Soft-Template Solvent Thermal Method Synthesis of Magnetic Mesoporous Carbon-Silica Composite For Adsorption of Methyl Orange From Aqueous Solution

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Abstract

A facile soft-template solvent thermal strategy was developed to prepare mesoporous carbon-silica composite (MMCS) by using furfuryl alcohol(FA) as carbon precursor, Pluronic copolymer P123 as template, hydrated iron nitrate as iron source, and tetraethylorthosilicate as silicon source and it was applied for the removal of methyl orange (MO). The as-synthesized MMCS with abundance of hydrophilic groups possessed a high specific surface area, large pore volume, and good magnetic response. With the increase amount of FA, the surface area and functional groups increased, promoting the adsorption effect. The adsorption isotherm, kinetic and thermodynamics were all studied in detail. Additionally, it was shown that the adsorption process could not be interfered by the co-existence of PO_4^{3-} , NO_3^- , CO_3^{2-} , SO_4^{2-} and real water matrix. Thus, the MMCS prepared in this study could be utilized as an alternative adsorbent for the removal of methyl orange from aqueous solution.

Introduction

It is no denying that synthetic dyes are ubiquitous in the wastewater discharged from textile, leather, paper, printing and other related industries, which could pose a severe threat to the environment and human beings' health even at low concentrations (Zhang et al., 2020). In view of the stability and recalcitrance to degradation of dyes, adsorption attracts considerable attention in dye-containing wastewater treatment because of its easy operation, high efficiency, non-secondary pollution, regeneration and recycle of adsorbents (Wang et al., 2015; Saroyan et al., 2017; Cao et al., 2019).

Carbon-based materials, with their particular properties such as controlled pore size distribution, high surface area and manipulatable surface chemistry, have been acknowledged as a promising class of adsorbents which are capable of adsorbing dyes from wastewater (Schneider et al., 2019). In the family of carbon-based materials, activated carbon (AC) is one of the most concerned adsorbents, which has been utilized to remove dyes conventionally. Nevertheless, AC exhibits some disadvantageous limitations like high cost, poor recovery, difficult regeneration and microporous nature, which has restricted its application in the adsorption of large dye molecules (Rashid et al., 2016). Therefore, a great deal of attention have been received on mesoporous carbon (MC) due to its advantages of uniform and tunable mesopores, high specific surface area, high pore volume, good chemical and thermal stability, as well as variety of modification (Wu et al., 2015; Jiang et al., 2019).

Even though MC has been proven to be a promising adsorbent, there is unavoidably problem in the practical treatment of dye-containing wastewater due to its difficulty to separate from aqueous phase (Zhai et al., 2009). It is undeniable that the separation of the spent adsorbent from treated solution after adsorption is an important step, which is conventionally carried out by centrifugation or filtration (Yan et al., 2014). However, these conventional separation techniques are too time-consuming and costly to be viable for a large-scale application. As an alternative, magnetic separation has been proved to be a superior strategy owing to its high accuracy and simplicity of operation by applying an external magnetic field (Guo et al., 2014).

Therefore, in order to achieve a more efficient wastewater treatment system, the preparation of magnetic mesoporous carbon materials (MMC) through the combination of magnetic nanoparticles and MC is of a great interest to the development of novel functional materials with excellent adsorption capability and convenient separation. The effective combination of magnetic nanoparticles and MC can provide a strong magnetic response resulting in easy separation and recovery in liquid-solid processes. Additionally, the introduction of magnetic particles into MC will provide the possibility of creating specific binding sites and reducing the mass transfer resistance, which can enhance the adsorption performance and shorten the adsorption equilibrium time of the adsorbent (Phenrat et al., 2009). Moreover, immobilization of the magnetic nanoparticles with carbon matrix can prevent the aggregation of magnetic nanoparticles and improve their stability to avoid oxidation or erosion (Liu et al., 2019).

