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Magnetically recyclable Fe₃O₄/Bi₂S₃ microspheres for effective removal of Congo red dye by simultaneous adsorption and photocatalytic regeneration



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ABSTRACT

Novel magnetic bayberry-like Fe₃O₄/Bi₂S₃ microspheres (Fe₃O₄/Bi₂S₃ MSs) combining highly effective adsorption and photocatalytic regeneration were prepared by a facile hydrothermal method. The resultant Fe₃O₄/Bi₂S₃ MSs were characterized by XRD, SEM, EDS, VSM, BET and DRS. Fe₃O₄/Bi₂S₃ MSs possessed a relative large surface area of 36.0 m² g⁻¹ and narrow pore size distribution around 4.72 nm. The equilibrium and kinetics of adsorption process followed the Langmuir isotherm model and pseudo-second-order kinetic model, respectively. Maximum adsorption capacity of CR as 92.24 mg g⁻¹ was achieved on Fe₃O₄/Bi₂S₃ MSs, while only 66.28 mg g⁻¹ was found on Bi₂S₃ MSs. High saturation magnetization, low coercivity and remnant magnetization values of Fe₃O₄/Bi₂S₃ MSs indicated that easy separation and fast re-dispersion in aqueous solution can be realized. What's more important, Fe₃O₄/Bi₂S₃ MSs with a stronger absorption in the visible light region can be regenerated by photocatalysis under simulated solar light irradiation. Fe₃O₄/Bi₂S₃ MSs also showed excellent stability and reusability for continuous removal of Congo red dye by synergistic adsorption and photocatalytic regeneration. As a result, Fe₃O₄/Bi₂S₃ MSs provided effective and conveniently recyclable materials for environmental remediation by means of providing the facile preparation, easy magnetic separation, high adsorption, and simple regeneration.

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1. Introduction

According to the Colour Index, over 10,000 types of dyes are being manufactured, and annual worldwide dye production is more than 700,000 tons. It is estimated that about 10% of dyes used in industry are finally discharged into the aqueous environment, which is quite harmful to the human health and aquatic ecosystem due to their high carcinogenicity and toxicity [1]. For effective removal of those dyes from industrial wastewater, various techniques, including adsorption [2,3], flocculation-coagulation [4], ozonation [5], sonocatalysis [6], and photocatalysis [7–9], have been developed recently. Among those approaches, synergistic method of adsorption and photocatalysis has been shown to be an effective method to treat containing-dye wastewater [8–13].

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As a direct band gap material with a gap energy (E_g) of 1.3 eV, bismuth sulfide (Bi₂S₃) has drawn intensive attention for its potential applications in photocatalysis [14–16], electrochemical applications [17–19], photodetector [20,21], environmental remediation [22–24], and solar energy conversion [25,26]. Recently, many Bi₂S₃-based nanocomposites, such as SiO₂/Bi₂S₃ [27], BiVO₄/Bi₂S₃ [14], Bi₂S₃/In₂S₃ [28], Bi₂S₃-BiOCl [29], CuS/Bi₂S₃ [30], Bi₂S₃/Bi₂SiO₅ [31], Bi₂S₃/g-C₃N₄ [22], and Bi₂S₃/Bi₂WO₆ [16], have been successfully fabricated by different techniques, and their novel and unique adsorption and photocatalytic properties have been extensively explored. Those studies have demonstrated that Bi₂S₃-based nanocomposites possess excellent photocatalytic performance for eliminating various toxic organic pollutants [22,23,27,28]. However, because of their small sizes, easy recovery and continuous reusability of Bi₂S₃-based nanocomposites are still a challenge in practical treatment system.

The separation and recovery of nanomaterials from solution with the use of magnetic fields is more selective, efficient and faster than centrifugation or filtration [32]. Magnetically recyclable

materials has become an active and important field of corresponding researches [33–35]. Some magnetic chemicals have been used as the magnetic carriers, such as Fe_3O_4 [32,36–38], $\gamma\text{-Fe}_2\text{O}_3$ [9,35] and MFe_2O_4 ($\text{M} = \text{Ni}, \text{Co}, \text{Zn}, \text{Cu}$) [13,39], to prepare all kinds of magnetic nanocomposites. Among them, Fe_3O_4 nanoparticles with good magnetic response can accomplish the simple magnetic separation and recovery of suspended nanocomposites using an external magnet [37,40,41]. In addition, the excellent adsorption ability of Fe_3O_4

