Magnetic Mesoporous Carbons Derived from In Situ MgO Template Formation for Fast Removal of Heavy Metal Ions

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ABSTRACT: In this paper, magnetic mesoporous carbon composites were prepared by calcination of the mixture of magnesium citrate and Fe3O4@SiO2 in an inert atmosphere. A high content of Fe3O4@SiO2 and MgO was in situ embedded in a carbon matrix. After removing the MgO template by diluted acid, the resulting material (Fe3O4@SiO2@mC) was subjected to further H2O2 oxidation treatment. The formed oxygen-containing functional groups on the products provided plenty of active sites for the adsorption of analytes of interest. The obtained composites (Fe3O4@SiO2@mC-H2O2) exhibited a mesoporous structure with a high specific surface area of 731 m2 g−1. The adsorption capacities of Fe3O4@SiO2@mC-H2O2 for Cu(II) and Pb(II) were calculated to be 86.5 and 156 mg g−1, respectively. Under optimal conditions, the adsorption isotherm of Cu(II) and Pb(II) onto Fe3O4@SiO2@mC-H2O2 fitted the Langmuir model and the adsorption kinetic was well-correlated with the pseudo-second-order model. Besides, Fe3O4@SiO2@mC-H2O2 exhibited fast removal dynamics (within less than 1 min) for Cu(II) and Pb(II), demonstrating great application potential in wastewater treatment.

1. INTRODUCTION

With the rapid development of modern industry and agriculture, environmental pollution, especially water pollution, has become one of the most serious social problems presently. Great efforts have been made on the treatment of polluted water, and a series of pretreatment techniques, for example, chemical precipitation,1 liquid–liquid extraction,2 membrane filtration,3 ion exchange,4 and adsorption,5 have been applied for heavy metal removal from wastewater. Among these technologies, adsorption has been demonstrated with the merits of high efficiency, low cost, and ease of operation. A variety of adsorbents have been employed for metal ion removal, such as metal–organic frameworks,6 nanocomposites,7 biomaterials,8 graphene oxide,9 and mesoporous carbons.9 Mesoporous carbons are one kind of porous carbons (PCs), featuring good chemical inertness and electrical conductivity, high specific surface area, and easily controlled pore structure.10–12 They are attractive for industrial applications as adsorbents,9 as electrode materials,13 as catalyst supports,14 as sensors,15 in drug delivery,16 in energy conversion, and as storage materials.17 A template method is generally adopted for the fabrication of mesoporous carbons, in which a template, such as zeolites and silica (hard template), or block/graft copolymer (soft template), is added into carbon precursors to produce mesopores in PCs. Generally, the hard template is dissolved by corrosive acid/alkali to form a porous structure; the soft template is removed by using a relatively high temperature. Comparatively, some sacrificial soft templates exhibit higher cost than commonly used hard templates. The templating process using mesoporous silica to generate mesoporous carbon is quite tedious and extremely difficult for manufacturing on a large scale.18 MgO has been demonstrated as a good alternative template for mesoporous carbon preparation.19 In comparison with zeolite/silica-based template methods for mesoporous carbon preparation, MgO can be easily dissolved by noncorrosive acids; the morphology of the PCs is tunable by varying the MgO precursor and carbon precursor; MgO can be recycled easily.20 Morishita et al.19 prepared mesoporous carbons via a MgO template method, and the surface area of the products without any activation process reached 2000 m2 g−1. The sizes of the formed mesopores were very similar to those of the MgO particles. As one of the MgO precursors, citrate salts with bulky organic anions are rich in carbon, of low cost, easy to obtain, and are good precursors for carbon materials. Zhuo et al.21 prepared mesoporous carbons via simple pyrolysis of magnesium citrate, which acted as a MgO precursor and a carbon precursor simultaneously. The one-step pyrolysis process without the need for a metal catalyst is very convenient and economical for preparing mesoporous carbons.

