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1. Introduction

Endocrine-disrupting chemicals (EDCs) can simulate, strengthen or inhibit the effect of natural hormones and may bring about hyperplasia and tumors in the tissue or organs.¹ Bisphenol A [2,2-bis(4-hydroxyphenyl) propane; BPA], however, as one of the most widely used endocrine disruptors in industry, serves as a monomeric material for the production of polycarbonate and epoxy phenolic resins and a stabilizer or antioxidant for numerous types of plastics.^{2,3} Reports have pointed out that BPA can leach out in heating cases from plastics and pollute food.4 Some reports have also revealed that BPA were detected in trade effluent, open water, ground water, even effluents of wastewater treatment plant and fish at a concentration ranging from microgram to nanogram per liter.^{5,6} Due to the wide use of BPA in our daily life, the public has paid great attention on the security of BPA. Thus, an effective, convenient and cheap method for quick removal of BPA in the contaminated water is of great importance and requirement herein.

Removal of bisphenol A by iron nanoparticle-doped magnetic ordered mesoporous carbon[†]

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Iron nanoparticle-doped magnetic ordered mesoporous carbon (Fe/OMC) was prepared by coimpregnation and carbothermal reduction methods, and used for highly effective adsorption and degradation of bisphenol A (BPA). Several techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption-desorption isotherms were applied to characterize the prepared composites. Batch experiments were conducted to explore the decontamination performance, and the results showed that the removal capacity can reach an equilibrium value of 311 mg g⁻¹ at an initial BPA concentration of 200 mg L⁻¹. Kinetic study showed that it agreed well with the pseudo-second-order model ($R^2 = 0.999$). In addition, the Langmuir and Freundlich models were used to describe the removal process. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis confirmed the existence of Fe⁰ nanoparticles in the obtained composites. The mechanism of interaction between Fe/OMC and BPA was investigated by Fourier transform infrared spectrometry (FTIR), XRD and XPS analyses. Furthermore, thermodynamics studies were carried out and the exhausted composites could be regenerated with ethanol and easily separated with a magnet.

> Recently, various methods were applied to deal with BPA contaminated water, such as adsorption,⁷ membrane separation,8 biological treatment,9 electrochemical10 and photochemical degradation,¹¹ and etc. Among these methods, adsorption is regarded as a preferred method due to its excellent properties of low investment, simple operation and small land occupation. In fact, the properties of the adsorptive material determine the adsorption effect. Therefore, researchers have been searching for a proper adsorbent for bisphenol A with larger adsorption capacity, wider working pH range and reusability for years. So far, ordered mesoporous carbon (OMC) with the characteristics of high chemical stability, large specific surface area, production feasibility was regarded as a promising adsorbents for BPA removal.12 Meanwhile, zero-valent iron has attracted researcher's great interest in contaminant treatment for its efficient reduction, micro electrolysis, adsorption and flocculation effects.^{13–15} It has been confirmed to be highly effective in the removal of numerous pollutants, including PCBs,16 bromides,17 dyes,18 heavy metals19 and BPA.20,21 In Yunfei Xi's work,²¹ the degradation of bisphenol A was a Fenton reaction where zero-valent iron was oxidized into ferrous ions by oxygen to produce hydrogen peroxide, then the hydrogen peroxide and bivalent iron oxidized BPA into inorganic state. Immobilizing the nano zero-valent iron on the ordered mesoporous carbon can effectively increase the contact area with pollutants, and prevent the agglomeration and further oxidation of nano zerovalent iron.²² Therefore, Fe/OMC was applied to the treatment

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of organic substances or heavy metals due to its high activity of adsorption and reaction.^{23,24} It can also be separated from liquid phase rapidly by an external magnet due to the magnetic property of the adsorbent endowed by the doped iron nanoparticles, and avoid the centrifugal separation or filtering operation. Therefore, the composite of Fe/OMC is a promising candidate to remove BPA without secondary pollution.