3. Results and discussion

3.1. Characterization of materials

3.1.1. XRD analysis and UV-vis diffuse reflectance spectra

Fig. 1a represents XRD patterns of pure Fe_3O_4 , Bi_2S_3 MSs and $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs. It can be easily found that the diffraction peaks of pure Fe_3O_4 at $2\theta = 30.32^\circ$, 35.64° , 43.36° , 53.66° , 57.26° and 62.87° match the reflections of (220), (311), (400), (422), (511) and (440), respectively, indexed to the cubic spinel structure of Fe_3O_4 (JCPDS 56-3107) (Fig. 1a) [44]. All of the diffraction peaks of Bi_2S_3 MSs are in good accordance with the standard card of orthorhombic Bi_2S_3 (JCPDS 75-1306) [17]. The pattern of $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs exhibit a coexistence of the Fe_3O_4 and Bi_2S_3 , indicating the formation of the nanocomposites. No additional phases are evident found from the XRD patterns of all samples. The crystalline sizes of Fe_3O_4 and Bi_2S_3 , determined by the Debye-Scherrer equation [40], were found to be 9 and 4 nm, respectively. Yavuz's research showed that 8–12 nm-size represents the optimal size for magnetic separations [32], which is further demonstrated below by VSM studies.

Fig. 1b displays the UV-vis diffuse reflectance spectra (DRS) of Fe_3O_4 , Bi_2S_3 MSs and $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs. It is worth noting that Bi_2S_3 MSs have strong absorption over the whole visible light region [14,29]. The band gap of pure Bi_2S_3 is about 1.3 eV [22]. Pure Fe_3O_4 has photo-absorption not only in UV light range, but also in visible light range. However, light absorption of Fe_3O_4 weakens with increasing wavelength in the range of visible light. The whole light absorption ability of the $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs increased obviously with the introduction of Bi_2S_3 , which should be attributed to the small band gap and large absorption coefficient of Bi_2S_3 [49]. Compared with the magnetic photocatalysts reported in literatures [29,43,44], $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs have strong absorption in the UV-visible-light region from 200 to 800 nm, implying it possible to regenerate the materials by photocatalysis under simulated solar light irradiation after $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs have adsorbed targeted pollutants.

3.1.2. Morphology and microstructure

The surface morphology, microstructure and sizes of Bi_2S_3 MSs and $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs were determined by SEM. Fig. 2a shows a low-magnification SEM image of Bi_2S_3 MSs by hydrothermal method using thiocarbamide as sulfur source. It reveals that Bi_2S_3 MSs consisted of bayberry-like microspheres with diameters in

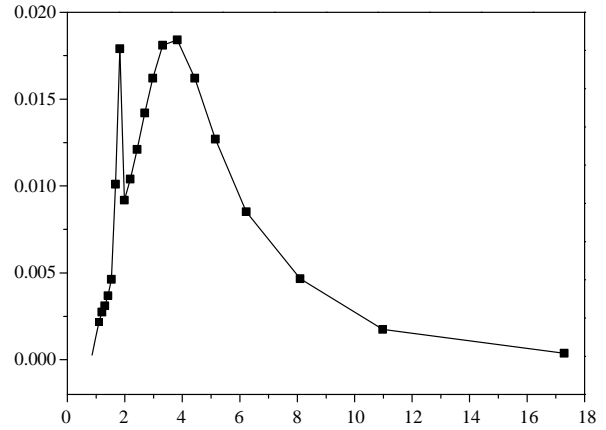
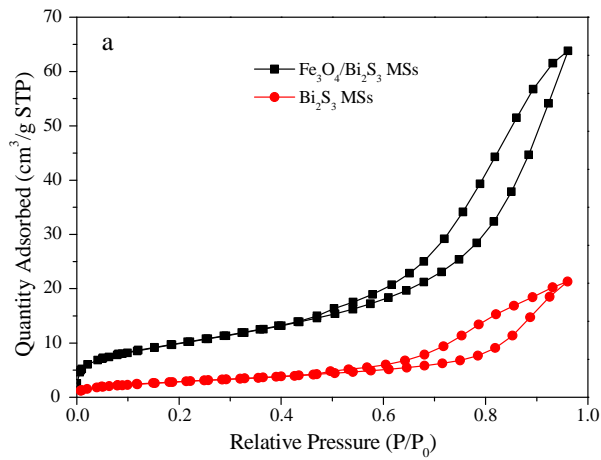
the range of 1.3–4.5 μm . The SEM image of Bi_2S_3 MSs shows that they were constructed with nanorods around the center of the microspheres. The hierarchical bayberry-like structure of ferroferric oxide (Fe_3O_4) on Bi_2S_3 MSs with an average diameter of 1.3–4.5 μm was obtained (Fig. 2c), and the Fe_3O_4 nanorods on Bi_2S_3 MSs and Fe_3O_4 nanoparticles on $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs were more unevenly distributed. The presence of Fe_3O_4 on Bi_2S_3 crystal to some extent is beneficial to the adsorption of Fe_3O_4 on Bi_2S_3 MSs. The dispersive spectra of $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs were analyzed by EDS, showing the presence of Fe, O, and S, which are the main elements of the nanorods. However, the microsphere structure of $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs was not destroyed.