Great progress has been made in adsorption of organic substances by developing various mesoporous carbons,22
although mesoporous carbons for heavy metal adsorption are still scarce so far, mainly because of the difficulty in the recovery process and lack of functional groups.

The integration of magnetism to PCMs can resolve the difficulty in recovery of PCs from aqueous solution with the aid of an external magnet. The separation of magnetic PCs from aqueous solution by an external magnetic field is easy to operate and fast, avoiding the tedious operation of centrifugation and filtration. Magnetic carbon nanoparticles (NPs) with a high Brunauer–Emmett–Teller (BET) surface area (918 m² g⁻¹) exhibited higher adsorption capacities than activated carbon and carbon nanotubes for metal ions.25 Cheng et al.24 prepared porous Fe₃O₄@C nanocapsules, which exhibited a high removal efficiency (99.6%), large adsorption capacity (79 mg g⁻¹ for Pb), and rapid removal dynamics (within 1 min) for heavy metal removal applications. However, for magnetic carbon materials carbonized at a high temperature (800–1000 °C), the oxygen-containing groups on their surface would be greatly lost, leading to low adsorption capacities for metals (e.g., 7.79 mg g⁻¹ for Cu(II)).25 To resolve this problem, oxidation treatments have been frequently used, and they contribute to the formation of numerous −OH and −COOH groups on the surface of carbon materials.25 H₂O₂ is a kind of mild oxidizing agent, which can generate −OH and −COOH groups on the surface of carbon framework and maintain the original mesoporous structure simultaneously. During the H₂O₂ oxidation process, the groups of −CH₂ and −CH on the carbon skeleton are first oxidized to C−OH and then converted to −C=O groups. It is attributed to the corrosion of the carbon wall, increasing the size of mesopores and pore volume.26

On the basis of these facts, this paper aimed to prepare magnetic mesoporous carbons by using magnesium citrate as both carbon precursor and magnesium precursor and Fe₃O₄@SiO₂ as an iron precursor; to functionalize the obtained magnetic mesoporous carbons via H₂O₂ oxidation process; and to adopt them for metal ion removal from aqueous solution.

2. EXPERIMENTAL SECTION

2.1. Apparatus and Chemicals. The determination of target metals was performed with an ITRIS Intrepid II XSP radial inductively coupled plasma optical emission spectrometry (ICP–OES) instrument (Thermo, USA), and the corresponding operation conditions are displayed in Table 1. A GL-12K model tubular quartz reactor (Kejing Materials Technology Co. Ltd., Hefei, China) was used to synthesize the magnetic nanocomposites. The pH measurement was conducted with a 320-S pH meter (Mettler Toledo, China). Magnetic separation process was performed by using an Nd–Fe–B magnet (15.0 × 6.0 × 1.6 cm).

Stock solutions of 1000 mg L⁻¹ Cu(II) and Pb(II) were obtained by dissolving analytical reagents of Cu(acac)₂ and Pb(NO₃)₂ (Shanghai Reagent Factory, China) in ultrapure water, respectively, and the working solutions with specific concentrations were obtained by stepwise dilution of the corresponding stock solution. FeCl₃·6H₂O, FeCl₂·4H₂O, HNO₃, ammonia, NaOH, and ethanol were of analytical grade and purchased from Sinopharm Chemicals Co., Ltd (Shanghai, China). Magnesium citrate was purchased from Aladdin Corporation (Shanghai, China). All solid reagents and solvents used in the whole experiment were of analytical grade or better. Ultrapure water (18.2 MΩ cm) used throughout the experiments was obtained from a Milli-Q water system (Molsheim, France).

2.2. Fabrication of Fe₃O₄@SiO₂. The naked Fe₃O₄ NPs and Fe₃O₄@SiO₂ NPs were synthesized via a co-precipitation method27 and a sol–gel method28 respectively. The details are provided in the Supporting Information.