In this study, a systematic and detailed investigation into the adsorption and degradation towards BPA by Fe/OMC has been explored for the first time. The carbon matrix of the composite can effectively adsorb large amount of BPA, increase the contact area of iron nanoparticles with BPA, and prevent the agglomeration and deactivation of nanoparticles. The composite is also easy to separate and reuse because of its magnetic property. Kinetic theory of adsorption was conducted to account for the removal of BPA. The Freundlich and Langmuir equations were simulated to determine the most appropriate isotherms. A plausible mechanism for the BPA removal pathway was also proposed through X-ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis. Besides, thermodynamic study and consecutive adsorption-desorption cycles were also researched. The adsorption and degradation capacity of this proposed approach is remarkably high compared with the reported materials. Because of its high removal capacity, favorable stability and reusability, Fe/OMC offers a promising application in removal of organic pollutants.

2. Materials and methods

2.1. Materials

Pluronic copolymer P123 (EO20PO70EO20, EO = ethylene oxide, PO = propylene oxide) were obtained from Sigma-Aldrich Corp. Bisphenol A (BPA, the purity of 98%), lysine, tetraethoxysilane (TEOS), oxalic acid, furan methanol and other chemical reagent (all of analytical reagent grade) were provided by Shanghai Chemical Corp. The water used throughout the study in lab was ultrapure water (18.25 M Ω cm⁻¹).

2.2. Synthesis of Fe/OMC

Firstly, the mesostructured SBA-15 silica template was synthesized according to our previously reports.^{25,26} Then the Fe/OMC composites were prepared following a co-impregnation and carbothermal reduction method by adding sucrose as carbon source and mesoporous SBA-15 as hard template in terms of a previous literature27 with some modification. The experiment steps were as follows: firstly, 2 mM FeCl₃ was put into a mixture of 10 mL aqueous solution containing 2.5 g sucrose and 0.28 g H₂SO₄. Then, the mixed solution was dropped into 2 g SBA-15 powder and stirred evenly into a paste in the crucible. Afterwards, put the crucible into an oven heating at 100 °C for 6 h and then at 160 °C for another 6 h. In the next moment, 10 mL of multicomponent solution including 1.6 g sucrose and 0.18 g H₂SO₄ were added once more to the pre-treated sample and do the same heating operation again. Next, to carbonize the sucrose, the obtained material was calcined from room temperature to 850 °C with a heating rate of 2 °C min⁻¹ and kept at this state for 3 h under the protection of nitrogen flow. Finally, in order to remove the silica template, the acquisition was put into the sodium hydroxide solution (2 mol L⁻¹) at 90 °C for an hour and then filtered, washed with ultrapure water over and over again until the pH value of wash water was close to neutral. Repeat the above steps at least twice and dried at 60 °C for 24 h. For comparison, pure OMC without iron was also prepared with the similar method.

2.3. Materials characterization

Scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscopy (TEM, Tecnai G20) were used to describe the morphology and inner structure of the material. Nitrogen adsorption-desorption isotherms were conducted on a quantachrome instruments (Quadrasorb SI analyzer). X-ray diffraction (XRD, BRUKER D8 Advance) and Fourier transform infrared spectrometer (FTIR, Nicolet Magna-IR 750) were used to verify the possible existence of physical forms and functional groups. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, UK) with a resolution of 0.05 eV was proposed to investigate the surface elemental composition. Vibrating sample magnetometer (Quantum Design MPMS-XL-7) and Zetasizer Nano (ZEN3600, Malvern) were applied to confirm the magnetization and isoelectric point of the composites at room temperature, respectively. To determine the amount of Fe nanoparticles in mesoporous carbon, thermogravimetric analysis (TGA) was performed by a SDTQ600 thermogravimetric analyzer from ambient temperature to 1000 °C in air with heating rate of 5 °C min⁻¹.