Up to date, considerable efforts have been put forth to explore advantageous methods to prepare MMC (Deng et al., 2011). For instance, Wu *et al.* synthesized a mesoporous magnetic iron oxide@carbon for arsenic removal by post-loading method through pre-synthesizing MC followed by impregnating with an iron precursor solution and converting the precursor into magnetic nanoparticles in situ (Wu et al., 2012). Tang *et al.* and Deng *et al.* prepared MMC for adsorption of rhodamine B by the same method, in which the iron precursors were replaced by a cobalt precursor and cobalt-iron precursor, respectively (Tang et al., 2014; Deng et al., 2017). Nejad *et al.* employed a nanocasting method to synthesize MMC through a consecutive-impregnation process, in which the precursors of carbon and metal sources were impregnated separately into the pre-synthesised hard template SBA-15 (Nejad et al., 2013). Another nanocasting method including a co-impregnation process where SBA-15 was impregnated with carbon source and metal source simultaneously was applied by Lui *et al.* and Wang *et al.* to prepare Fe/Ni doped MMC for dye adsorption (Liu et al., 2015; Wang et al., 2015). Nevertheless, an unavoidable problem was that most of the magnetic nanoparticles were readily to block the main pores of mesoporous materials or to expose surrounding media, resulting in the loss of magnetism and dispersibility. Meanwhile, most of these methods were either too costly or too time-consuming due to the presynthesis of the silica template and the additional impregnation steps. As a consequence, it is crucial to develop a facile strategy to eliminate the complex fabricating process, such as forming mesoporous carbonaceous matrix with simultaneously generating magnetic nanoparticles in situ in one pot. Yuso *et al.* synthesized MMC via a one-pot microwave-assisted self-assembly strategy which allowed the formation of mesoporous carbon and the growth of the particles at the same time (Yuso et al., 2016). Ma *et al.* reported a simple one-pot route to synthesize MMC using the biomass chitosan and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursors and NaCl as template agent (Ma et al., 2017). In particular, one-pot method combined with surfactant-assisted soft template can greatly simplify the synthesis of MMC and reduce the cost, which has been applied in the preparation of magnetic mesoporous carbon intensively (Zhang et al., 2016).

In this paper, MMC materials were successfully fabricated by a facile soft template one-pot method, where furfuryl alcohol (FA) was used as a carbon precursor, Pluronic copolymer P123 as a template agent and hydrated iron nitrate as an iron source. Furthermore, tetraethylorthosilicate (TEOS), which is rich in silicon hydroxyl and easy to form hydrogen bond with other molecule, was used in this work to facilitate

the formation of organic polymer networks. Although etching silica from the network of organic and inorganic phases can further increase the surface area of the material, the rigid framework of silica can ensure the mesoscopic structure of the material will not collapse when removing the template agent. Thus, the aim of this work is to prepare a novel magnetic mesoporous carbon-silica composite (MMCS) and to investigate the effect of the content of carbon precursor on the structure and performance of MMCS. At last, The as-synthesized MMCS were systematically evaluated by charactering with X-ray diffraction (XRD), transmission electron microscopy (TEM), specific surface area (BET), Fourier transform infrared (FTIR), energy dispersive spectroscopy (EDS) mapping, Zeta potential and vibrating sample magnetometry (VSM). Methyl orange (MO), as a typical cationic dye usually exists in dye wastewater, was selected to examine the adsorption capability of the obtained materials. To improve the adsorption performance of MO by MMCS, the effects of coexisting ions were intensively examined. Batch experiments were proceeded to reveal the adsorption mechanism towards MO by discussing the influence factors like pH, initial concentration, temperature, contact time, as well as calculating adsorption kinetics, isotherms and thermodynamics.

Experimental

2.1 Materials and standard solution

Furfural alcohol was purchased from Aladdin (Shanghai, China); Polyethylene oxide-polypropylene oxide-polyethylene oxide (P123) was purchased from Aldrich (Shanghai, China); hydrated iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and tetraethylorthosilicate (TEOS) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China); ethanol was purchased from Guangdong Guanghua Sci-tech Co., Ltd (Shantou, China); hydrochloric acid was purchased from Nanjing Chemical Reagent Co., Ltd (Nanjing, China); ammonia (25%~28% in water) was purchased from Shanghai Pilot Chemical Corporation (Shanghai, China); sodium hydroxide was purchased from Longxi Chemical Industry Co., Ltd (Lanzhou, China); MO was purchased from Shanghai Ruiyong Biotechnology Co., Ltd (Shanghai, China). All chemicals used in this paper were of analytical grade without further purification. MO standard solution (1 g L^{-1}) used in this paper was prepared by dissolving 1 g MO powder with 1 L ultrapure water.

2.2 Synthesis of magnetic mesoporous carbon

Magnetic mesoporous carbon materials were prepared via co-assembly of FA, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, P123 and tetraethylorthosilicate, followed by a carbonization treatment under inert gas. Typically, 1.0 g of P123 and 0.909 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 10 mL of ethanol solution with stirring until clarification, followed by mixing with 10 mL of ethanol solution contained a certain content of FA (0.25 g, 0.5 g and 1.0 g). After stirring for 30min, 3 mL of TEOS was dropped into the mixture and continually stirred for 3 h at room temperature. Afterwards, the mixture was transferred into a Teflon reactor and cooled to room temperature after heated in an oven at 383 K for 24 h. The obtained gel was dried in an oven at 333 K for 12 h and then calcinated at 1173 K for 6 h under the atmosphere of nitrogen. Finally, 0.3 g of the product

after carbonization was crushed and added into 50 mL of 20% NaOH with stirring for 8 h, followed by washed with deionized water to neutral, and then dried to obtain magnetic mesoporous carbon material.