2.3. Fabrication of Fe₃O₄@SiO₂@mC. The fabrication of Fe₃O₄@mC was referred from ref 16 with some modifications. In a typical synthesis, magnesium citrate and Fe₃O₄@SiO₂ NPs, with the weight ratio varying from 5/5 to 9.5/0.5, were ground together for 1 h in a mortar to get a homogeneous mixture. For carbonization process, the obtained mixture was placed in a tube furnace and calcined at 600 °C (at a heating rate of 5 K min⁻¹) for 2 h in Ar. The obtained composites were treated with 0.5 mol L⁻¹ HNO₃ to remove the MgO template, and magnetic mesoporous carbons (Fe₃O₄@SiO₂@mC) were obtained. For comparison, mesoporous carbons were prepared using the same procedure by carbonizing magnesium citrate without adding Fe₃O₄@SiO₂ NPs.

2.4. Fabrication of Fe₃O₄@SiO₂@mC-H₂O₂. To introduce enough hydroxyl and carboxyl functional groups on the carbon matrix without damaging the original mesoporous structure, the obtained Fe₃O₄@mC was further treated by H₂O₂ oxidation according to ref 26 with some modifications. Specifically, 0.15 g of the above-prepared Fe₃O₄@mC (Fe₃O₄@SiO₂/magnesium citrate = 0.5/9.5) was treated with 8.0 mL of H₂O₂ (30 wt %) solution for 30 min under an ultrasonic bath at room temperature. Finally, the resultant magnetic NPs were separated, washed, and subsequently dried at 100 °C for 4 h. The obtained products were denoted as Fe₃O₄@SiO₂@mC-H₂O₂.

2.5. Characterization. Fourier transform infrared (FT-IR) spectroscopy (Thermo, USA) (4000–400 cm⁻¹) in KBr pellets was used for the characterization of the prepared materials. The crystalline structure was identified using a Rigaku Miniflex 600 X-ray diffractometer (Rigaku Corporation, Japan). S_BET was measured by N₂ adsorption at −196 °C with a micromeritics ASAP 2020 analyzer (USA), and all samples were outgassed at 120 °C for 12 h before measurements. S_BET values were calculated from the BET theory, whereas the total pore volume was estimated from the amount adsorbed at a relative pressure of 0.99. The images of the microstructure were taken by an X-650 scanning electron microscope (Tokyo, Japan) and a JEM-2010 transmission electron microscope (Tokyo, Japan). A PPMS-9 model vibrating sample magnetometer (VSM, Quantum, USA) was employed for the characterization of the magnetic properties.

2.6. Adsorption Studies. In the adsorption experiments, 4 mL of sample solution containing Cu(II) and Pb(II) adjusted

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Table 1. Operation Parameters of Intrepid XSP Radial ICP–OES

| operating conditions | value |
|---------------------|-------|
| incident power (W)  | 1150  |
| frequency of rf generator (MHz) | 27.12 |
| outer argon flow rate (L min⁻¹) | 14 |
| auxiliary gas flow rate (L min⁻¹) | 0.5 |
| carrier gas flow rate (L min⁻¹) | 0.5 |
| solution uptake rate (L min⁻¹) | 1 |
| analytical wavelength (nm) | Cu 324.754, Pb 220.353 |
to pH 6 was spiked with 4 mg of Fe₃O₄@SiO₂@mC-H₂O₂, followed by shaking at room temperature for 5 min to reach equilibrium. Subsequently, the mixed solutions were subjected to magnetic separation, and the obtained aqueous solution was subjected to ICP–OES detection. The adsorption capacity (qₑ, mg g⁻¹) for Cu(II) and Pb(II) on Fe₃O₄@SiO₂@mC-H₂O₂ was calculated, and the details are presented in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Fabrication of Fe₃O₄@SiO₂@mC-H₂O₂