2.4. Batch experiments

The adsorption and degradation experiments of BPA by Fe/OMC were studied with a batch equilibrium manner. All batch studies were proceeded in a series of 50 mL conical flask containing 10 mL various initial concentrations of BPA and 5 mg composites, then agitated on an air-bathing constant temperature vibrator at



Fig. 1 Synthesis procedure of Fe/OMC.

the speed of 150 rpm. Illustration of the synthesis procedure of Fe/OMC is presented in Fig. 1. In this study, initial concentration (75–400 mg L⁻¹), pH of the solution (3–13), contact time (5–360 min) and temperatures (25–45 °C) were investigated. At each preset sampling time, Fe/OMC in aqueous were extracted by external magnet, the residual concentration of each solution was determined by UV-Vis spectrophotometer (Shimadzu, UV-2550, Japan) at the wavelength of 276 nm. All the experiments were performed three times and the outcomes were the average of three duplicates. The amount of removed BPA (q_t) at time t and the removal percentage (R) were calculated by the following equations.

$$q_t = \frac{(C_0 - C_t) \times V}{W} \tag{1}$$

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\%$$
⁽²⁾

where C_0 and C_t (mg L⁻¹) represent the concentration of BPA at the initial and time t (mg L⁻¹), respectively; V (mL) is the volume of BPA solution; W (mg) is the quality of composites.

3. Results and discussions

3.1. Characterization of materials

SEM and TEM images of the OMC and Fe/OMC were shown in Fig. 2. SEM image of OMC shows that the sample presented rodlike morphology and those rods were slightly aggregated (Fig. 2a). From the upper right corner of the insert in Fig. 2a, many villous tiny holes were observed uniformly distributed throughout the rods. These tiny holes could increase the surface area of the material and are conducive to the adsorption and degradation process. The SEM image of Fe/OMC in Fig. 2b shows similar structures. To further study the conformational difference of OMC and Fe/OMC, TEM images of the two samples were obtained as Fig. 2c and d, respectively. It is clear to see that



Fig. 2 SEM images of OMC (a) and of Fe/OMC (b) and HRTEM images of OMC (c) and of Fe/OMC (d).

the ordered stripe-like structures of OMC were clearly visible, but the degree of order was slightly lower as for Fe/OMC, indicating the occurrence of damaging of mesoporous structure after the doping of iron. Fig. 2d also demonstrated that the iron nanoparticles with an average diameter about 20 nm were dispersed evenly on the carbon rod matrix including α -Fe, Fe₃O₄ or γ -Fe₂O₃ particles, and the details can be seen in XRD

diffraction patterns. The isotherm curves (Fig. S1[†]) show hysteresis loops of OMC and Fe/OMC in the P/P_0 ranging 0.6–0.9, which was regarded as the type IV isotherm with H1 hysteresis loop. This indicates that the Fe/OMC composite possesses uniform mesopores in accordance with what was shown in TEM image (Fig. 2c and d).28 The corresponding pore size distributions in the inset of Fig. S1[†] inferred from adsorption branches of isotherms by BIH method clearly confirm that OMC possessed a pore size distribution centered near 4.9 nm, while for Fe/OMC it appeared at 3.8 nm. The new peak might be relative with the introduction of iron, and it also results in a distinct decrease in both BET surface area (from 1620 to 536 $m^2 g^{-1}$) and pore volume (from 2.3 to 1.1 cm³ g⁻¹). Pore structure parameters of the two mesoporous materials were summarized in Table S1.† This distinct decrease might be due to that the iron destroyed the surface structure of carbon matrix in the process of calcinations or entered into channels partially occupying or even blocking the mesopores. The zeta potential of Fe/OMC under different pH is shown in Fig. S2.† The zero point of zeta potential was at pH of 4.76. The vibrating sample magnetometer (VSM) measurement was shown in the inset of Fig. S2.† The saturation magnetization strength of Fe/OMC was 10.54 emu g⁻¹, which was more beneficial for separation compared with the saturated magnetization values (6.1 emu g^{-1} and 2.5 emu g^{-1}) reported in previous studies.29,30

To determine the amount of Fe nanoparticles in mesoporous carbon, thermogravimetric analysis was performed from ambient temperature to 1000 °C in air with heating rate of 5 °C min⁻¹. As shown in Fig. S3,† the weight loss curve of Fe/OMC showed three different stages: (i) the first 4.5% weight loss below 100 °C was attributed to the departure of the moisture; (ii) the second 4% mass loss at 100–440 °C was ascribed to the sublimation and/or decomposition of the carbon impurity (such as amorphous carbon); and (iii) when the temperature increased further, the third 55.9% mass loss between 450 and 861 °C corresponded to carbon combustion, which is a decomposition of mesoporous carbon skeleton. Last, the relative weight of Fe/OMC can be remained with increasing of temperature from 861–1000 °C. So the actual weight of percentage of Fe nanoparticles in mesoporous carbon is 35.6 wt%.