2.3 Characterization

Wide-angle X-ray diffraction (XRD) patterns were collected on an X'TRA X-ray diffractometer (ARL, Switzerland). The morphology of magnetic mesoporous carbon were investigated by an S-3400N II transmission electron microscope (TEM) (Hitachi, Japan). N₂ adsorption/desorption isotherm was conducted on a V-Sorb 2800P specific surface area analyzer (Gold APP Instrument, China) to analyze the surface areas and pore nature. Infrared absorption spectra were achieved using the KBr pellets technique on a Thermo Nicolet 300 Fourier transform infrared spectrometer (Thermo Nicolet, USA) with a frequency range of 4000 – 400 cm⁻¹. Energy dispersive X-ray spectroscopy (EDS) images were taken with a Regulus 8230 scanning electron microscope (Hitachi, Japan). Zeta potential was determined by a 90 plus Zetasizer Nano (Brookhaven, America). The analysis of the magnetic properties was taken on a vibrating sample magnetometer (VSM) (Quantum, America).

2.4 Adsorption experiments

Batch equilibrium adsorption experiments were carried out in an ultrasonic bath to determine the MO adsorption characteristics of MMCS. In a typical procedure, 2 mg MMCS was dispersed in 10 mL MO solutions with desired pH value and concentrations. Then the mixture was soaked in the ultrasonic bath for desired time at the desired temperature. After the adsorption was completed, the adsorbent was magnetically separated from the solution by an external magnet. The concentration of the MO dyes was measured by using UV-Vis spectrophotometer at a wavelength of 470 nm. The adsorption capacity (Q) of MO was calculated according to following equation:

$$Q = (C_0 - C_e) \times V/m \text{ Eq. 1}$$

where Q is the adsorption capacity (mg g⁻¹) at equilibrium, C_0 and C_e are the initial concentration of MO (mg L⁻¹) before adsorption and the equilibrium concentration of MO (mg L⁻¹) after adsorption, V is the volume of MO solution (mL), and m is the mass of the adsorbent (mg).

In order to investigate the effect of pH, solution pH was varied over a wide range from 2 to 8 by adding NH₃·H₂O and HCl. To examine the kinetic characteristics, kinetic experiments were performed at 308 K by controlling the contact time from 5 to 100 min, respectively. To reveal the equilibrium adsorption characteristics, isothermal adsorption experiments were studied over a range of initial MO concentrations from 10 to 200 mg L⁻¹.

2.5 Desorption and regeneration study

In each cycle, 2 mg of S-doped MMCS was added to 10 mL 150 mg L⁻¹ MO solution at the pH of 4.5, and the mixture was sonicated for 80 minutes. Then, 10 mL different solvents including 0.1 mol L⁻¹ NaOH, 0.1 mol L⁻¹ HCl, methanol and ethanol were used to desorb MO. After desorption, the supernatant was

collected to detect the concentration of MO by using UV-Vis spectrophotometer. Recycled materials were washed to neutrality and reused in the next adsorption cycle.

The adsorption capacity of MO in each cycle was calculated by the following equation:

$$D = (m_d/m_0) \times 100\% \text{ Eq. 2}$$

where m_0 is the amount of MO absorbed on the adsorbent and m_d is the amount of CR desorbed in the solution.

Results And Discussion

3.1 Characterization of materials

3.1.1 XRD analysis

Wide-angle XRD analysis of MMCS was carried out to identify their crystallographic structure. As illustrated in Fig. 1, the diffraction peak at 2θ of about 1° is characteristic diffraction peak of mesoporous carbon (Zhang et al., 2018). It is clear from the spectrum that there are diffraction peaks centered at 2θ of about 22° , which is assigned to amorphous carbon, indicating the formation of carbon skeleton through calcination of the FA precursor (Chen et al., 2020). The peaks located at 2θ values of 30.2° , 35.5° , 42.6° and 55.6° are due to diffraction from (220), (311), (400), and (511) planes of Fe_3O_4 , demonstrating that Fe_3O_4 nanoparticles are successfully incorporated in the carbon matrix (Zhu et al., 2017). The peak at 44.6° can be indexed to 110 reflection attributed to $\alpha\text{-Fe}$ phase, which is in agreement with the reported values in the literature (Tang et al., 2016). As a consequence, the coexistence of Fe and Fe_3O_4 is found in the obtained MMCS materials, which may be explained by the reduction of ferric iron (Ma et al., 2017).

3.1.2 TEM images

TEM images were conducted to obtain surface morphology information of MMCS with different FA contents and the results were shown in Fig. 2. It can be seen that the produced MMCS materials with different FA contents exhibit amorphous morphology. Clearly, there are a lot of black spherical particles with different diameters distributing in the amorphous carbon walls of the three MMCS materials, which is in agreement with XRD results, demonstrating magnetic nanoparticles (*i.e.*, Fe or Fe_3O_4) have been successfully embedded into the carbon matrix. As shown in Fig. 2a, the black spherical particles about 400–500 nm in diameter are obviously a little bit large may due to the further growth of the particles with excessive iron content, which may penetrate the pore walls and block the main mesopore channels (Yuso et al., 2016). With the increasing of FA content, the nanocrystallization and distribution uniformity of the black particles increase (Fig. 2b, 2c).