3.1.1. Calcination Temperature. The calcination temperature was optimized according to carbonization yield and the adsorption capacity of the obtained products for Cu(II) and Pb(II). As the pyrolysis temperature of magnesium citrate is around 500 °C, the effect of calcination temperature on the carbonization was investigated by calcining pure magnesium citrate at 600, 700, and 800 °C under an Ar atmosphere. The carbonization yield is calculated by dividing the product mass obtained after calcination with the mass of pure magnesium citrate before calcination. It was found that when we increased the carbonization temperature from 600 to 800 °C, the carbonization yield decreased from 43 to 36%. Thermogravimetric (TG) analysis was performed for Fe₃O₄@SiO₂@mC and the mixture of Fe₃O₄@SiO₂ and Mg citrate (0.5/9.5) in an inert atmosphere to monitor pyrolysis process, and the result is shown in Figure S1. After calcination and removal of MgO template by washing with diluted acid, the obtained products are denoted as MgC-T, where T stands for the calcination temperature (600, 700, or 800 °C). It was found that the adsorption capacities of 43.9, 25.9, and 24.3 mg g⁻¹ were obtained for Cu(II) and 74.8, 61.5, and 60.9 mg g⁻¹ were obtained for Pb(II) by MgC-600 °C, MgC-700 °C, and MgC-800 °C, respectively. The decreasing sorption capacity of the products along with the increase of the calcination temperature is probably due to the loss of oxygen-containing groups under high temperature. On the other hand, it was found that magnetism of the products was increased with the increase of the calcination temperature from 600 to 800 °C. Thus, a calcination temperature of 600 °C was adopted for the synthesis of the composites.

3.1.2. Mass Ratio of Fe₃O₄@SiO₂ NPs/Magnesium Citrate. To evaluate the adsorption capacity of magnetic composites, the mass ratio of Fe₃O₄@SiO₂ NPs to magnesium citrate in the precursor was investigated in the range of 5/5–0.5/9.5. The sorption capacity of Cu(II) and Pb(II) on the obtained magnetic composites was evaluated. The results are shown in Figure 1. With the increase of magnesium citrate mass in the precursor mixture, the sorption capacities for Cu(II) and Pb(II) were gradually increased. When the ratio of Fe₃O₄@SiO₂ NPs to magnesium citrate was decreased to 0.5/9.5, the adsorption capacity was close to that of pure mesoporous carbon material. Thus, the mass ratio of Fe₃O₄@SiO₂ NPs to magnesium citrate as 0.5/9.5 was employed for subsequent experiments.

3.1.3. Pretreatment Time of H₂O₂ Oxidization. To improve the hydrophilicity and adsorption capacity of Fe₃O₄@SiO₂@mC, the mild oxidizing agent H₂O₂ was adopted to introduce more oxygen-containing groups to the carbon surface. It was found that the specific surface area of Fe₃O₄@SiO₂@mC seriously decreased (70 m² g⁻¹) after H₂O₂ (30 wt %) treatment at room temperature after 12 h, mainly because of the cleavage of part C–C bonds by H₂O₂ and the mesostructure collapses in Fe₃O₄@SiO₂@mC. According to ref 26, H₂O₂ treatment was processed for 30 min for the obtained Fe₃O₄@SiO₂@mC in this work. The specific surface area of Fe₃O₄@SiO₂@mC-H₂O₂ (731 m² g⁻¹) was close to that of Fe₃O₄@SiO₂@mC (781 m² g⁻¹); the porous structure of Fe₃O₄@SiO₂@mC remains almost unchanged after H₂O₂ treatment. Relevant information is included in section 3.2.3.

