Controllable synthesis of magnetic carbon composites with high porosity and strong acid resistance from hydrochar for efficient removal of organic pollutants: An overlooked influence

Xiangdong Zhu a, Feng Qian a, Yuchen Liu a, Daniel Matera b, Gang Wu b, Shicheng Zhang a, *, Jianmin Chen a

a Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China
b Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA

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A B S T R A C T

Facile fabrication of magnetic carbon composites (MCs) via pyrolysis of hydrochar in the presence of ZnCl₂ and an iron salt has been attracting enormous interest to simultaneously realize high-surface area and magnetization. During this synthesis, the interactions between the carbon matrix and iron salts have remained unknown. In this work, a closer look was taken on iron salt interactions and their respective effect on MC characteristics. These newly fabricated MCs can provide guidance for further design of efficient MCs. It was discovered that ferric chloride (FeCl₃) promoted the enhancement of MC porosity, largely due to the strong reduction reaction between amorphous carbon and iron oxide (γ-Fe₂O₃ and Fe₃O₄). Various other iron salts (including ferrous oxalate (FeC₂O₄), ferric citrate (FeC₆H₅O₇), and ferric sulfate (Fe₂(SO₄)₃)) were also evaluated. These compounds inhibited pore structure development, resulting from decreased carbonization seen in the composite. This phenomenon was observed from complexation reactions between Zn²⁺ and the corresponding anions of these salts. Also, high Fe content and low γ-Fe₂O₃:Fe₃O₄ ratios led to decreased acid resistance of the MC. Finally, higher porosity in resultant MCs resulted in larger adsorption capacity for organic pollutants (roxarsone). This study will aid in further optimization of MCs to ultimately maximum performance.

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1. Introduction

Recently, the modification and application of hydrochar obtained by hydrothermal carbonization (HTC) of biomass has received increased attention because of the ever-increasing energy crisis and environment-related concerns [1–8]. Magnetic carbon composites (MCs) with high porosity and strong acid resistance are largely required in fields of environment and agriculture, due to their high adsorption capacity for organic pollutants and facile magnetic separation [9–11].

The facile one-step fabrication of MC samples with sufficient porosity and magnetism (via thermal pyrolysis of hydrochar utilizing ZnCl₂ and an iron salt) has been well documented in literature [12,13]. The porosity and acid resistance of the MC could be tuned by controlling the activation temperature, ZnCl₂ content, and properties of the hydrochar material [13,14]. In this method, iron salts were incorporated to increase magnetic composition, while ZnCl₂ was added as a porogen to increase pore development in the sample. Recently, it has been observed that the iron salt can also improve the porosity of the carbonaceous material [15–18], and MC samples derived from simultaneous activation and magnetization have higher porosity than those activated by only ZnCl₂ [12]. Thus, it was evident that iron salts may have played dual role in the preparation process. However, during the synthesis process, the interaction mechanism between the iron salt and carbon matrix has been overlooked and thus has not been optimized.

Several iron salts have been used in the preparation of MC sample, for example, ferric chloride (FeCl₃) [12,19], ferric nitrate (Fe(NO₃)₃) [20,21], ferrous oxalate (FeC₂O₄) [22], ferric citrate (FeC₆H₅O₇) [20,22], and ferric sulfate (Fe₂(SO₄)₃) [15,23]. During heating, the transformation of Fe-species was governed by the following equations numbered 1 to 5 below [15,20,24]. Initially,
2Fe2O3 and ZnCl2 and iron salts, including FeCl3, Fe(NO3)3, FeC2O4, FeC6H5O7, and Fe2(SO4)3 were of analytical grade, and were used as-received without further purification. Reagent grade ROX was purchased from Aladdin Reagent Corporation.

2.2. Synthesis of magnetic carbon composites

MCs were prepared using a previously reported simultaneous activation and magnetization method [12]. Typically, 10 g of ZnCl2 and a desired amount of iron salt was mixed in 50 mL of deionized water. Then, 10 g of hydrochar was added to the solution. Samples were prepared with 0, 0.01, 0.02, 0.04, and 0.08 mol FeCl3 to discern its role. For comparison, different iron salts, including FeCl3, Fe(NO3)3, FeC2O4, FeC6H5O7, and Fe2(SO4)3, were used with 0.02 mol Fe content. These mixtures were shaken for 24 h and were then dried in air at 80 °C for 4 h. Subsequently, these dried mixtures were heat-treated at 600 °C for 90 min under a nitrogen gas flow of 1 l/min. The resultant carbonized sample was successively washed with diluted HCl (0.1 M) and water and finally dried at 100 °C for 4 h.