3.1.3. Vibrating sample magnetometry

The magnetic properties of $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs were measured by VSM. The magnetic hysteresis loop of $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs was shown in Fig. 3. The coercive field (H_c) was 66.50 Oe, which is much smaller than the literature value of Fe_3O_4 (100–200 Oe) [50]. The $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs showed a typical superparamagnetic behavior of bismuth ferrite (BiFeO_3) [51]. The saturation magnetization (M_s) reported in this work is 0.016 emu/g, which is much smaller than the reported M_s of $\text{Fe}_3\text{O}_4/\text{ZnO}$ (0.025 emu/g) [52]. The small M_s indicated that the Fe_3O_4 on Bi_2S_3 MSs was not completely covered by Fe_3O_4 nanorods.

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3.2. Adsorption isotherms

Adsorption isotherm is one of important data to explain the adsorption mechanism of contaminant on novel nanocomposite [27]. In addition, the adsorption of dye on nanocomposites is an important prerequisite for a synergistic adsorption-photocatalytic degradation process [8]. Therefore, Langmuir and Freundlich isotherm models were used to analyze the equilibrium adsorption

characteristics for CR dye on Bi₂S₃ MSs and Fe₃O₄/Bi₂S₃ MSs. Langmuir and Freundlich equations is represented for Eqs. (3) and (4), respectively [3].

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (4)$$

where c_e (mg L^{-1}) is equilibrium concentration of CR in solution, q_e (mg g^{-1}) is the adsorption capacity of CR adsorbed at equilibrium, q_m (mg g^{-1}) is maximum amounts of CR adsorbed per unit mass of adsorbent required for monolayer coverage of the surface, b (L mg^{-1}) is a constant related to the heat of adsorption. The slope and intercept of linear plots of c_e/q_e against c_e yield the values of $1/q_m$ and $1/bq_m$ for Eq. (3). K_F ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$) is related to the adsorption capacity of the adsorbent and $1/n$ is another constant related to the surface heterogeneity. The slope and intercept of linear plots of $\ln q_e$ against $\ln c_e$ yield the values of $1/n$ and $\ln K_F$ for Eq. (4).

Fig. 5 shows the isotherms of CR adsorption on Bi_2S_3 MSs and $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs, while their maximum adsorption capacities (q_m) and some theoretical parameters (q_m , b , K_F , n , and R^2) are summarized in Table 1. It was notable that an increase in temperature resulted in a corresponding increase in adsorption capacity of CR on both Bi_2S_3 MSs and $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs, which showed that the adsorptions of CR onto Bi_2S_3 MSs and $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs are endothermic process. In general, the Langmuir isotherm model describes monolayer adsorption process while the Freundlich isotherm model describes the adsorption on heterogeneous surfaces associated with several adsorbent–adsorbate interactions [27]. For the CR adsorption on Bi_2S_3 MSs, the R^2 values ($R^2 > 0.968$) from the Freundlich equation (Eq. (4)) were all higher than those ($R^2 < 0.890$) from the Langmuir model (Eq. (3)), which is responsible for the observed multilayer adsorption. However, for the CR adsorption on $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs, the Langmuir equation represented the adsorption process and all R^2 values were higher than 0.972, indicating that monolayer coverage of the dye adsorbed on the surface of $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs. With the introduction of Fe_3O_4 , magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs have bayberry-like structures, rough and porous surfaces and exposed more adsorption sites. As a result, the adsorption of CR on $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs presents monolayer adsorption process. This result is in good agreement with the observations in SEM and BET analysis of Bi_2S_3 MSs and $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs.