3.2. Characterization. 3.2.1. Powder X-ray Diffraction Measurements and X-ray Photoelectron Spectroscopy Characterization. X-ray diffraction (XRD) pattern of Fe₃O₄@SiO₂@mC is shown in Figure 2a. For the obtained magnetic PCs before acid washing, the characteristic diffraction peaks of MgO (200 and 220) can be seen clearly. The intensities of diffraction peaks are very strong and sharp, and they are in a highly crystalline state, indicating that a large quantity of MgO NPs were in situ embedded in the carbon matrix after high-temperature calcination. On the other hand, carbons formed from magnesium citrate are amorphous (002) and difficult to detect in the XRD pattern. Besides, the products obtained under 700 and 800 °C have been characterized by XRD, and it also showed an amorphous state for these carbons. For Fe₃O₄@SiO₂@mC obtained after 0.5 mol L⁻¹ HNO₃ washing, MgO diffraction peaks disappeared from the XRD spectrum, indicating a complete dissolution of MgO particles. The XRD pattern of Fe₃O₄@SiO₂@mC-H₂O₂ is very similar to that of Fe₃O₄@SiO₂@mC, indicating that the oxidation treatment does not change the crystalline phase of Fe₃O₄@SiO₂@mC. Besides, Fe₃O₄ (311) at a 2θ value of 35° is observed for all three curves, which demonstrates that the magnetic core of Fe₃O₄ is embedded in the obtained PCs. X-ray photoelectron spectroscopy (XPS) was employed to monitor the elemental contents for the prepared Fe₃O₄@SiO₂@mC before and after oxidation treatment, and the result is shown in Table S1. It demonstrated the existence of C, Fe, O, and Si.

3.2.2. FT-IR Measurements. The FT-IR spectra of the prepared magnetic adsorbents (Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@mC, and Fe₃O₄@SiO₂@mC-H₂O₂) are presented in Figure 2b. The FT-IR spectra of Fe₃O₄@SiO₂ exhibit a wide and strong band at 1095 cm⁻¹, which is assigned to O–Si–O stretching vibrations, indicating that the naked Fe₃O₄ was coated by Si. The FT-IR spectrum of Fe₃O₄@SiO₂@mC shows a broad band at 3425 cm⁻¹, attributed to –OH stretching vibrations. The absorption bands appearing at 1612 and 1384 cm⁻¹ are ascribed to the asymmetric vibrations and symmetric stretching vibrations of –COOH, respectively. After H₂O₂ oxidation treatment, a new diffraction peak appears at 1708 cm⁻¹, which
is ascribed to the C=O vibrational stretching of −COOH, indicating that more −COOH groups are generated in the carbon matrix.26

3.2.3. N2 Adsorption−Desorption Isotherms. The specific surface area of the obtained magnetic PCs was determined by the BET method. Table 2 shows the \( S_{\text{BET}} \) values and the properties of pores of the magnetic nanocomposites. For Fe\(_3\)O\(_4@\)SiO\(_2@mC\), a high BET surface area of 781 m\(^2\) g\(^{-1}\) was obtained, with a large pore volume of 0.47 cm\(^3\) g\(^{-1}\) and an average pore width of 3.65 nm. After the oxidation treatment, no obvious variation was observed for the surface area and pore structure for Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\). Figure 2c displays the N\(_2\) adsorption−desorption isotherm curves for Fe\(_3\)O\(_4@\)SiO\(_2@mC\) and Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\). It indicates that the adopted H\(_2O_2\) treatment did not damage the structure of the obtained magnetic PCs.

3.2.4. Magnetic Properties. The hysteresis curves for the magnetic core and two magnetic composites were measured by a VSM. The magnetic susceptibility of Fe\(_3\)O\(_4@\)SiO\(_2\) is 39 emu/ g. As shown in Figure 2d, the magnetic susceptibility is 4.8 emu/ g for Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\), a little higher than that of Fe\(_3\)O\(_4@\)SiO\(_2@mC\) (3.4 emu/ g). It is possibly attributed to the carbon loss during the oxidation process.26 Because of the superparamagnetic property, the suspension can be easily separated via an external magnet. A clear solution was obtained after separation by a magnet within 1 min, and the photographs of an aqueous solution before and after separation are shown in the insets of Figure 2d, with Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\) as the example.