The as-prepared MCs are henceforth denoted as MC-X-Y, where X represents the iron salt used (i.e., Cl for FeCl3, N for Fe(NO3)3, O for FeC2O4, Cl for (FeC6H5O7), and S for Fe2(SO4)3), Y is the content of Fe in mole (i.e., 0, 0.01, 0.02, 0.04, and 0.08).

2.3. Characterizations of magnetic carbon composites

The elemental composition (C, H, N) was analyzed with an elemental analyzer (Vario EL III). The ash contents (including magnetic composition) of the MCs were measured after heating at 600 °C for 2 h in air. The surface area and porosity of each sample was analyzed using nitrogen adsorption–desorption isotherms which were obtained using a Tristar 3000 apparatus. The crystal structures of the samples were characterized by powder X-ray diffraction (XRD) at a scan rate of 4°/min and a step size of 0.02° in 2θ. Fourier transform infrared spectroscopy (FTIR, Nexus470) was used to examine the functional groups on the samples, over a wavenumber range of 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹. Raman spectra were obtained using the LabRam-1B spectrometer with the He–Ne laser operating at a wavelength of 514 nm. Curve fitting was then performed with a combination of Gaussian line shapes which were employed to minimize fitting error. X-ray photoelectron spectroscopy (XPS) was carried out on a RBD-upgraded PHI–5000 ESCA system (Perkin Elmer) with Mg Kα radiation (hv = 1253.6 eV). In general, the X-ray anode was run at 250 W and the voltage was maintained at 14.0 kV with a detection angle at 54°. Binding energies were calibrated by setting C to 1 s at 284.6 eV. The morphology of samples was examined through scanning electron microscopy (SEM, Phenom Prox).

Magnetic measurements were performed using a vibrating sample magnetometer (VSM, MPMS, SQUID) with a maximum magnetic field of ±20 K Oe at room temperature. Fe leaching of the samples (to test acid resistances) was performed at an MC concentration of 2000 mg/L with a 24 h contact time under a pH of 2.0 or 3.0, respectively. Additionally, the extracted Fe content in the MCs were determined by inductively coupled plasma (ICP, P-4010), following acid digestion (HCl–HNO3). The experiments of Fe leaching and Fe content were performed in duplicate.

2.4. Adsorption performance of magnetic carbon composites

Adsorption isotherm experiments were performed using a batch equilibrium technique by placing 0.02 g of MC in a glass vial containing 50 mL ROX solutions of various concentrations (50–500 mg/L). The mixtures were then shaken at 25 °C for 24 h. All adsorption experiments were performed in triplicate. After the adsorption equilibrium was attained, the solid adsorbent was filtered from the liquid phase by a 0.22-μm polytetrafluoroethylene
3. Results and discussion

3.1. Effect of FeCl₃ content on the characteristics of MCs

Firstly, the effect of FeCl₃ content on the characteristics of the resultant MCs was determined. As shown in Table S1, the ash content of the MCs gradually increased with increasing FeCl₃ content, and contributed to the increase of yield. This was further indicated by the strong positive correlation between the ash content and the yield ($R^2 = 0.99$, Fig. S1). Recently, FeCl₃ has emerged as a good porogen in the activation of carbonaceous materials [15,25,30]. As expected, a slight increase in $N_2$ adsorption with increasing FeCl₃ content was observed (Fig. S2). In addition, the first four MC (MC-Cl-0.01, 0.02, 0.04, and 0.06) exhibited a typical isotherm of type IV, indicating dominant microporous properties. The last MC (MC-Cl-0.08) exhibited an isotherm of type IV, suggesting formation of mesoporous structures.