3.1.3 BET analysis

The specific surface area, total pore volume and pore size distribution of three MMCS materials were determined by N₂ adsorption-desorption isotherm analysis. As listed in Table 1, the corresponding pore size of the MMCS materials cover a range of 8.64 to 6.77 nm, which is indicated the presence of mesopores structure according to the IUPAC classification (Chen et al., 2010). It can be observed that with the increase of FA content from 0.25 to 0.5 g, the specific surface area increases from 150.4 to 328.6 m² g⁻¹, and the pore volume increases from 0.36 to 0.62 cm³ g⁻¹, while the pore size decreases slightly, illustrating that the increase of FA content is conducive to the formation of well-developed pores after carbonization. When the FA content increased from 0.5 g to 1.0 g, there is no significantly difference in the textural properties of the three MMCS materials, which is mainly ascribed to the influence on the mesoporous structure tended to be stable with the further increasing of FA content.

Table 1
The parameters of porous structure of MMCS with different FA amounts.

FA amount (g)	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
0.25	150.4	0.36	8.64
0.5	328.6	0.62	7.32
1.0	317.7	0.56	6.77

3.1.4 FT-IR spectra

The FT-IR absorbance spectra of MMCS materials are exhibited in Fig. 3. It can be seen that there is a broad band at 3142 cm⁻¹, arising from vibrational stretching of the C-H groups. The peaks at 3412cm⁻¹, 1631 cm⁻¹ and 1092 cm⁻¹ are due to the stretching vibration of -OH, C = O and C-O, respectively, which leads to the hydrophilic nature of MMCS. Especially, the band at 470 cm⁻¹ is assigned to the Fe-O characteristic absorbance, further indicating that magnetic nanoparticles have been successfully embedded into the carbon matrix.

3.1.5 EDS analysis

The elemental composition of MMCS materials with the FA contents of 0.25, 0.5, and 1.0 g was determined by EDS analysis, respectively. As shown in Table 2, C, O, Si, and Fe elements are coexisting in the three MMCS materials, suggesting that Fe has been successfully incorporated into mesoporous carbon matrix. Besides, it can be seen that the content of carbon increases with the increasing of content of FA from 0.25 g to 0.5 g and then decreases with the further increase content of FA to 1.0 g, however the content of Si increases with it during the whole content range of FA. The possible reason may be due to the interaction among FA, P123 and TEOS. Based on the theory proposed by Stucky (Firouzi et al., 1995), mesoporous materials were assembled by template molecules and inorganic reagents (FA and TEOS) through cooperative formation. At the same time, the polycondensation reaction of FA and TEOS takes

place respectively. So, the interaction among FA, TEOS and P123 such as hydrogen bond enhances with the increasing of content of FA at first, resulting in increasing content of C and Si, which means cooperation is dominant at this time. With the further increase of FA content, the polycondensation reaction of TEOS proves dominant and more and more Si can be entered into the network structure of composite, which squeezes out some of the carbon in the network structure, hence the content of Si increases and the content of C declines instead. These results have demonstrated that the content of carbon precursor has a very important effect on the structure of prepared material.

Table 2
The removal rates of MO by MMCS in different water samples

Sample	Added (mg·L ⁻¹)	Residual (mg·L ⁻¹)	R (%)
Yangtze water	0	ND*	/
	10	0.007911	99.8
	30	0.1022	99.6
	50	3.1103	93.8
River water	0	ND*	/
	10	0.01570	99.8
	30	0.4978	98.3
	50	3.5864	92.8
Yueya Lake water	0	ND*	/
	10	0.007962	99.9
	30	0.4847	98.3
	50	3.2709	93.5
ND*: not detected			

3.1.6 Zeta potentials analysis

Zeta potentials of MMCS materials containing 0.25, 0.5, and 1.0g FA contents before and after MO adsorption were measured in a wide range of pH to predict the nature of the charge of the materials. As shown in Fig. S1, before MO adsorption, the pH at the zero point charge of MMCS materials containing 0.25, 0.5, and 1.0 g FA contents are determined to be 2.2, 2.7, and 3.7, respectively. The measurements indicate that these MMCS materials are positively charged when the pH values are less than their corresponding isoelectric point (pI) and conversely negatively charged when the pH values are over their

pl. Besides, after MO adsorption, the pl of the three MMCS materials shifts to lower pH values because of the incorporation of anionic MO molecules.