3.3. Effect of Sample pH. Solution pH would determine the protonation degree of the active sites on the adsorbents and affect the existing form of target ions. Thus, the pH effect on the adsorption performance of the prepared Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\) for the removal of Cu(II) and Pb(II) was investigated in the range of 2−8 at room temperature. As shown in the results presented in Figure 4a, the removal efficiency of Cu(II) and Pb(II) increases rapidly with the increase of pH from 2 to 6 and levels off with further increase of solution pH. A complete removal of Cu(II) and Pb(II) can be achieved in the pH range of 6−8 by using Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\). Considering that the pH range for domestic sewage is 6−9, no pH adjustment is needed in the practical application of Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\). For a comparison, the removal efficiency of Cu(II) and Pb(II) obtained by Fe\(_3\)O\(_4@\)SiO\(_2@mC\) over pH 2−8 is also

Figure 2. XRD patterns of Fe\(_3\)O\(_4@\)SiO\(_2@mC\) (a). FT-IR spectra of Fe\(_3\)O\(_4@\)SiO\(_2\), Fe\(_3\)O\(_4@\)SiO\(_2@mC\), and Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\) (b). Nitrogen adsorption/desorption isotherms of Fe\(_3\)O\(_4@\)SiO\(_2@mC\) and Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\) (c). Room-temperature magnetization curves of Fe\(_3\)O\(_4@\)SiO\(_2@mC\) and Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\) (d). The insets show the digital images before and after magnetic separation under an external magnetic field.

Table 2. BET Specific Surface Area and Pore Size of Fe\(_3\)O\(_4@\)SiO\(_2@mC\) and Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\) Based on BET Technique

| materials            | \( S_{\text{BET}} \) (m\(^2\) g\(^{-1}\)) | micropore area (m\(^2\) g\(^{-1}\)) | external surface area (m\(^2\) g\(^{-1}\)) | pore volume (cm\(^3\)g\(^{-1}\)) | pore size (nm) |
|----------------------|------------------------------------------|------------------------------------|------------------------------------------|---------------------------------|----------------|
| Fe\(_3\)O\(_4@\)SiO\(_2@mC\) | 781                                      | 303                                | 478                                      | 0.47                            | 3.65           |
| Fe\(_3\)O\(_4@\)SiO\(_2@mC-H_2O_2\) | 731                                      | 245                                | 486                                      | 0.42                            | 3.56           |
presented in Figure 4b. As can be seen, complete removal of Cu(II) and Pb(II) is obtained at a pH of approximately 7−8. This suggests that the H₂O₂ oxidization process helps to broaden the pH range for the application of magnetic PCs to some extent.

3.4. Adsorption Kinetics. The studies on adsorption kinetics can not only estimate the adsorption rate but also speculate the adsorption mechanism. The impact of reaction time for the adsorption of Cu(II)/Pb(II) on Fe₃O₄@SiO₂@mC and Fe₃O₄@SiO₂@mC-H₂O₂ was investigated by spiking 50 mg of adsorbents into 50 mL of sample solution containing Cu(II)/Pb(II) (50.0 mg L⁻¹). The results (Figure 5a,b) show that the adsorption equilibrium could be achieved in less than 1 min, suggesting that Fe₃O₄@SiO₂@mC and Fe₃O₄@SiO₂@mC-H₂O₂ possess fast adsorption dynamics for removing Cu(II) and Pb(II) from wastewater.

The adsorption kinetic processes of Cu(II) and Pb(II) onto Fe₃O₄@SiO₂@mC and Fe₃O₄@SiO₂@mC-H₂O₂ were investigated by using pseudo-first-order and pseudo-second-order kinetic models. The details are provided in the Supporting Information. The experimental data were well-correlated with the pseudo-second-order model, and the fitting curves are shown in Figure 5c,d along with the relevant kinetics parameters listed in Table S2. It indicates that Cu(II)/Pb(II) adsorption on Fe₃O₄@SiO₂@mC and Fe₃O₄@SiO₂@mC-H₂O₂ is rapid and controlled by chemical adsorption, which follows the second-order kinetic model.