Porosity is a key factor influencing the adsorption ability of MCs. The porosities of synthesized MCs are summarized in Table 1. Clearly, FeCl₃ exhibited an activation effect on the development of pores. Thus, FeCl₃ was not only used as the source of magnetic composition, it also contributed to the production of pores (i.e., acted as a porogen). The microporosity of the MC samples (indicated by $S_{mic}/S_{BET}$ and $V_{mic}/V_t$) were also directly related to their respective FeCl₃ contents. Notably, there was an obvious decrease in the microporosity at the highest FeCl₃ content.

The activation effect of FeCl₃ and the phase transformation of Fe species were interpreted using XRD analysis. XRD analyses were also conducted on samples before and after acid washing (0.1 M HCl). In the heat activation process, several Fe species could be generated on the basis of the aforementioned Equations (1–5). The formation of a ZnO (JCPDS 36–1451) phase, derived from the transformation of ZnCl₂, was significant during the heat treatment. The XRD pattern of FeCl₃ (Fig. S1 and Fig. S3). Fig. 1 indicated that metallic Fe (JCPDS 65–4899) was dominant in samples before acid washing, which was formed by the reduction of Fe₂O₃ and Fe₃O₄ with amorphous carbon (Equations (4) and (5)). FeCl₂ (JCPDS 16–0123) was also formed in the sample with the highest FeCl₃ content. Notably, there was an obvious decrease in the microporosity at the highest FeCl₃ content.

Surface areas and porosities of MCs as functions of FeCl₃ contents. Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$</th>
<th>$S_{mic}$</th>
<th>$S_{mic}^{jet}$</th>
<th>$V_{mic}$</th>
<th>$V_{mic}^{jet}$</th>
<th>$V_{mic}/V_t$</th>
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<tr>
<td>MC-Cl-0</td>
<td>829</td>
<td>779</td>
<td>94.0</td>
<td>0.453</td>
<td>0.387</td>
<td>85.4</td>
</tr>
<tr>
<td>MC-Cl-0.01</td>
<td>921</td>
<td>854</td>
<td>92.8</td>
<td>0.497</td>
<td>0.420</td>
<td>85.1</td>
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<tr>
<td>MC-Cl-0.02</td>
<td>910</td>
<td>849</td>
<td>93.2</td>
<td>0.482</td>
<td>0.416</td>
<td>86.2</td>
</tr>
<tr>
<td>MC-Cl-0.04</td>
<td>962</td>
<td>894</td>
<td>92.9</td>
<td>0.519</td>
<td>0.439</td>
<td>84.7</td>
</tr>
<tr>
<td>MC-Cl-0.08</td>
<td>1000</td>
<td>893</td>
<td>89.3</td>
<td>0.559</td>
<td>0.435</td>
<td>77.8</td>
</tr>
</tbody>
</table>

a. Brunauer–Emmett–Teller (BET) surface area measured using N₂ adsorption at $P/P_0$ of 0.04–0.3.

b. Micropore surface area calculated using the t-plot method.

c. Total pore volume determined at $P/P_0 = 0.99$.

d. Micropore volume calculated using the t-plot method.

After acid washing (0.1 M HCl) of the samples, iron oxide phases ($\gamma$-Fe₂O₃ JCPDS 39–1346 or Fe₃O₄ JCPDS 19–0629) were exposed, which could be explained according to Equations (2) and (3) (Fig. 1). A graphite peak (JCPDS 65–6212), derived from the calcination of biomass [15], also could be founded in the MC-Cl-0.01 sample. The disappearance of graphite peak in the other three samples (MC-Cl-0.02, 0.04 and 0.08) was resulted from the inhibition effect of coexisted substance ($\gamma$-Fe₂O₃ or Fe₃O₄), similar with the change of ZnO phase in the samples before acid washing. Based on Scherrer’s equation, the sizes of iron oxide crystals could be calculated as 42.9, 43.2, 41.9, and 41.8 nm for the MC-Cl-0.01, 0.02, 0.04, and 0.08 samples, respectively. Obviously, when the FeCl₃ content increased to 0.04 mol, the growth of crystalline phases was progressively restricted. Generally, the iron oxide phases would become aggregated due to the decrease of carbon coating [31].