3.2. The effect of initial pH on removal of BPA

The initial pH of the solution had a great influence on the properties of the objects, reagent and treating processes, because it can change the surface charge of reagent and the degree of ionization of the target molecule. In this study, the effect of initial pH of the solution on removal of BPA by Fe/OMC was studied in the pH ranging from 3 to 13 with initial BPA

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concentration of 200 mg L^{-1} , contact time of 360 min and the temperature of 25 °C. As shown in Fig. S4,† the removal capacity remained in high level (around 280 mg g^{-1}) at a wide pH range from 3 to 9, indicating that the binding affinity between the BPA molecule and the binding sites did not vary significantly under acidic, weak acidity and neutral conditions. However, the removal capacity dropped a lot from 294.9 to 76.6 mg g^{-1} when the solution pH increased from 9 to 13. Thus, unless stated otherwise, all BPA removal experiments in this study were done by pure water. The reason can be attributed to the following points, first of all, the p K_a value of BPA ranged from 9.6 to 10.2,³¹ and more than half of BPA molecules in aqueous solution were ionized into mono or divalent anions at pH values above 9 while the surface charge of Fe/OMC is neutral at pH of 4.76 (Fig. S2,† pH PZC). When the solution pH is very high, as a result, the electrostatic repulsion occurred between the BPA anions and the negatively charged composites. What is more, in alkaline condition, nanoscale zero-valent iron may change into metal hydroxide precipitated form a passivation layer that may make it inactive due to the following reactions.32,33

 $Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + OH^-$ (in alkaline solution) (3)

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (K_{sp} = 4.87 \times 10^{-17})$$
 (4)

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^-$$
(5)

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \quad (K_{sp} = 2.79 \times 10^{-39})$$
 (6)

3.3. Effect of contact time on BPA removal

Fig. S5[†] shows the effect of contact time and initial concentration on removal of BPA by Fe/OMC at 25 °C. The remaining concentration of BPA in aqueous solution was measured at different preset times with initial BPA concentrations of 100, 200, 400 mg L⁻¹ and a composite dosage of 500 mg L⁻¹. Results showed that a rapid removal rate takes place during the first 60 min and then slows down until the balance occurred at about 6 h.

Here, a simple and popular model, pseudo-second-order model, was applied to inspect the removal process. The equation of pseudo-second-order model could be expressed in general as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{7}$$

where q_e (mg g⁻¹) was the removal capacity of BPA at equilibrium, k (g mg⁻¹ min⁻¹) was the constant rate of pseudo-secondorder model at equilibrium. The statistic plots of t/q_t versus t are shown in Fig. S6.† Table 1 shows the value of q_e and k calculated from the slope and intercept of Fig. S6.† The values of correlation coefficient constants (R^2) assessed from the linear fitting of pseudo-second-order model were quite high at all tested concentrations (exceed 0.999). Hence, the experiment data exhibited good accordance with pseudo-second-order model, and make clear that the removal process of BPA may be

Table 1 Parameters of pseudo-second-order model for removal of BPA onto Fe/OMC at 25 $^\circ\text{C}$

$C_0 (\mathrm{mg g}^{-1})$	$k_2 \ (\min^{-1})$	$q_{ m e} ({ m mg \ g}^{-1})$	R_{adj}^{2}
100	0.0017	189.8	0.9998
200	0.0058	302.1	0.9996
400	0.0005	326.8	0.9993

a chemical adsorption and the rate-controlling step of chemisorption was probably the valence forces produced by sharing or exchanging electrons between Fe/OMC and BPA.³⁴

