. However, the adsorption rate of $Fe_3O_4/SiO_2@SA$ beads was significantly slower. The MB adsorption increased sharply within the initial 80 min, indicating a strong interaction between MB molecules and the porous structure of the beads. Subsequently, the adsorption rate decreased gradually and approached equilibrium after 320 min, with a removal efficiency of 91.75%. The adsorption capacity reached 183.77 mg/g, much higher than that of Fe_3O_4 and Fe_3O_4/SiO_2 powders. The decreased adsorption rate of $Fe_3O_4/SiO_2@SA$ is that numerous active sites are embedded within the SA gel network. MB molecules must first penetrate the gel layer on the bead surface and then diffuse gradually to the adsorption sites via the three-dimensional internal channels. The internal diffusion resistance is significant, resulting in a relatively long equilibrium time. However, the bead structure enables more active sites and provides an effective adsorption interface, resulting in a substantially enhanced equilibrium adsorption capacity [31].

3.2.1. Adsorption isotherms study

Fig. 5b shows that the Langmuir and the Freundlich isotherm models for the adsorption of MB by $Fe_3O_4/SiO_2@SA$. The results (Table 3)

indicate that the R^2 of the Langmuir model was 0.9646, which was higher than that of the Freundlich model (0.9318). Meanwhile, the RMSE value of the Langmuir model was 46.82, lower than the 65.02 obtained for the Freundlich model, indicating that the Langmuir model provided a better fit to the experimental data. Therefore, it can be inferred that the adsorption process of MB onto $Fe_3O_4/SiO_2@SA$ is more consistent with the Langmuir isotherm model, suggesting that adsorption mainly occurred on uniform active sites of the adsorbent surface and was dominated by monolayer adsorption. The maximum adsorption capacity calculated from the Langmuir model was 925.77 mg·g⁻¹, demonstrating the excellent adsorption capability of the material toward MB. In addition, the $1/n$ value obtained from the Freundlich model was 0.41, which was lower than 1, indicating that the adsorption process could proceed favorably [32].

3.2.2. Adsorption kinetics study

As seen in Fig. 5c and d, the pseudo-first-order model has a higher R^2 than the pseudo-second-order model (parameters are listed in Table 4), and the RMSE value of the pseudo-first-order model is lower than that of the pseudo-second-order model, indicating that the MB adsorption by $Fe_3O_4/SiO_2@SA$ beads is mainly driven by physisorption. However, the high correlation of the experimental data with both kinetic models implies a complex adsorption involving both chemisorption and physisorption.

3.2.3. Effect of pH on the adsorption of MB

The pH value plays a critical role in the adsorption of MB onto an adsorbent surface. Changes in pH can alter the surface charge of $Fe_3O_4/SiO_2@SA$. For adsorbents containing surface functional groups, these groups may acquire different charges depending on the pH, which affects the electrostatic interactions between the adsorbent and the MB molecules [33]. As shown in Fig. 5e, the surface of $Fe_3O_4/SiO_2@SA$ contains abundant -COOH and -OH groups, so the weakly charged ions are always present in the solution. Under low-pH conditions, high H^+ concentration leads to more H^+ binding to the adsorbent's active sites, thus impeding the MB adsorption. As the pH value increases, the -COOH and -OH groups gradually deprotonate into -COO⁻ and -O⁻. The negative charge facilitates electrostatic adsorption and complexation of MB. When the pH is 9, the adsorption performance reaches its maximum. However, upon a further increase in pH to 11, the adsorption capacity of $Fe_3O_4/SiO_2@SA$ for MB slightly decreases. High pH solutions usually have a higher ionic strength and a strong electrostatic repulsion, which hinders the diffusion and adsorption of MB* to the surface of the adsorbent. Overall, $Fe_3O_4/SiO_2@SA$ exhibits good adsorption performance across the pH range 5–11 [19].