XRD analysis cannot distinguish the $\gamma$-Fe₂O₃ and Fe₃O₄ phases effectively because these two species have similar characteristic peaks [31,32]. Hence, XPS analysis was used to further determine the Fe species on the synthesized MCs. The Fe₂p spectrum of $\gamma$-Fe₂O₃ shows peaks at 725.8 (Fe₂p₁/₂) and 712.4 eV (Fe₂p₃/₂), while the peaks corresponding to Fe₂p₁/₂ and Fe₂p₃/₂ for Fe₃O₄ are located at 723.5 and 710.2 eV [31,33]. As shown in Fig. S4, only the Fe₂p₃/₂ peak can be observed, because it was very likely that the iron oxides were enclosed by the carbon matrix. Furthermore, the Fe₂p₃/₂ peak can be well-fitted into two peaks, indicating that the $\gamma$-Fe₂O₃ and Fe₃O₄ phases coexisted in the synthesized MCs. The MC-Cl-0.04 sample had the higher Fe₃O₄ content, evidenced by a lower $\gamma$-Fe₂O₃/Fe₃O₄ peak area ratio. According to the Equation (3), Fe₃O₄ could be produced through the reduction of $\gamma$-Fe₂O₃ with a proper reductive agent, such as amorphous carbon and CO gas.

Magnetic property analysis indicated that the saturated magnetization of the prepared MCs was in the 8.4–28.9 emu/g range (Fig. 3), which was sufficient for application in magnetic separations from aqueous solution. Also, the highest magnetization was observed in the MC-Cl-0.08 sample, which was related to the Fe content in the MCs. In addition, acid resistance of MCs is particularly important during their recycling. As shown in Fig. S5, XPS spectra of the synthesized MCs showed very low iron content (<1 wt%), revealing that the iron oxide phases were well coated by the carbon layers [31]. This indicated that the synthesized MCs should have strong acid resistance. Table 2 shows that only ~1 wt% Fe for all samples was leached out and further verified the high acid–resistance of the prepared MCs. However, the concentration of leached Fe was strongly regulated by the Fe content of the MCs (Table 2), as further confirmed by the strong correlations between the Fe leaching concentration and the Fe contents of the synthesized MCs (Fig. S6).

It was reported that the graphitization degree ($I_{D}/I_{G}$ value obtained from Raman spectra) of porous carbon could be changed by the addition of a metal species [34,35]. Here, when the amount of loaded FeCl₃ increased up to 0.04 mol, the $I_{D}/I_{C}$ value increased, indicating a decrease in graphitization. However, further increasing FeCl₃ content beyond 0.04 mol, the $I_{D}/I_{C}$ value started decreasing slightly. Interestingly, a positive correlation between the iron oxide crystal sizes (obtained from the XRD results) and the $I_{D}/I_{C}$ value was observed (Fig. S7), suggesting that the crystal size, rather than Fe
content (seen with a very low correlation), controlled the graphitization degree of sample. These results indicated that the iron oxide with bigger size would better disperse into the carbon matrix to yield more Fe carbide, finally improving the degree of graphitization.

3.2. Effect of iron salt types on the characteristics of MCs

In Table S1, the types of the iron salts used for synthesis of MCs had a significant effect on the yield of the MCs, indicating that their properties would also be affected by the nature of the iron salt. FeCl₃-derived MCs had the highest carbon content and lowest H/C ratio among the synthesized MCs, indicating the highest degree of carbonization. Oppositely, the Fe₂(SO₄)₃-derived MC exhibited the lowest degree of carbonization.

N₂ adsorption isotherms shown in Fig. S8 indicated significant differences between the MCs derived from the various iron salts. In particular, the porosity of the MCs was strongly affected by the iron salt type. Among others, FeCl₃ was the most effective for porosity development. This was further confirmed by the porosity analysis of MCs synthesized only involving iron salt without added ZnCl₂ (Table S2). Fig. 4 compares the BET surface area of the resultant MCs as function of the iron salt type, indicating that only FeCl₃ has a promotional role in porosity improvement. During the synthesis process, FeCl₃ had a significant effect on the yield of the MCs, indicating that their properties would also be affected by the nature of the iron salt. FeCl₃-derived MCs had the highest carbon content and lowest H/C ratio among the synthesized MCs, indicating the highest degree of carbonization. Oppositely, the Fe₂(SO₄)₃-derived MC exhibited the lowest degree of carbonization.