3.4. Sorption isotherms

In this study, two classic adsorption isothermal models, Langmuir and Freundlich isotherms were used to analyze the experiment data. The Langmuir isotherm model assumes that the adsorption occurred in a monolayer.³⁵ The Freundlich model was shown to be in accord with an exponential distribution of active sites which hypothesis that a multilayer adsorption takes place on the heterogeneous surface.³⁶ Their equations are expressed in eqn (8) and (9):

Langmuir:

$$q_{\rm e} = \frac{q_{\rm m} K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{8}$$

Freundlich:

$$q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n} \tag{9}$$

where $q_{\rm m} \,({\rm mg g}^{-1})$ is the maximum removal capacity, $q_{\rm e}$ is the same as eqn (3), $C_{\rm e} \,({\rm mg L}^{-1})$ is the equilibrium concentration of BPA in solution, $K_{\rm L} \,({\rm L mg}^{-1})$ is the Langmuir constant, and $K_{\rm F}$ and *n* are Freundlich constants and intensity factors, respectively.

The temperature and initial concentration are critical factors in the respect of the maximum removal capacity of the Fe/OMC for BPA.³⁷ The fitted curves by Langmuir and Freundlich model at three different temperatures (298, 308 and 318 K) are shown in Fig. S7,† and the relative parameters are counted and listed in Table 2. It could be found that the Freundlich isotherm model was more suitable for the consequence of higher correlation coefficient (R^2).

 Table 2
 Adsorption parameters for the Langmuir and Freundlich isotherm models

	Langmuir			Freundlich			
Т (К)	$K_{\rm L}$ (L mg ⁻¹)	$q_{ m m} \ (m mg~g^{-1})$	$R_{\rm adj}^2$	$K_{\rm F}$ (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	n	$R_{\rm adj}^2$	
298	2.87	347.2	0.794	141.86	5.19	0.970	
308	2.10	286.0	0.888	146.17	7.21	0.975	
318	1.52	256.1	0.892	149.68	9.24	0.944	

The performance of this resultant Fe/OMC was also compared with previously reported adsorbents^{35,38-44} for BPA removal (shown in Table 4). The adsorption and degradation capacity of the proposed approach in this work is remarkably high compared with these reported materials. The ordered mesoporous carbon holds large adsorption capacity for BPA and effectively increases the contact area of iron nanoparticles with pollutants, and the carbon skeleton can prevent the agglomeration and deactivation of nanoparticles.²² Moreover, the treatment method of BPA is very simple and convenient since the composite is easy to separate and reuse because of the magnetic property of the embedded iron oxide. It is indicated that Fe/OMC is a fairly promising candidate for the treatment of BPA contaminated water.

3.5. Effect of temperature on BPA removal

It is well known that temperature is an important factor in influencing the removal process. Three thermodynamic properties, enthalpy change (ΔH), entropy change (ΔS) and free energy change (ΔG) were applied to study the removal process of BPA at three different temperatures (298, 308 and 318 K). In addition, they can be obtained by the following expression:

$$\ln K_{\rm d} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(10)

$$K_{\rm d} = \frac{C_{\rm ad,e}}{C_{\rm e}} \tag{11}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{12}$$

where *R* is the universal gas constant (8.314 J mol⁻¹ K⁻¹), *T* is the solution temperature in Kelvin, K_d is the distribution coefficient; $C_{ad,e}$ (mg L⁻¹) is the equilibrium concentration of BPA on Fe/OMC and C_e is the same as eqn (8). The thermodynamic parameters are summarized in Table 3. The negative value of ΔH demonstrates the exothermic nature of the sorption process which is proved by much less removal capacity at high temperature. However, the negative value of ΔS indicated stability, good affinity and decrease of randomness of BPA by Fe/OMC in the whole removal process.⁴⁵ For another, the negative values of ΔG at different temperatures implied that the removal process of BPA by Fe/OMC was thermodynamic feasible, unconscious, and spontaneous.⁴⁶