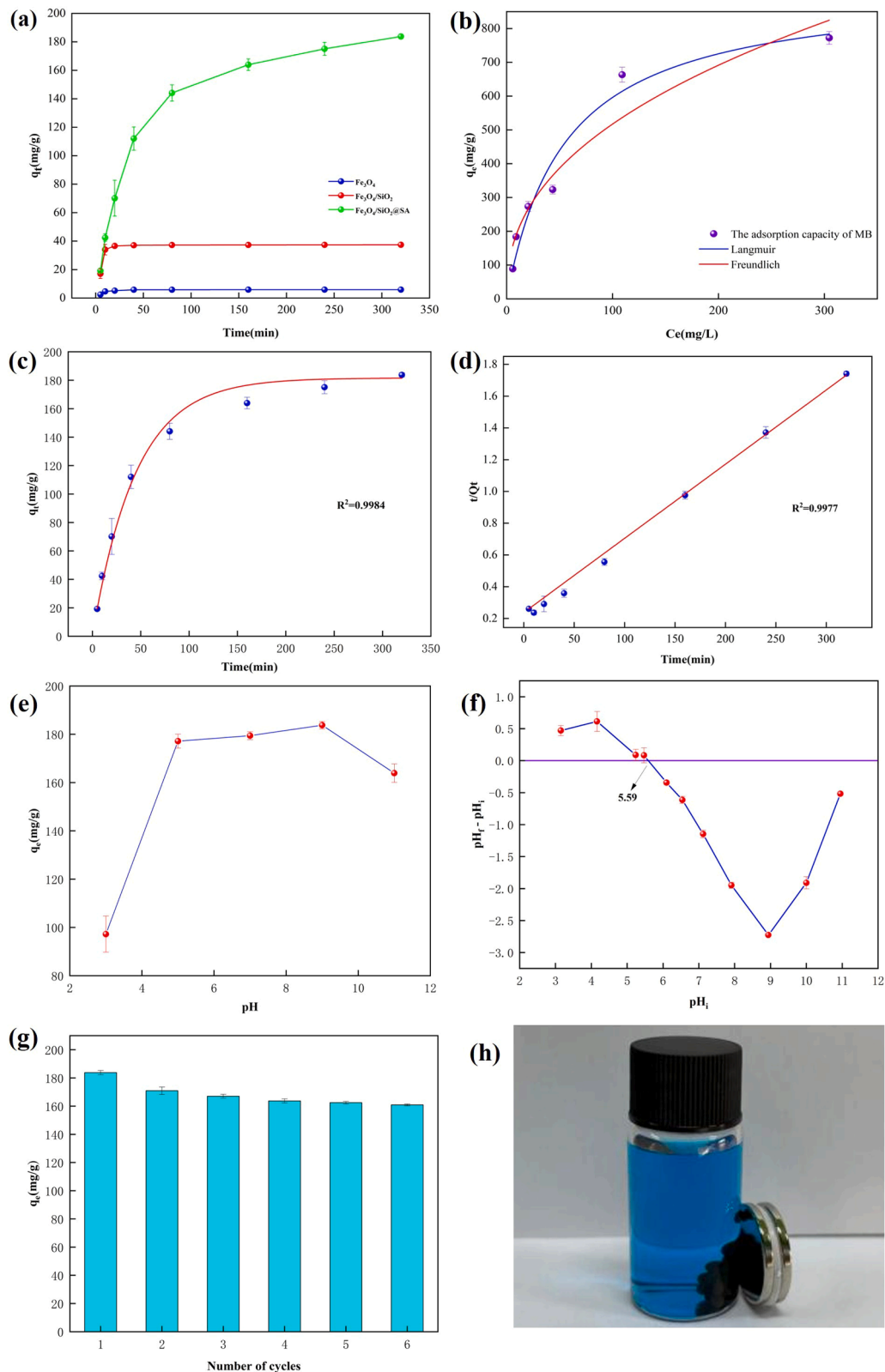


Fig. 5. (a) Adsorption kinetics of MB on Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ (25 °C, pH 9, 0.5 g/L adsorbent dosage, 100 mg/L initial MB concentration); (b) Non-linear adsorption isotherms of MB on $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ (25 °C, pH 9, 0.5 g/L adsorbent dosage, 320 min reaction time); (c) Pseudo-first-order kinetic and (d) Pseudo-second-order kinetic of MB on $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ (25 °C, pH 9, 0.5 g/L adsorbent dosage, 100 mg/L initial MB concentration); (e) Influence of pH of MB on $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ (25 °C, 0.5 g/L adsorbent dosage, 100 mg/L initial MB concentration, 320 min reaction time); (f) Determination of the point of zero charge (pH_{zpc}) on $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ (25 °C, 0.5 g/L adsorbent dosage, 100-mg/L initial MB concentration, 24 h reaction time); (g) Adsorption cycles performance of MB on $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ (25 °C, pH 9, 0.5 g/L adsorbent dosage, 100 mg/L initial MB concentration, 320 min reaction time) and (h) photograph of $\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{SA}$ attracted by a magnet.