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Fig. 1. - Effect of FeCl₃ content on the XRD pattern of synthesized magnetic carbon composites (before and after acid washing, activation temperature of 600 °C). (A color version of this figure can be viewed online.)

Fig. 2. - Correlations between the loss in Fe content and obtained BET surface areas and total pore volume for MCs synthesized from various FeCl₃ contents. (A color version of this figure can be viewed online.)

Fig. 3. - Effect of FeCl₃ loading on the hysteresis loop of the as-prepared magnetic carbon composites.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe leaching concentration (mg/L)</th>
<th>Fe leaching percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>pH 3</td>
<td>pH 2</td>
</tr>
<tr>
<td>MC-Cl-0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MC-Cl-0.01</td>
<td>1.91 ± 0.01</td>
<td>1.40 ± 0.01</td>
</tr>
<tr>
<td>MC-Cl-0.02</td>
<td>2.74 ± 0.05</td>
<td>2.30 ± 0.01</td>
</tr>
<tr>
<td>MC-Cl-0.04</td>
<td>4.06 ± 0.03</td>
<td>2.87 ± 0.05</td>
</tr>
<tr>
<td>MC-Cl-0.08</td>
<td>6.23 ± 0.06</td>
<td>5.09 ± 0.08</td>
</tr>
</tbody>
</table>

In Table S1, the types of the iron salts used for synthesis of MCs...
preparation of MCs using different salts, a strong inverse correlation was observed between the yields and the porosities (including BET surface area, micropore area, pore volume, and micropore volume) of the different iron-salt-derived MCs (Fig. S9), indicating that the development of porosity was partially determined by the extent of carbonization. In addition, all of the prepared MCs from various iron salts were typical microporous materials, indicated by their proportion of microporosity (i.e., $S_{\text{mic}}/S_{\text{BET}}$ and $V_{\text{mic}}/V_{\text{t}}$ shown in Table 3).

Morphological details of the MC-Cl-0.02 and MC-S-0.02 sample were compared by SEM studies for the further comparison of porosity. As shown in the Fig. 5, the samples appeared to be bulk structures with different porosities. Abundant surface pores were produced in the MC-Cl-0.02 sample, which contributed to the increase of surface area. However, a small pore count was observed in the MC-S-0.02 sample, confirming its decrease of surface area.

When FeC$_2$O$_4$, FeC$_6$H$_5$O$_7$, and Fe$_2$(SO$_4$)$_3$ were used as the iron sources, ZnCl$_2$ would lose its efficacy for pore development. This is largely the result of complexation reactions between Zn$^{2+}$ cations and the C$_2$O$_4$$^{2-}$, C$_6$H$_5$O$_7$$^{3-}$, and SO$_4$$^{2-}$ anions. To further verify this assumption, the XRD analyses were performed on the mixtures of hydrochar, ZnCl$_2$, and various iron salts treated by impregnation and drying (without heat activation). As shown in Fig. 6, the XRD pattern of the hydrochar mixture showed some new crystalline phases, ZnC$_2$O$_4$ (JCPDS 25-1029) and ZnSO$_4$ (JCPDS 33-1476), indicating that the Zn$^{2+}$ cations were complexed by the C$_2$O$_4$$^{2-}$ and the SO$_4$$^{2-}$ anions. Due to the weak crystalline structure, the possible Zn$_3$(C$_6$H$_5$O$_7$)$_2$ phase was not observed in the XRD pattern. The metallic Fe phase was also observed, resulting from the reducing ability of the carbonyl groups within the hydrochar [36].

The porosities for the hydrochar samples activated with these new complexes (ZnC$_2$O$_4$, Zn$_3$(C$_6$H$_5$O$_7$)$_2$ and ZnSO$_4$) were also determined. As shown in Table S2, compared with the ZnCl$_2$ activator, ZnC$_2$O$_4$, Zn$_3$(C$_6$H$_5$O$_7$)$_2$, and ZnSO$_4$ were not effective porogens for hydrochar activation. Thus, combined with XRD and porosity analyses, it can be confirmed that the porogen mechanism of ZnCl$_2$ is inhibited in the presence of iron salts (other than FeCl$_3$). This complexation decreased the degree of carbonization in the MC, finally inhibiting the porosity development and adsorption capacity of the carbon material.