3.1.7 Magnetic properties of MMCS

To investigate the magnetic properties of MMCS materials, magnetic saturation strength of three MMCS materials containing 0.25, 0.5 and 1.0 g of FA were measured respectively and the results are presented in Fig. 4. It can be seen that the magnetization curves of the three materials are all S-shaped with magnetic hysteresis loops, suggesting that the MMCS materials have ferromagnetic properties and can be separated rapidly from aqueous solution via an external magnetic field. Clearly, the MMCS material containing 0.25g of FA presents the strongest saturation magnetizations and the corresponding saturation magnetization value is about 10 emu g^{-1} . The saturation magnetization value of the MMCS material containing 1.0 g FA is approximate 5 emu g^{-1} , which is lower than that of 0.25 g FA and higher than that of 0.5 g FA. As we all know that the content of Fe determines the magnetism of materials and the results of magnetism performance agree well with the results of EDS. Considering the fact that the MMCS material containing 0.25 g FA possesses poor nanocrystallization and distribution uniformity (Fig. 2), as well as small special surface area (Table 1), the MMCS material containing 1.0 g FA is more suitable as a candidate adsorbent for subsequent experiments.

3.1.8 The effect of the amount of carbon precursor FA on adsorption capacity

As discussed earlier, the network structure of MMCS is generated by the cooperation of FA, TEOS and P123, therefore the amount of carbon precursor FA will have an important influence on adsorption capacity and structure of the materials and the results are showed in Fig.S2. As can be seen that, the specific surface area of single point of MMCS increases with the increase of the content of FA from 0.25 g to 0.5 g and then stays unchanged when further increasing the content of FA to 1.0 g. This phenomenon can be explained from the above analysis. When the content of FA increases from 0.25 g to 0.5 g, more and more network structure and porous pores are produced by the cooperation among FA, TEOS and P123, leading to the increasing specific surface area from 150.4 to $328.6 \text{ m}^2 \text{ g}^{-1}$. Whereas the specific surface area of MMCS keeps stable after further increasing the content of FA to 1.0 g, which is possibly because the network has already been formed and the scale is no longer growing. These results are in good agreement with the EDS results. Besides, the saturated adsorption capacity of MO on MMCS also increases with the content of FA and then remains unchanged. The change trend of adsorption capacity of MO on MMCS with FA content is the same as that of specific surface area, thus it can be inferred that large surface area can provide more active sites, contributing to high adsorption capacity of MO on MMCS.

3.2 Effect of pH

Solution pH is one of the most influential operational factors controlling the adsorption process, which affects not only the surface charge of the adsorbent but also the chemistry of dye (Hu et al., 2019). In this

study, the effect of pH on adsorption of MO by MMCS containing 1.0 g FA was investigated in the range of pH values from 2 to 8. Since the pI of MMCS is 3.7 according to the zeta potential results (Fig. S1), when the pH value ranges from 2 to 3.7, the surface of MMCS can offer positively charged adsorption sites, increasing the electrostatic attraction with anionic MO dye. As the pH increases, the negatively charged sites of the surface increase, which decreases the adsorption of anionic dye due to electrostatic repulsion. However, as seen in Fig. 5, the adsorption capacity of MO is less sensitive to the solution pH variation and remains almost a constant in the range of pH values from 2 to 8, suggesting that the electrostatic interaction is not the primary process for MO adsorption by MMCS. A similar phenomenon was reported for the removal of MO onto CNTs-A (Ma et al., 2012). Based on FT-IR study (Fig. 3), a larger number of hydrophilic groups (-OH, C = O, C-O) are found on the surface of MMCS. These hydrophilic groups may provide additional affinity and available anchoring sites for MO molecules, demonstrating that hydrogen bonding interaction may be an important process for MO adsorption. When the concentration is too high (100 mg L^{-1}), MO is easy to precipitate at low pH, thus the optimal adsorption condition is considered as pH 4.

3.2 Effects of concentration of MO and temperature

Concentration and temperature are two important factors affecting the adsorption properties of the materials and the effects of concentration and temperature on the adsorption of MO by MMCS were investigated in detail. Considering the results of VSM that the saturation magnetization value of MMCS containing 1.0 g FA is higher than that of 0.5 g FA (Fig. 4), the FA content set at 1.0 g is selected for the studies of concentration and temperature.

As presented in Fig. 6 and Fig. S3, the adsorption capacity of MO by MMCS increases sharply with increasing MO concentration from 10 to 50 mg L^{-1} , followed by a much slow increase, and finally reaches equilibrium. This phenomenon can be explained by that higher initial MO concentration will provides greater driving force to overcome the mass transfer resistance of MO molecules between the aqueous phase and the solid phase, meanwhile, the driving force of the concentration gradient increases with the increase of initial concentration (Peng et al., 2014). Additional, it can be observed in Fig. S2 that the adsorption capacity increases with the increase of temperature, which reveals the adsorption process of MO by MMCS is endothermic in nature. It is worth to note that at each of the three temperatures (298, 308, 318 K), the adsorption capacity reaches its maximum at MO concentration of 150 mg L^{-1} , which is regarded as the optimal concentration for MO adsorption.