Table 2 compares the adsorption capacity of the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs with the other reported inorganic adsorbents. The maximum adsorption capacity of the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs towards CR is 92.24 mg g^{-1} , which is higher than those of adsorbents reported earlier, such as $\text{Fe}_{3-x}\text{La}_x\text{O}_4$ ferrite [53], $\text{Zn-Fe}_2\text{O}_4$ [54], Ca-bentonite [55], chitosan coated magnetic Fe_3O_4 particle [56], activated carbon [57]. It is worth mentioning that the maximum adsorption capacity (92.24 mg g^{-1}) of CR on $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs was almost 12.76 times higher than that of the reported activated carbon (6.7 mg g^{-1}) [57]. Therefore, $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs are suitable and promising for CR removal from aqueous solutions since it has a relatively high adsorption capacity and easy magnetic separation.

3.3. Effect of initial CR concentration on adsorption

Fig. 6 presents the time-dependent adsorption performance of the Bi_2S_3 MSs and magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs towards the removal of CR at different initial dye concentrations in aqueous solutions.

Table 1
Adsorption isotherm constants for CR adsorption onto Bi_2S_3 MSs and magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs.

Adsorbent	T ($^{\circ}\text{C}$)	$q_{e,\text{exp}}$ (mg g^{-1})	Langmuir isotherm constants			Freundlich isotherm constants		
			q_m (mg g^{-1})	b	R^2	K_F ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$)	n	R^2
Bi_2S_3 MSs	25	37.44	33.39	0.250	0.830	15.75	6.27	0.982
	35	48.48	41.36	0.736	0.813	22.81	7.69	0.972
	45	54.62	46.86	0.826	0.861	24.45	6.98	0.968
	55	66.28	56.27	0.912	0.890	26.91	6.08	0.980
$\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs	25	53.33	55.25	0.376	0.981	23.63	5.51	0.963
	35	72.23	70.97	0.629	0.972	28.50	4.93	0.968
	45	77.24	78.064	1.073	0.973	32.45	5.07	0.962
	55	92.24	90.580	1.302	0.987	35.72	4.79	0.958

Table 2
The q_m values for the adsorption of CR on different adsorbents.

Adsorbents	q_m (mg g^{-1})	Ref.
$\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs	92.24	This study
Chitosan coated magnetic Fe_3O_4 particle	42.62–56.66	[56]
$\text{Fe}_{3-x}\text{La}_x\text{O}_4$ ferrite	37.4–79.1	[53]
Zn- Fe_2O_4	16.58	[54]
Ca-bentonite	23.25–85.29	[55]
Activated carbon	6.7	[57]

For Bi_2S_3 MSs, as the initial concentration increased from 5 mg L^{-1} to 30 mg L^{-1} , the removal rate of CR decreased from 99% to 60% (Fig. 6a). However, the percentage of CR adsorption on $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs reached up to 85% within 90 min for all the studied concentrations (Fig. 6b). Compared with CR adsorption process on Bi_2S_3 MSs, the fast adsorption over the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs was clearly observed for all the studied concentrations. This higher efficiency and faster rate of CR adsorption on $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs can be ascribed to abundant unoccupied active sites on the adsorbent's surface as well as the porous hierarchical structure of the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs [3]. On the basis of the above results, the observed high adsorption capacity and the short time needed to achieve adsorption equilibrium confirm the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs would be an effective adsorbent for CR removal.

3.4. Adsorption kinetics

Adsorption kinetics is one of the most important characters which govern the solute uptake rate and represent adsorption efficiency of adsorbent for design operation and optimization. To investigate adsorption kinetics of CR on Bi_2S_3 MSs and magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs, three different kinetic models, i.e. Lagergren-first-order model, pseudo-second-order kinetic model and intraparticle diffusion model were used to fit the adsorption kinetic data.

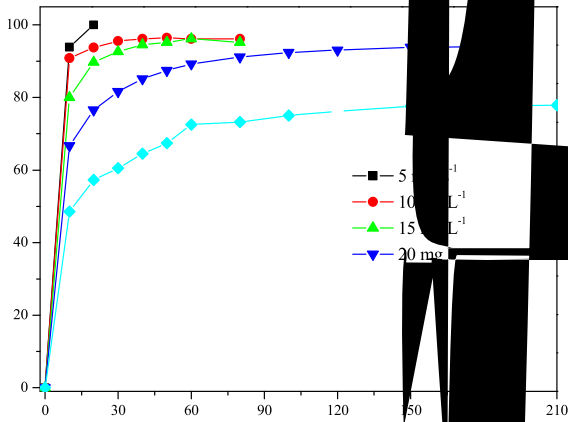
The Lagergren-first-order kinetic, pseudo-second-order kinetic model and intraparticle diffusion model can be given by Eqs. (5)–(7) [55].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