3.5. Adsorption Capacity and Adsorption Isotherms. Adsorption capacity is one of the important indexes for the evaluation of the adsorbents, which depends on the specific surface area and the density of active sites on the adsorbent. To estimate the adsorption capacity, the sorption isotherm of Cu(II)/Pb(II) on the prepared adsorbents is shown in Figure 6a,b. Remarkably, the adsorbed amount of Cu(II)/Pb(II) increases with the increase of Cu(II)/Pb(II) initial concentration and then reaches a plateau, which indicates the saturated adsorption of heavy metal onto the adsorbents. The adsorption capacities of Cu(II) and Pb(II) on the prepared Fe₃O₄@SiO₂@mC-H₂O₂ were calculated to be 86.5 mg g⁻¹ (1.36 mmol g⁻¹) and 156 mg g⁻¹ (0.75 mmol g⁻¹), respectively. The difference in adsorption capacity of Cu(II) and Pb(II) is possibly due to their difference in ionic size. The ionic radii of Cu(II) and Pb(II) are 0.073 and 0.132 nm, respectively, and Cu(II) with a smaller size would occupy the adsorption sites on a certain adsorbent in larger mole quantities than Pb(II).

The adsorption capacity of Cu(II) and Pb(II) on Fe₃O₄@SiO₂@mC-H₂O₂ is nearly twice that obtained by Fe₃O₄@SiO₂@mC, indicating the improvement of adsorption capacity by H₂O₂ treatment. Moreover, a comparison of adsorption capacity of Fe₃O₄@SiO₂@mC-H₂O₂ with those of some other adsorption materials is shown in Table 3. The adsorption capacity obtained by Fe₃O₄@SiO₂@mC-H₂O₂ for Cu(II) and Pb(II) is obviously higher than that obtained by the reported carbon-based materials. Although the surface area of the prepared material is lower than that of activated carbon, its adsorption capacity is significantly higher than that of activated carbon. This indicates that the mesoporous structure and oxygen-containing functional groups, rather than the surface area, significantly contributed to the adsorption process.

The isotherms of Cu(II)/Pb(II) adsorption onto Fe₃O₄@SiO₂@mC-H₂O₂ were analyzed using both monolayer (Langmuir) and multilayer (Freundlich) adsorption models. The details are provided in the Supporting Information. The experimental data fit better with Langmuir over Freundlich model (Figure 6c,d), and the results are presented in Table S3. The linear regression between Cₑ/qₑ.

Figure 4. Effect of pH on the removal of Cu(II) and Pb(II) by Fe₃O₄@SiO₂@mC-H₂O₂ (a) and Fe₃O₄@SiO₂@mC (b). Adsorbent, 4 mg; sample volume, 4 mL; and initial concentration of Cu(II) and Pb(II), 10.0 mg L⁻¹.
and Ce is fitted with a high correlation coefficient of 0.999, and the calculated maximum sorption capacities for Cu(II) and Pb(II) (94.5 and 154 mg g$^{-1}$) agree well with the experimental values (86.5 and 156 mg g$^{-1}$), demonstrating that the sorption of Cu(II) and Pb(II) ions on the as-prepared composites fits the Langmuir model, and the adsorption on the surface of composites is a monolayer adsorption.$^{31}$

### 3.6. Selectivity

Selectivity is another index to evaluate the properties of the as-prepared materials. Selective adsorption of single elements or a class of similar elements is the focus and hotspot in current research. Therefore, the effect of coexisting ions (Mn(II), Co(II), Ni(II), Zn(II), and Cd(II)) on the adsorption of Cu(II) and Pb(II) by Fe$_3$O$_4$@SiO$_2$@mC and Fe$_3$O$_4$@SiO$_2$@mC-H$_2$O$_2$ was investigated, and the results are displayed in Figure S2. For Fe$_3$O$_4$@SiO$_2$@mC, the removal efficiencies of Cu(II) and Pb(II) at pH 6 are about 60 and 90%, whereas for Fe$_3$O$_4$@SiO$_2$@mC-H$_2$O$_2$, the removal efficiencies are more than 90%. The removal efficiency of other ions is all