To further interpret the influence of various iron salts on the formation of the Fe species, XRD analyses were performed at

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**Table 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}^{a}$ (m$^2$/g)</th>
<th>$S_{\text{mic}}^{b}$ (m$^2$/g)</th>
<th>$S_{\text{mic}}/S_{\text{BET}}$ (%)</th>
<th>$V_{\text{t}}^{c}$ (cm$^3$/g)</th>
<th>$V_{\text{mic}}^{d}$ (cm$^3$/g)</th>
<th>$V_{\text{mic}}/V_{\text{t}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC-Cl-0.02</td>
<td>910</td>
<td>849</td>
<td>93.2</td>
<td>0.482</td>
<td>0.416</td>
<td>86.2</td>
</tr>
<tr>
<td>MC-N-0.02</td>
<td>823</td>
<td>772</td>
<td>93.8</td>
<td>0.450</td>
<td>0.381</td>
<td>84.7</td>
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<tr>
<td>MC-Ox-0.02</td>
<td>692</td>
<td>650</td>
<td>94.0</td>
<td>0.396</td>
<td>0.322</td>
<td>81.5</td>
</tr>
<tr>
<td>MC-Ci-0.02</td>
<td>604</td>
<td>556</td>
<td>92.0</td>
<td>0.338</td>
<td>0.274</td>
<td>81.2</td>
</tr>
<tr>
<td>MC-S-0.02</td>
<td>492</td>
<td>456</td>
<td>92.6</td>
<td>0.304</td>
<td>0.227</td>
<td>74.7</td>
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</tbody>
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*a* Brunauer–Emmett–Teller (BET) surface area measured using N$_2$ adsorption at $P/P_0$ of 0.04–0.3.

*b* Micropore surface area calculated using the t-pplot method.

*c* Total pore volume determined at $P/P_0$ = 0.99.

*d* Micropore volume calculated using the t-pplot method.
Fig. 7. - Effect of iron types on the XRD patterns of resultant magnetic carbon composites activated at 500 and 600 °C (before and after acid washing). (A color version of this figure can be viewed online.)
different activation temperatures (Fig. S10 and Fig. 7). The peaks associated with Fe species cannot be detected until the activation temperature was above 400 °C. However, ZnO was produced from 400 °C onwards, indicating a low formation temperature compared to iron oxides. When the temperature increased to 500 °C, the metallic Fe and iron oxide (γ-Fe2O3 or Fe3O4) phases were observed in the samples before acid washing (MC-Cl-0.02 and MC-S-0.02), and the intensity of the peak corresponding to the metallic Fe phase was greatly increased at 600 °C for all samples (Fig. 7). It should also be pointed out that the peak intensity of metallic Fe at 600 °C was closely related to the porosity of the synthesized MC; the highest peak intensity of the metallic Fe phase was observed for the MC-Cl-0.02 sample with the highest porosity. This suggested that a high-porosity sample is related to the formation of metallic Fe species, partly due to the better coating effect from the carbon matrix and the greater reduction reaction between iron oxide and the carbon matrix. For the MC-S-0.02 sample, FeS (JCPDS 23–1123) and ZnS (JCPDS 36–1450) were also obtained at the activation temperature of 500 °C, further confirming the possible complication reaction between the SO42– anions and Zn2+ cations.