3.3 Effect of contact time and adsorption kinetics

The effect of contact time on the adsorption of MO by MMCS was evaluated ranging from 5 to 120 min and the result is present in Fig. S4. It can be seen that the adsorption of MO is quite rapid in the initial stage, subsequently, a slight fluctuation occurs, and followed by apparent equilibrium with the prolongation of contact time. A similar trend was reported for the adsorption of MO onto other adsorbents (Tang et al., 2014). As shown in Fig. S4, when the MO concentration is 150 mg L^{-1} , the adsorption rate is the fastest and the adsorption equilibrium is achieved after 15 min of contact time,

which is consistent with higher MO concentration presents higher adsorption capacity. Due to the short adsorption equilibrium contact time favors the application of economical wastewater treatment, 15 min is taken as the equilibrium time in batch adsorption experiments.

The pseudo-first-order and pseudo-second-order kinetic models were applied to estimate adsorption rate and simultaneously reveal the conceivable reaction mechanisms of MO adsorption, which are expressed by Eq. (3) and Eq. (4) (Peng et al., 2019) as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Eq. 3}$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad \text{Eq. 4}$$

where q_e and q_t are the adsorption capacity (mg g^{-1}) of MO at equilibrium and time t (min); k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constants of pseudo-first-order and pseudo-second-order kinetic process, respectively.

The obtained results analyzed by kinetics models are shown in Table 3. It can be seen that the correlation coefficient R^2 values of pseudo-second-order model (> 0.996) are all higher than pseudo-first-order model, indicating pseudo-second-order model is more suitable to describe the adsorption kinetics data. Moreover, the equilibrium adsorption capacity q_e values calculated by the pseudo-second-order model are approximate with the experimental equilibrium q_e values, which further confirm the adsorption process could be well fitted with pseudo-second-order model.

3.4 Adsorption isotherms and thermodynamics

The adsorption isotherms of MO over MMCS were explored at three varies temperatures over a range of initial MO concentrations from 10 to 200 mg L^{-1} to reveal the equilibrium relations between the MO concentration on the solid phase and that in the liquid phase. The isotherm adsorption data were determined by two isotherms models, namely Langmuir and Freundlich. The linear equations can be described by Eq. (5) and Eq. (6):

Langmuir isotherm model:

$$C_e/q_e = C_e/q_m + 1/q_m K_L \quad \text{Eq. 5}$$

Freundlich isotherm model:

$$\ln q_e = \ln K_F + \ln C_e/n \quad \text{Eq. 6}$$

where C_e (mg L^{-1}) and q_e (mg g^{-1}) are the equilibrium concentration of MO and the equilibrium adsorption capacity, respectively; q_m (mg g^{-1}) is the maximum adsorption capacity; K_L (L mg^{-1}) and K_F (L g^{-1}) are the constants of Langmuir and Freundlich, respectively; and n is adsorption intensity index (dimensionless) related to the intensity of adsorption.

The fitting parameters of Langmuir and Freundlich models are summarized in Table 4. It is apparent that the Langmuir isotherm with higher correlation regression coefficients ($R^2 > 0.99$) yields a much better fit of adsorption data for MO compared with Freundlich model, revealing that monolayer adsorption of MO takes place on a uniform surface with distinct homogeneous adsorption sites. The equilibrium adsorption capacity q_e value calculated by Langmuir model is close to the experimental equilibrium q_e value and increases with the increase of temperature, demonstrating the adsorption is endothermic in nature. As for the Freundlich model, the value of K_F increases with the increase of temperature, indicating that adsorption capacity increases with temperature. These results are consistent with the effect of temperature discussed above. The values of $1/n$ are all less than 1, confirming that the adsorption processes are favorable (Liang et al., 2016).

To further elucidate the effect of temperature on adsorption, various thermodynamics parameters such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated using the following equations (Peng et al., 2015):

$$\Delta G^0 = -RT \ln K_d \quad \text{Eq. 7}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{Eq. 8}$$

$$\ln K_d = -\Delta H^0/RT + \Delta S^0/R \quad \text{Eq. 9}$$

where R is the gas constant; T represents the adsorption temperature (K); K_d denotes the thermodynamic equilibrium constant.

The values of ΔH^0 and ΔS^0 were measured from the slope and intercept of the plots of $\ln K_d$ versus $1/T$, respectively. The thermodynamic parameters at different temperatures are shown in Table 5. It can be seen that all of the calculated ΔG^0 values are negative, indicating the spontaneous nature of adsorption process. The positive value of ΔH^0 suggests the adsorption process is endothermic. The positive value of ΔS^0 reflects the good affinity and increase of randomness at the solid-solution interphase in the whole adsorption process.