$$q_t = k_{id} t^{1/2} + c \quad (7)$$

where q_e and q_t (mg g^{-1}) are the amounts of CR adsorbed at equilibrium and at time t (min), respectively; k_1 is the rate constant of Lagergren-first-order kinetic model (min^{-1}). Values of k_1 can be calculated from the plots of $\log(q_e - q_t)$ versus t for Eq.(5). k_2 is the rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) of pseudo-second-order kinetic model for adsorption. The slope and intercept of the linear plots of t/q_t against



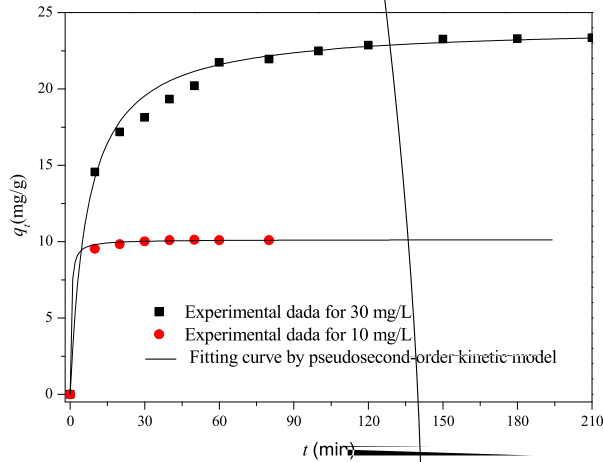
t yield the values of $1/q_e$ and $1/k_2q_e^2$ for Eq. (6). c (mg g^{-1}) is the intercept and k_{id} is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$), which can be calculated from the slope of the linear plots of q_t versus $t^{1/2}$.

Different kinetic parameters of CR adsorption onto Bi_2S_3 MSs and $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs for different CR initial concentrations were shown in Table 3. The relatively low correlation coefficient (R^2) and the large difference between the calculated value of adsorption capacity ($q_{e,cal}$) and the experimental value ($q_{e,exp}$) indicated that the adsorption kinetics of CR on the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs does not obey the pseudo-first-order kinetic model. However, all the experimental data showed better compliance with pseudo-second-order kinetic model in terms of higher correlation coefficient values ($R^2 > 0.998$) and closer values between $q_{e,cal}$ and $q_{e,exp}$ (Table 3). It could be found that pseudo-second-order kinetic model was more valid to describe the adsorption behavior of CR onto $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs, indicating that the adsorption of CR on both Bi_2S_3 MSs and magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs are mainly controlled by chemisorption. Fig. 7 showed the regression plots of pseudo-second-order kinetic model about CR adsorption on both Bi_2S_3 MSs and magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs. It was likely that the adsorption behavior may involve valence forces by sharing of electrons between anions and bio-adsorbent.

3.5. Photocatalytically recycling under simulated solar light

In addition to efficiency, the lifetime of water-treatment materials is also very important for practical applications. The reuse ability can be realized if $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs can self-clean CR dye molecules absorbed on it. Therefore, the reutility and stability of the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs were examined through the repeated experiments based on the two different experimental procedures: (1) only adsorption in dark and (2) simultaneous adsorption and photocatalytic regeneration in one step for cycling under simulated solar light irradiation. Fig. 8 shows the successive