3.6. The removal mechanism analysis

The proposed mechanism of BPA removed by Fe/OMC is presented in Fig. 3. After the adsorption of BPA onto Fe/OMC, a Fenton-like reaction possibly occurred on the surface. First, zero-valent iron on OMC was oxidized into bivalent iron by the naturally existing oxygen in water to produce hydrogen peroxide, and then the hydrogen peroxide reacted with bivalent iron to form hydroxyl free radical which would oxidize BPA into inorganic state. The possible reactions are proposed as follows:

$$Fe^{0} + O_{2} + 2H^{+} \rightarrow Fe^{2+} + H_{2}O_{2}$$
 (13)

$$2Fe^{3+} + Fe^0 \to 3Fe^{2+}$$
 (14)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
 (15)

$$OH + BPA \rightarrow CO_2 + H_2O$$
(16)

Table 3 Thermodynamic parameters for BPA removed by Fe/OMC (initial concentration, 150 mg L^{-1})

T (K)	Adsorption capacity $(mg g^{-1})$	K _d	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (KJ mol ⁻¹)	$R_{\rm adj}^2$
298	248.96	4.88	-20.84	-56.74	-3.93	0.999
308	236.59	3.73			-3.36	
318	222.56	2.87			-2.80	

 Table 4
 The comparison of removal performance of several adsorbents used for BPA removal

Adsorbent	$q_{\rm m} ({ m mg \ g^{-1}})$	рН	T (°C)	Isotherm model	References
Modified fibric peat	29	_	25	Langmuir model	38
$CNTs/Fe_2O_4^a$	46	6.2	25	Freundlich model	39
rGO-MNPs-3 ^b	106	6	25	Langmuir model	40
MMIPs ^c	122	_	_	Langmuir model	41
Hydrophobic zeolite	125	7	25	Langmuir model	42
Graphene	182	6	24	Langmuir model	35
Activated carbon–PCB ^d	227	7	25	Freundlich model	43
Lignin	237	6	23	Langmuir–Freundlich model	44
Fe/OMC	311	9	25	Freundlich model	This study

^{*a*} Carbon nanotubes grafted by magnetic Fe₃O₄ particles. ^{*b*} Reduced graphene oxide-magnetic nanoparticles. ^{*c*} Magnetic molecularly imprinted polymers. ^{*d*} Activated carbon–PCB (coconut shell-based).



Fig. 3 The proposed mechanism of BPA removed by Fe/OMC.





Fig. 4 XRD spectra of Fe/OMC (a) and BPA-adsorbed Fe/OMC (b).

Fig. 5 FTIR spectra of Fe/OMC (a), BPA-adsorbed Fe/OMC (b), BPAdesorbed Fe/OMC (c) and BPA (d).

where the process of BPA oxidation need to be further studied. To test whether the intermediate product H_2O_2 can directly oxidize BPA, different H_2O_2 (30%) dosage (0.1, 0.5, 1 mL) were added in 10 mL of BPA (100 mg L⁻¹) to react under the same conditions of the Fe/OMC removal process, and according to the measurement result, BPA was not oxidized, which indicated that the intermediate product H_2O_2 could not directly oxidize BPA, but react with Fe²⁺ to form 'OH.

From the wide-angle XRD diffractograms (Fig. 4), there exist two main forms of iron in the Fe/OMC. The two typical diffraction peaks at 44.6° and 65° could be identified to be the (110) and (200) planes of body-centered cubic α -Fe (JCPDS card no. 65-4899). In the process of calcination, elemental carbon and negative valent carbon in sucrose may restore the trivalent iron in FeCl₃ into zero-valent iron in acid medium with the protection of inert atmosphere.⁴⁷ The other four residual peaks emerged at 30.2°, 35.5°, 57° and 62.6° coincide with the planes of (220), (311), (511) and (440) from face centered cubic Fe_3O_4 (JCPDS card no. 65-3107) or cubic γ -Fe₂O₃ (JCPDS card no. 39-1346). The number and position of peaks in the spectra of BPA-adsorbed Fe/OMC (b) are most consistent with that of Fe/OMC. However, the peak corresponding to α -Fe became weak and shifted a little, and instead the peaks for Fe₃O₄ or γ -Fe₂O₃ were intensified. The valence states of elemental iron getting higher demonstrated that iron nanoparticles in the OMC matrix were oxidized by oxygen or participated in the degradation reactions of BPA.¹³