3.5 Effect of coexisting anions

It is common that dye wastewater contains a wide variety of coexisting ions, which might potentially compete with the active adsorption sites of the adsorbents and thus affect the adsorption the adsorption of MO by MMCS. The effects of commonly coexisting ions (including PO_4^{3-} , NO_3^- , CO_3^{2-} , SO_4^{2-}) on the adsorption of MO were investigated individually. As seen in Fig. S5, in the presence of PO_4^{3-} , NO_3^- , CO_3^{2-} or SO_4^{2-} , the adsorption capacity of MO remains almost constant, suggesting that the participation of these four anions has no interference in the adsorption process.

3.7 Desorption and regeneration study

The regeneration and reuse of the adsorbents is a crucial factor in practical application of the adsorbent, which can evaluate the economic practicability of materials, so adsorption-desorption experiments were carried out in this work. Several common desorption reagents such as hydrochloric acid, sodium hydroxide, methanol and ethanol, were used to desorb MO from S-doped MMCS. The results showed that hydrochloric acid and sodium hydroxide couldn't elute MO from S-doped MMCS, but methanol and ethanol could both quantitatively desorb MO from S-doped MMCS. Although the adsorption capacity of MO by the desorbed S-doped MMCS decreased obviously, MO could be desorbed from the adsorbents and collected together to avoid the second pollution.

3.8 The removal of MO by MMCS from real water samples

The prepared **MMCS** was applied to remove MO in Yangtze water, river water and Yueya Lake water and the removal rates and residual concentration in all the water samples and spiked water samples are given in Table 6. As can be seen, the removal rates of 93.5–93.8% were obtained for all the spiked water samples, which illustrated that MMCS could efficiently remove MO during real water matrix and thus showed MMCS's efficiency and very good prospects.

Conclusions

In this study, we demonstrated a facile route for the synthesis of magnetic mesoporous carbon (MMCS) via a soft template one-pot solvent thermal strategy by co-assembly of furfuryl alcohol, metal ion sources $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Pluronic copolymer P123 and TEOS. The MMCS was characterized by various techniques and used for the removal of MO from aqueous solution. The results of the effects of the content of carbon precursor FA on adsorption performance of MO by MMCS indicate that with the increasing of content of carbon precursor FA, adsorption performance of MMCS increases obviously, demonstrating the content of carbon precursor can facilitate the adsorption performance of adsorbents. At the same time, it was found that magnetic particles mixture of Fe_3O_4 and Fe were well embedded in the mesoporous carbon and silica matrix, exhibiting ferromagnetic property, and the higher content of carbon precursor results to lower magnetic performance, possibly due to the declining content of iron content per unit mass. These studies can supply some practical guidance for designing new materials with high adsorption efficiency. As suggested by the effect of pH, the adsorption of MO by MMCS might not be due to electrostatic interaction, but may be attributed to the present of abound of hydrophilic groups on the surface of MMCS, which increased with FA content increasing, leading to the improving adsorption capacity. In addition, initial dye concentration, temperature and contact time were effective on the adsorption of MO by MMCS. Kinetic calculations showed that pseudo-second-order kinetic model had a higher accuracy in adsorption kinetics data. The equilibrium data could be better interpreted with the Langmuir model, indicating that adsorption took place by monolayer coverage. The thermodynamic parameters revealed the spontaneous and endothermic nature of MO adsorption. Moreover, it was suggested that the co-existence of PO_4^{3-} , NO_3^- , CO_3^{2-} and SO_4^{2-} had no interference in the adsorption process. At last, the prepared MMCS was applied for removing MO in some real water samples with good results, suggesting it's a promising and efficient adsorbent in practical application.

Declarations

Compliance with Ethical Standards

Ethical Approval: We approve and agree all the ethical guidelines proposed by the journal and make sure to respect third parties rights such as copyright and/or moral rights.

Research involving Human Participants and/or Animals: This research doesn't involve Human Participants and/or Animals.

Consent to Participate: All the authors content to participate in this research work.

Consent to Publish: All the authors content to publish this manuscript.

Authors Contributions: All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Bo Zhu and Jiangyan Xu. The first draft of the manuscript was written by Bo Zhu and the manuscript was revised by Jiangyan Xu. Some supplementary experiments were carried out by Zhihui Xu. And all the work was under the supervision of Meisheng Wu and Hongmei Jiang. All authors read and approved the final manuscript.

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Competing Interests: The authors declare no competing interest.