Table 3

Langmuir and Freundlich parameters of MB adsorption on Fe₃O₄/SiO₂@SA. (25 °C, pH 9, 0.5 g/L adsorbent dosage, 320 min reaction time).

Models	Parameters			
Langmuir	$q_{\max}$ (mg g ⁻¹)	K_L (min ⁻¹)	R^2	RMSE
	925.77	0.01807	0.9646	46.82
Freundlich	1/n	K_F ((mg/g)·(L/mg) ^{1/n})	R^2	RMSE
	0.41	75.15	0.9318	65.02

Table 4

Adsorption kinetic parameters of MB adsorption on the Fe₃O₄/SiO₂@SA. (25 °C, pH 9, 0.5 g/L adsorbent dosage, 100 mg/L initial MB concentration, 320 min reaction time).

Kinetic model	Parameters			
Pseudo-first-order model	q_e (mg g ⁻¹)	K_1 (min ⁻¹)	R^2	RMSE
	181.59	0.022	0.9984	1.857
Pseudo-second-order model	q_e (mg g ⁻¹)	k_2 (g (mg ⁻¹ min ⁻¹))	R^2	RMSE
	214.13	0.0001	0.9977	2.054

3.2.4. Evaluation of the point of zero charge (pH_{ZPC})

The pH_{ZPC} of Fe₃O₄/SiO₂@SA shown in Fig. 5f is determined to be 5.59. Under the conditions of pH > 5.59, the deprotonation of the -COOH and -OH surface functional group makes the surface negatively charged, thereby significantly enhancing the adsorption performance of the cationic dye MB through electrostatic attraction [34]. This conclusion is consistent with the kinetic analysis, indicating that physical adsorption played a dominant role, revealing the application potential of the material in complex water environments with varying pH conditions.

3.2.5. Reusability study

Additionally, the reusability of the Fe₃O₄/SiO₂@SA adsorbent is of great significance for practical applications. Therefore, adsorption-desorption cycling experiments were performed to evaluate the recycling performance of Fe₃O₄/SiO₂@SA, and the results are shown in Fig. 5g. Benefiting from the superparamagnetic property of Fe₃O₄/SiO₂@SA, the material exhibits excellent magnetic separation performance. After the adsorption test, Fe₃O₄/SiO₂@SA can be rapidly separated using a magnet (Fig. 5h) and regenerated with an aqueous NaCl solution as the eluent. With increasing adsorption-desorption cycles, the adsorption efficiency of Fe₃O₄/SiO₂@SA gradually decreased from 91.75% in the first cycle to 80.10% in the sixth cycle, and the adsorption capacity decreased from 183.50 to 161.58 mg/g, indicating good reusability and considerable potential for large-scale engineering applications.

3.2.6. Adsorption performance in real water

To further evaluate the application potential of Fe₃O₄/SiO₂@SA in a real water environment, after completing the adsorption performance study in the DI water system, MB adsorption experiments under actual water body conditions were further conducted. The water samples used were taken from the Big Almaty River, and MB was added to the real water samples. The initial MB concentration reached 100 mg/L, and the composite eventually achieved an MB removal efficiency of 81.1%. Compared with the DI water system, the adsorption efficiency slightly decreases, which may be attributed to the competitive adsorption effect of natural organic matter in the real water matrix. Meanwhile, inorganic ions in the water may also occupy some surface-active sites, thereby causing interference in the adsorption process. Nevertheless, the material exhibited strong resistance to ion competition, maintaining efficient adsorption performance even in the presence of coexisting ions, indicating its good environmental adaptability and application potential, which can provide an important reference for the real treatment of dye

wastewater. Thank you for your valuable suggestion. In response to this comment, additional MB adsorption experiments were carried out using real water samples collected from the Big Almaty River to evaluate the influence of coexisting ions and complex water matrices on the adsorption performance. The results showed that the material still maintained a relatively high MB removal efficiency under real water conditions, demonstrating good ion competition resistance and environmental adaptability. The corresponding experimental results and discussion have been added to the revised manuscript, which further strengthen the potential practical application value of the developed adsorbent.

3.3. Comparison of MB adsorption with various adsorbents

MB is a common dye discharged in the textile industry and is regarded as an important water pollutant. To effectively remove MB from water, researchers have dev studied various adsorbents. Table 5 compares the maximum adsorption capacity and optimal operating conditions of different adsorbents for MB. Among them, PVA/Alg/AC/Fe₃O₄ exhibited the highest MB adsorption capacity, which was 769.23 mg/g. In comparison, the MB adsorption capacity of Fe₃O₄/SiO₂@SA in this study reached 925.77 mg/g, exceeding that of all reference adsorbents [35].