FTIR spectroscopy is a useful instrument in identifying the presence of specific functional groups on the surface of the substance. The FTIR spectrum of Fe/OMC (a), BPA-adsorbed Fe/OMC (b), BPA-desorbed Fe/OMC (c) and BPA (d) were analyzed and shown in Fig. 5. The broad and strong peak at 3351 cm⁻¹ can be attributed to the stretching vibration of O–H.⁴⁸ However, the stretching frequency of the O–H group had a shift from 3351

to 3391 cm⁻¹ after adsorption, which could be ascribed to hydrogen bonding between hydroxyl groups contained both in BPA and Fe/OMC.⁴⁹ Meanwhile, it can be found that many new peaks were recommended in the FTIR spectrum of Fe/OMC after BPA adsorbed. These new peaks at 2800-3000 and 500-1800 cm⁻¹ were in accordance with the peaks from the FTIR spectrum of BPA and presented significant intensities. These additional bands indicate that a mass of BPA molecules were adsorbed onto Fe/OMC. The peaks at 572 cm⁻¹ in Fe/OMC and BPA-adsorbed Fe/OMC spectra are ascribed to the Fe-O bond vibration, which turned out that magnetic iron nanoparticles were successfully introduced into the OMC matrix.50 BPAadsorbed Fe/OMC spectra showed aromatic ring deformation vibration of di-substituted benzenes at 551 cm⁻¹ and C-H vibrations out of the plane at 817 cm⁻¹.⁵¹ The peak at 1500 cm⁻¹ is assigned to the aromatic C=C stretching vibration,⁴⁹ and it also shifted a little after adsorption, indicating that there might be the π - π interaction between the benzene rings of BPA and Fe/OMC planes.⁵² These could also been proved by the following XPS analysis. Besides, comparing to Fe/OMC (a), there is a tiny

or no change occurred in the FTIR spectrum of BPA-desorbed Fe/OMC (c), indicating that the desorption of BPA from Fe/OMC by ethanol was efficient.

The results of XPS are shown in Fig. 6. Fig. 6a presented the full scan of two samples (fresh and after treated with the aqueous solution containing 200 mg L^{-1} BPA at 25 °C). Detailed XPS spectrum of the regions for Fe 2p, O 1s and C 1s of the fresh and spent composites are shown in Fig. 6b-f. As shown in Fig. 6b(i), there are two obvious peaks corresponding to the high energy (Fe 2p_{1/2}, around 725 eV) and low energy (Fe 2p_{3/2}, around 711 eV) asymmetric bands, respectively.53 In addition, a small peak at 707.5 eV corresponded to Fe^{0 27} and then vanished after reaction with BPA [Fig. 6b(ii)], which was possibly on account of the oxidation of Fe⁰ in the OMC matrix during the process of adsorption and degradation of BPA. XPS analysis was also used to study the variation of the Fe oxidation state in Fe/ OMC. As shown in Fig. 6b, the Fe 2p spectra of Fe/OMC before interaction with BPA were in the forms of FeO (710.8 eV) and Fe₂O₃ (714.7 eV). However, the peak of Fe–O had a shift from 710.8 eV to 708.1 eV and Fe₂O₃ had a shift from 714.7 eV to 711.6



Fig. 6 XPS survey of full scan of Fe/OMC before (i) and after (ii) reaction (a), Fe 2p before (i) and after (ii) reaction (b), O 1s before (c) and after (d) reaction and C 1s before (e) and after (f) reaction on Fe/OMC.