Availability of data and materials: Original data about adsorption method

Original Data for the effect of pH

T=35 °C; C_{MO}: 50 ppm; V: 10mL m: 2mg; t: 50min

pH	Q ₁	Q ₂	Q ₃	Q _{average}
2	26.09034	15.234375	19.98432602	19.9044586
3	27.41935	23.73417722	26.84294872	22.5
4	35.48387	19.67213115	37.02229299	23.51485149
5	16.02564	29.20560748	23.69281046	18.79084967
6	18.08682	37.0795107	35.36977492	26.87296417
7	22.76358	28.42679128	28.57142857	13.39285714
8	23.65931	25.63091483	21.82539683	20.48494983

Original Data for the effect of concentration and temperature

T=25 °C (pH: 4; V: 20 mL; m: 2mg; t: 50min)

C_o	A_o	A_1	A_2
20	0.05	0.032	0.031
50	0.135	0.1	0.104
80	0.225	0.185	0.18
100	0.279	0.229	0.231
150	0.395	0.35	0.351
200	0.514	0.467	0.471

T=35 °C (pH: 4; V: 20 mL; m: 2mg; t: 50min)

C_o	A_o	A_1	A_2
20	0.051	0.02	0.02
50	0.139	0.089	0.073
80	0.22	0.165	0.16
100	0.276	0.212	0.217
150	0.404	0.34	0.343
200	0.527	0.468	0.467

T=45 °C (pH: 4; V: 20 mL; m: 2mg; t: 50min)

C_o	A_o	A_1	A_2
20	0.051	0.009	0.01
50	0.127	0.039	0.039
80	0.224	0.111	0.115
100	0.279	0.155	0.151
150	0.389	0.265	0.273
200	0.513	0.393	0.396

Original Data for the effect of time

T=35 °C (pH: 4; V: 20 mL; m: 2mg; C_{CR} : 20 mg L⁻¹)

t	A ₀	A ₁	A ₂
10	0.057	0.034	0.037
20	0.057	0.03	0.03
30	0.057	0.029	0.028
50	0.057	0.02	0.024
80	0.057	0.023	0.02

T=35 °C (pH: 4; V: 20 mL; m: 2mg; **C_{CR}**: 50 mg L⁻¹)

t	A ₀	A ₁	A ₂
10	0.14	0.11	0.112
20	0.14	0.098	0.1
30	0.14	0.09	0.09
50	0.14	0.084	0.082
80	0.14	0.083	0.082

T=35 °C (pH: 4; V: 20 mL; m: 2mg; **C_{CR}**: 150 mg L⁻¹)

t	A ₀	A ₁	A ₂
10	0.378	0.348	0.351
20	0.378	0.34	0.339
30	0.378	0.331	0.33
50	0.378	0.319	0.322
80	0.378	0.32	0.32

Original Data for the effects of different dyes on the adsorption capacity of CR on N-MCA

C_{CR}: 100 mg L⁻¹

C_{MO}	A_o	A_1	A_2
0	0.276	0.212	0.217
50	0.503	0.391	0.408
$C_{Orange\ II}$	A_o	A_1	A_2
0	0.276	0.212	0.217
50	0.483	0.389	0.401
$C_{Rhodamine}$	A_0	A_1	A_2
0	0.276	0.212	0.217
50	0.284	0.245	0.234

Original Data for CR adsorption on N-MCA with four adsorption-desorption cycles

Cycle 1

A_o	A_{e1}	A_{e2}
0.256	0.191	0.211
	$A_{eluent1}$	$A_{eluent2}$
	0.06	0.043
Cycle2		
A_o	A_{e1}	A_{e2}
0.256	0.203	0.201
	$A_{eluent1}$	$A_{eluent2}$
	0.049	0.046
Cycle 3		
A_o	A_{e1}	A_{e2}
0.256	0.205	0.198
	$A_{eluent1}$	$A_{eluent2}$
	0.045	0.049
Cycle 4		
A_o	A_{e1}	A_{e2}
0.256	0.196	0.199
	$A_{eluent1}$	$A_{eluent2}$
	0.05	0.048

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Tables

Tables 3-6 are not available with this version

Figures

Figure 1

XRD patterns of MMCS with 0.25 g FA (a), 0.5 g FA (b), and 1.0 g FA (c).

Figure 2

TEM images of MMCS with 0.25 g FA (a), 0.5 g FA (b), and 1.0 g FA (c).

Figure 3

FTIR spectra of MMCS with 0.25 g FA (a), 0.5 g FA (b), and 1.0 g FA (c).

Figure 4

Magnetization curves of MMCS with 0.25 g FA(a), 0.5 g FA (b), and 1.0 g FA (c).

Figure 5

The effect of pH value on the adsorption capacity of MO by MMCS (Adsorption conditions: $C_0=50 \text{ mg L}^{-1}$, $T=308 \text{ K}$, contact time=50 min)

Figure 6

The effects of FA content on the adsorption capacity of MO by MMCS with 0.25 g FA (a), 0.5 g FA (b), and 1.0 g FA (c) (Adsorption conditions: pH=4, time=50 min, T=318 K)

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