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**Figure 5.** Adsorption curves of Cu(II) (a) and Pb(II) (b) vs contact time. The pseudo-second-order sorption kinetic of Cu(II) (c) and Pb(II) (d) onto Fe$_3$O$_4$@SiO$_2$@mC and Fe$_3$O$_4$@SiO$_2$@mC-H$_2$O$_2$.

**Figure 6.** Effect of the initial Cu(II) (a) and Pb (II) (b) concentration on the adsorption capacity of Fe$_3$O$_4$@SiO$_2$@mC and Fe$_3$O$_4$@SiO$_2$@mC-H$_2$O$_2$. Langmuir adsorption isotherm for Cu (II) (c) and Pb (II) (d) on Fe$_3$O$_4$@SiO$_2$@mC and Fe$_3$O$_4$@SiO$_2$@mC-H$_2$O$_2$. [Graphs and images]
below 30%. After H2O2 treatment, the removal efficiency for copper was improved by about 30%, probably because of the introduced −OH and −COOH groups on the surface of PCs by H2O2. The results indicate that H2O2 oxidation greatly improves the selectivity of magnetic PCs for Cu(II).

3.7. Regeneration and Reuse Time. The regeneration of adsorbents is the process of desorbing target ions from the adsorbents. An ideal adsorbent should not only have excellent adsorption properties but also can be regenerated easily. Thus, the regeneration of Fe3O4@SiO2@mC-H2O2 was further investigated. The experimental results showed that Fe3O4@SiO2@mC-H2O2 could be regenerated easily by dispersing the recovered Fe3O4@SiO2@mC-H2O2 in 0.5 mol L−1 HNO3 (4 mL) solution and sonicating the mixture for 2 min. The recoveries for Cu(II) and Pb(II) obtained by the reused Fe3O4@SiO2@mC-H2O2 were above 95%. Moreover, the reusability experiment revealed that the removal efficiency was still above 90% after five adsorption—regeneration cycles (Figure S3), indicating a good application potential of Fe3O4@SiO2@mC-H2O2 for removing Cu(II) and Pb(II) from wastewater.

4. CONCLUSIONS

In this paper, magnetic PCs as highly efficient adsorbents were prepared via simple one-step pyrolysis of magnesium citrate, which acted as a MgO precursor and a carbon precursor simultaneously. The obtained magnetic mesoporous carbon was further functionalized via H2O2 oxidation process. The obtained Fe3O4@SiO2@mC-H2O2 exhibited a mesoporous structure with a high specific surface area and presented fast adsorption dynamics (less than 1 min) and high adsorption capacities of 86.5 and 156 mg g−1 for Cu(II) and Pb(II), respectively. It exhibited high removal efficiency, good selectivity, reusability, and easy separation ability and has a great application potential in industrial wastewater treatment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01989.

Fabrication of Fe3O4@SiO2: adsorption capacity calculation; adsorption kinetics; adsorption isotherms; relative content (%) of elements in the prepared Fe3O4@SiO2@mC obtained by XPS; simulation of the pseudo-second-order sorption kinetic and corresponding parameters; simulation of Langmuir sorption model and corresponding parameters; TG curve of 0.5/9.5 Fe3O4@SiO2/Mg citrate and Fe3O4@SiO2@mC; selectivity of the Fe3O4@SiO2@mC and Fe3O4@SiO2@mC-H2O2 adsorbents for Cu(II) and Pb(II) in the mixture of different divalent ion solutions; and adsorption/desorption cycles of Cu(II) and Pb(II) by Fe3O4@SiO2@mC-H2O2 (PDF).

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Notes

The authors declare no competing financial interest.

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