eV after adsorption which could be ascribed to BPA adsorbed or degraded by Fe/OMC. As shown in Fig. 6c, the O 1s peaks can be decomposed into four components originating from O-H (around 533.8 eV), O-C (around 532.7 eV), O=C (around 531.5 eV) and Fe-O (around 530.5 eV). The O-H on the surface of Fe/ OMC shifted from 533.8 eV to 534.9 eV after adsorption (Fig. 6d), which also proved that the hydrogen bonding could apply to explain the mechanism of adsorption between BPA and Fe/OMC. The OH⁻ occupied area of the spectra of O 1s changed from 27% to 33%, probably as a result of the formation of metalhydroxide in the process of reaction.³² In the O 1s spectra, the presence of the Fe–O group proved the oxidation of surface Fe⁰, which is in accordance with the Fe 2p and XRD analysis. As shown in Fig. 6e and f, the C 1s peaks was decomposed into four peaks of curve-fitting assigned to the C=C/C-H (around 284.9 eV), C-O (around 286.3 eV), C=O (around 288.7 eV) and C-C (around 291.1 eV). The C 1s band at around 286.3 eV and 288.7 eV may correspond to the C-O in carboxyl or phenol groups in the Fe/OMC skeleton and C=O in quinone group as BPA intermediates, respectively,54 and the total content of the two peaks changed from 20% to 23% after the reaction with BPA, which was possibly due to the adsorption and degradation of BPA on the surface of composites. Meanwhile, in Fig. 6f, C=C shifted a little after adsorption, thus, the result of the XPS spectroscopy was a new proof in demonstrating the presence of the π - π interaction between BPA and Fe/OMC. However, the C 1s spectra for the two samples changed almost nothing, indicating that the features of the skeleton of Fe/OMC are very stable.

3.7. Regeneration of Fe/OMC

For a good removal agent, regeneration and reuse are essential for practical application. In this study, regeneration experiments for Fe/OMC were conducted using ethanol as stripping solvent and magnet to separate, and the successive adsorptiondesorption cycles of removal amount and removal efficiency are shown in Fig. S8.† It can be observed that approximate 73% removal efficiency was reached in the first three cycles. With the increase of cycling times, little decrease was observed, and in the sixth absorption–desorption cycle, as high as 68% efficiency was obtained. All the above results suggested that Fe/OMC had a good performance for regeneration and reusability.

3.8. Application in real water samples

From a practical point of view, the composition of wastewater is extremely complex. To test the practical application of Fe/OMC for the removal of BPA in real water samples, tap water (pH 7.26) taken from the laboratory and river water (pH 7.8) from Xiangjiang River, Hunan, China were used for preparation of 200 mg L⁻¹ BPA contaminated water samples. After the adsorption process, more than 73%, 64% of BPA is removed by Fe/OMC for BPA-obtained tap water and river water, respectively, which is a little bit lower than that in ultrapure water (78.3%). It is suggested that Fe/OMC displays high removal capacity, and might offer an easy and effective method to treat BPA-contaminated water in industrial application.

4. Conclusions

In this study, a mesoporous carbon impregnated with iron nanoparticles was successfully prepared and used to remove BPA in wastewater. The synthesized composites possessed high ordering, high specific surface area (536 m² g⁻¹), excellent magnetic properties (10.54 emu g^{-1}) due to the magnetic nanoparticles (Fe⁰, Fe₃O₄ or γ -Fe₂O₃) inside. Batch experiments showed a high capacity (311 mg g^{-1}) for BPA removal performance over a wide range of pH at low temperature. Equilibrium experiment data were fitted well by pseudo-second-order kinetic model (0.999) and Freundlich model. Thermodynamic studies demonstrated that the removal is an exothermic and spontaneous process with a negative value of standard enthalpy change and free energy change. Discussions on the removal mechanisms with respect to XRD, FTIR and XPS analysis inferred that a lot of BPA molecules were adsorbed onto Fe/ OMC by hydrogen bond and π - π interaction. Besides, the process of adsorption may be accompanied by the redox reaction attributed to the changing form of nanoscale zero-valent iron before and after reaction. Moreover, the composites could be regenerated and reused by ethanol and magnet, and kept a relative high removal efficiency and the removal ability could still reach up to 272 mg g^{-1} even after six cycles of adsorption-desorption at initial concentration of 200 mg L^{-1} . The chemical characterization results obtained by each analytical technique were summarized in Table S2.† In conclusion, asprepared Fe/OMC composites own great removal capacity, favorable stability and reusability, and could be regarded as a promising candidate for organic pollutant removal in practical application.

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