3.4. Adsorption mechanism

From the results of adsorption experiments and the characterization results of before and after adsorption, the adsorption mechanism of Fe₃O₄/SiO₂@SA for MB removal can be systematically elucidated (Fig. 6). Research shows that the main MB adsorption is a complex adsorption involving both chemisorption and physisorption, with MB molecules forming a monolayer adsorption on the surface. The adsorption mechanism mainly involves electrostatic interaction, hydrogen bonding, and coordination interaction. Under relatively high pH conditions, the -COOH and -OH groups on the material surface gradually deprotonate to form -COO⁻ and -O⁻ active sites, which can generate strong electrostatic attraction toward positively charged MB molecules. Meanwhile, the hydroxyl and carboxyl groups on the adsorbent surface can also form hydrogen bonds with MB molecules. SiO₂ surface silanol (Si-OH) groups may also contribute to adsorption through hydrogen bonding interactions with MB molecules. In addition, the Fe-O active sites in Fe₃O₄ may undergo coordination interactions with nitrogen- or sulfur-containing groups in MB molecules, thereby further enhancing the adsorption stability and adsorption capacity of the material. Therefore, electrostatic interaction, hydrogen bonding, and coordination interaction collectively constitute the primary adsorption mechanisms of MB onto Fe₃O₄/SiO₂@SA.

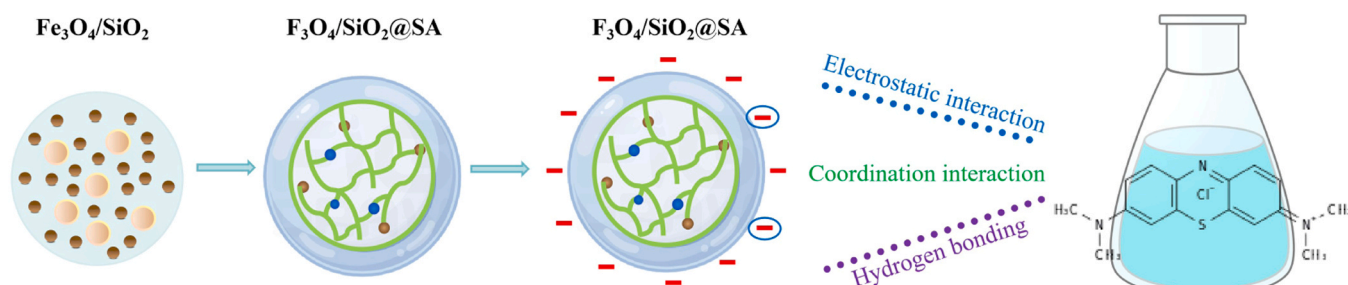
Fe₃O₄/SiO₂@SA combines the functional groups and structural advantages of each component, thereby achieving efficient adsorption of MB. SA is rich in -OH and -COO⁻ functional groups, which can interact with MB molecules through hydrogen bonding and electrostatic interactions. Meanwhile, SA forms a three-dimensional porous hydrogel network structure, providing excellent adsorption capability and enhancing its structural stability and reusability. Bio-based SiO₂ possesses abundant -Si-OH functional groups and a porous structure, which can effectively increase the specific surface area and act as a stable framework to promote the uniform

loading and dispersion of Fe₃O₄ nanoparticles, thereby inhibiting the agglomeration of Fe₃O₄ particles, increasing surface active sites and promoting the diffusion of pollutants. In addition, Fe₃O₄ nanoparticles not only endow the material with excellent magnetic separation performance but also further enhance the adsorption performance through Fe-O active sites. Therefore, the components of Fe₃O₄/SiO₂@SA interact through structural support and multiple interfacial interactions, collectively contributing to the efficient adsorption performance toward MB.

Table 5

Comparative MB adsorption over various adsorbents.