cycles of two different experimental procedures. The adsorption capacities for $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs decreased noticeably during the repeated adsorption operations. An obvious decrease from 91.60% to 40.3% in the removal efficiency was observed when the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs were reused as adsorbent for the first cycle (Fig. 8 curve a). After the successive fifth cycles, the removal efficiency was only 25.3% by only adsorption in dark. The decreased efficiency after five cycles may be due to the decreased surface active sites. Interestingly, when the adsorption and photocatalytic regeneration were simultaneously performed during the repeated experiments under simulated solar light irradiation, the recyclability of the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs can be improved efficiently compared with the reuse of Bi_2S_3 MSs. As shown in Fig. 8 curve b, the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs exhibited good stability and maintained high removal efficiency in successive five cycles under simulated solar light irradiation. What's more, the magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs did not show a clear decrease in photodegradation efficiency after $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs were used for fifth time recycles for the decolorization of CR under simulated light irradiation. The enhanced decolorization of CR solution by $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs resulted from two main reasons. Firstly, $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs can concentrate the targeted CR dye on the surface of water-treatment materials from the diluted water to promote the CR transfer process. Secondly, CR adsorbed on the surface of $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs can be photocatalytically oxidized and the adsorbent can be regenerated and reused in further cycles [27]. Several studies have shown that CR molecules can be photodecolorized by appropriated photocatalysts under light irradiation [9,58]. Bi_2S_3 with a typical narrow band gap can be used to photodegrade organic pollutant since $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs have a stronger absorption in the visible light area. In addition, the fact that adsorption and photocatalytic regeneration of organic compounds occur continuously in the presence of $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs avoids two independent processes and reduces the actual processing cost. As a result, magnetically recyclable $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs could be regenerated via the

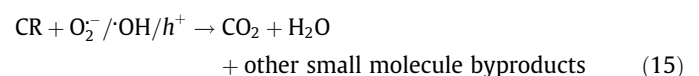
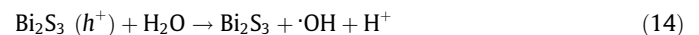
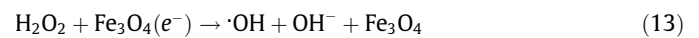
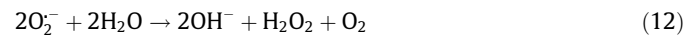
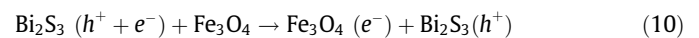
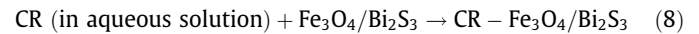


economical, green photocatalytic treatment and maintain higher processing removal efficiency of CR dye by adsorption and photocatalytic regeneration.

3.6. The possible mechanism of dye removal by $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs

As previous studies mentioned [29,46], the photodegradation of dye pollutants on photocatalyst is mainly driven by a series of reactive species including active holes (h^+), hydroxyl radicals ($\cdot\text{OH}$), and superoxide radicals ($\text{O}_2^{\cdot-}$) generated. Based on the above experimental results and corresponding Refs. [44,46], a possible mechanism of successful CR removal by $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs under simulated solar light irradiation was proposed as follows (Fig. 9). Firstly, CR molecules in aqueous solution were adsorbed fast onto $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs (Eq. (8)) due to the high relative large surface areas and mesoporous channels of magnetic $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$. At the same time, electrons (e^-) in the valence band (VB) of Bi_2S_3 in $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs can be photoexcited to its conduction band (CB) under simulated light irradiation, causing the photoproducted holes (h^+) in the VB of Bi_2S_3 simultaneously (Eq. (9)). The CB level of Fe_3O_4 (1 V vs. NHE) is much lower than that of Bi_2S_3 (0.12 V vs. NHE) [22,46], so the photoproducted $\text{Bi}_2\text{S}_3(e^-)$ may quickly migrate from conduction band of Bi_2S_3 MSs into that of the Fe_3O_4 and the

chance of e^-/h^+ recombination is greatly reduced (Eq. (10)). Following, the migrated e^- reacted with the oxygen molecule (O_2) that dissolved in aqueous solution to yield $\text{O}_2^{\cdot-}$ (Eq. (11)) [29], which further react with H_2O and to produce H_2O_2 and $\cdot\text{OH}$ (Eqs. (12) and (13)). The photoinduced holes (h^+) at the VB top of Bi_2S_3 with potential of about 2.07 eV [31], which is more positive than the standard reduction potential of OH^-/OH (1.99 eV), can react with H_2O to produce $\cdot\text{OH}$ radicals (Eq. (14)). At last, all the produced active species including $\cdot\text{OH}$, e^-/h^+ and $\text{O}_2^{\cdot-}$ can attacked the N=N bonds of CR molecules adsorbed on $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs and further oxidize the broken CR molecules into CO_2 , H_2O and other small molecule byproducts (Eq. (15)) [29].



4. Conclusions

In summary, magnetically recyclable $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs combining the highly effective adsorption and green photocatalytic regeneration were prepared by a facile hydrothermal method. The as-obtained $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs possessed a relative high surface area, low coercivity value and remanent magnetization value. The $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{S}_3$ MSs can be easily and economically separated, regenerated and re-dispersed in aqueous solution, which is desirable

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