Adsorbent	Pollutant	$q_{\max}$ (mg/g)	Optimal operating conditions					Ref.
			T (°C)	pH	Adsorbent dosage (g/L)	Contact time (min)	MB concentration (mg/L)	
$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$	MB	24	25	6	2	120	10–150	[36]
$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{MOFs}$	MB	58.67	25	7	8	120	20–150	[4]
Magnetic-Biochar/Alginate (MBA) Bead	MB	69.76	25	6	2	150	50–150	[37]
Sodium alginate/silica hybrid	MB	178.6	45	6	0.5	160	50–800	[38]
ALG-Op@ Fe_3O_4	MB	188.7	25	6	3	120	10–300	[39]
$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{MgAl-Cl-LDH}$	MB	389.11	25	7	3	240	50–700	[40]
$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{MBH-CR}$	MB	408.15	25	6	0.5	350	100–250	[31]
SA- SiO_2 -PAMPS	MB	564.97	45	9	1	240	100–1200	[19]
$\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$	MB	660.38	25	11	0.25	200	5–200	[41]
PVA/Alg/AC/ Fe_3O_4	MB	769.23	45	6	1	420	5–800	[42]
$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$	MB	925.77	25	9	0.5	320	50–700	Present study

Fig. 6. Proposed adsorption mechanism of MB onto $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$.

4. Future perspectives

Although the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ exhibits excellent adsorption performance for MB, its practical application potential still needs further research. In this study, when the concentration of MB reached 400 mg/L, the material began to show a softening phenomenon and further increases to 700 mg/L, the phenomenon of material softening becomes more pronounced. In addition, under the condition that the NaCl concentration reached 0.1 M, the phenomenon of material softening was also observed. This indicates that the structural stability of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ still has certain limitations in high-concentration dye and high-salinity environments.

Meanwhile, in the real water, the adsorption process is not only affected by factors such as the initial pollutant concentration, pH, but also easily interfered with by complex components such as high salinity, coexisting ions and natural organic pollutants, thereby weakening the multi-mechanism synergy, reducing the selectivity and competitive adsorption capacity, and further affecting its long-term operational stability.

Therefore, further research needs to enhance the mechanical strength, structural stability and salinity resistance to meet the practical application requirements of complex water systems. At the same time, expand its application in the removal of other organic dyes, antibiotics and heavy metal ions, which provides an important theoretical basis and practical foundation for the large-scale application of bio-based Magnetic adsorbents in the field of water treatment.

5. Conclusions

In the current study, an innovative and highly efficient bio-based magnetic composite bead ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$) was successfully synthesized, and its adsorption mechanism was investigated. Under the optimized adsorption conditions (25 °C, pH 9, 100-mg/L initial MB concentration, 20-mL solution volume, and 10 mg adsorbent dosage),

the MB removal rate of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ reached 91.75%, and the adsorption capacity was 183.77 mg/g, significantly superior to Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{SiO}_2$ powders. In addition, the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ can be rapidly and conveniently recovered through magnetic separation in the solution. The removal efficiency remained at 80.1% after six adsorption-desorption cycles, and the removal rate reached 81.1% in real river water, demonstrating excellent reusability and effectively reducing the operating costs in practical applications.

The adsorption mechanism is mainly driven by the combined effects of electrostatic interaction, hydrogen bonding interaction and coordination complexation. The -OH and -COO⁻ groups in sodium alginate, the porous structure and dispersion effect of SiO_2 , as well as the Fe-O active sites in Fe_3O_4 , collectively contribute to multi-interface interactions, thereby enhancing the adsorption performance.

However, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ still shows certain limitations under high dye concentration and high-salinity conditions, where softening was observed. Moreover, coexisting ions and natural organic matter in real water systems may interfere with the adsorption process and affect long-term stability. Therefore, future work should focus on improving the structural stability and salinity resistance, as well as expanding its application toward the removal of other emerging pollutants.

In summary, the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ composite beads possess a three-dimensional network structure, abundant active binding sites, outstanding adsorption performance, convenient magnetic separation capability, and excellent reusability, making them a new type of adsorbent with dual advantages of “highly efficient and easy regeneration.” The research offers fresh perspectives on the development of high-performance bio-based magnetic adsorbents. It provides a robust experimental basis for the practical application of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SA}$ in treating dye wastewater, demonstrating its broad potential for large-scale MB wastewater treatment.

CRediT authorship contribution statement

Seitkhan Azat: Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition. **Jia Li:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mohd Ridhwan Adam:** Writing – review & editing, Supervision, Resources, Methodology. **Kydyr Askaruly:** Writing – review & editing, Validation. **Alzhan Baimenov:** Writing – review & editing, Supervision, Resources, Methodology. **Zhexenbek Toktarbay:** Writing – review & editing, Supervision, Resources, Project administration. **Jechean Lee:** Writing – review & editing, Validation, Supervision, Methodology.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used ChatGPT in order to improve language. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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