In Table 3, the porosity of the MC-N-0.02 sample was smaller than that of the MC-Cl-0.02 sample. The complication reaction between the Zn2+ and NO3– could not occur in this case. However, the content of Fe loss (12.4%) for the MC-N-0.02 sample was obviously lower than that for the MC-Cl-0.02 sample (24.2%), even lower than that of the MC-Cl-0.01 sample (24.2%). This suggested that a lesser amount of iron oxide was reduced by the amorphous carbon in the MC-N-0.02 sample (Equations (4) and (5)), leading to a decrease in the porosity of MC-N-0.02 sample. After the samples were washed with 0.1 M HCl, both the metallic Fe and the ZnO phases were removed, and the iron oxide (γ-Fe2O3 and Fe3O4) phases were exposed (Fig. 7). Moreover, both the FeS and ZnS phases in the MC-S-0.02 sample were retained, indicating a strong acid resistance due to the protection of carbon layers. It was observed that 600 °C was favorable for the formation of the iron oxide phases. Based on Scherrer’s equation, the sizes of the iron oxide crystals could be calculated as 43.2, 34.5, 30.8, 37.1, and 48.8 nm for the MC-Cl-0.02, MC-N-0.02, MC-Ox-0.02, MC-Cl-0.02, and MC-S-0.02 samples (activation temperature of 600 °C), respectively. Thus, the crystal sizes were somewhat affected by the iron salt type.

XPS analysis was used to explore the relative ratio between the γ-Fe2O3 and Fe3O4 phases in the various MCs. As shown in Fig. S11, the Fe2p1/2 peak (~725 eV) was not apparent for all samples, and only a weak Fe2p3/2 peak (~711 eV) can be observed. Furthermore, the detected Fe2p3/2 peaks matched well to those of γ-Fe2O3 (712.4 eV) and Fe3O4 (710.2 eV). Notably, the relative ratio between the γ-Fe2O3 and Fe3O4 phase was greatly affected by the type of iron salt. Both the MC-Ox-0.02 and MC-Cl-0.02 MCs yielded lower γ-Fe2O3:Fe3O4 ratios, indicating that these two samples had higher Fe3O4 contents. An MC with a high γ-Fe2O3 to Fe3O4 ratio exhibited a low graphitization degree (high Ip/Ig value), this was in good agreement with the positive correlation between the γ-Fe2O3:Fe3O4 ratio and the Ip/Ig value (Fig. S12).

Fig. 8 indicated a nonlinear and reversible behavior with a weak magnetic hysteresis loop, indicating a fine grain size for the embedded iron oxide crystals [37]. The saturation magnetization of the MCs derived from the chosen salts was in the 15.3–21.7 emu/g range (Fig. 8). As shown in Fig. S13, a low Fe content on the surface (<1%) was observed for all the iron-salt-derived MCs, suggesting that the iron species were well enclosed by the carbon layers [31]. Accordingly, the various MCs had strong acid resistance as summarized in Table 4. Under a leaching condition at pH 2, the MC-Ox-0.02 and the MC-Cl-0.02 samples had relatively higher Fe leaching concentrations, mostly due to the difference in the type of iron oxide involved in their syntheses. A strong positive correlations between the γ-Fe2O3:Fe3O4 ratio and the percentage of Fe leaching (at pH 2) was observed in Fig. S14, indicating that Fe3O4 had lower acid-resistance than γ-Fe2O3. It should also be pointed out that the leaching ability of the MC-S-0.02 sample is also partially due to solubility of the FeS phase. Hence, the MC-S-0.02 sample cannot be included in the aforementioned correlation (Fig. S14).

The SEM images of various iron-salt-derived MCs partly confirmed their degree of acid resistance. As shown in Fig. 9, the iron oxide particles (light dots) in the MC-Cl-0.02 and MC-N-0.02 sample were uniformly coated by the carbon matrix, indicating their strong acid resistance. However, in the MC-Ox-0.02, MC-Cl-0.02 and MC-S-0.02 samples, part of iron particles were dispersed on the surface of porous carbon without obvious aggregation, confirming their relatively weak acid resistance at pH 2.

### 3.3. Adsorption of roxarsone onto the prepared MCs

The variations in ROX adsorption as a function of the ROX concentrations at equilibrium are shown in Fig. S15. The Langmuir model was used to fit the adsorption data:

\[
\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}
\]

where \( C_e \) (mg/L) is the equilibrium concentration of ROX in the solution, \( q_m \) (mg/g) is the maximum adsorption capacity, and \( b \) (L/mg) is the Langmuir constant [38]. The linear forms of the Langmuir equation for the adsorption data are shown in Fig. S16. High regression coefficient \( R^2 = 0.99 \) for all the cases revealed that the Langmuir equation was well fitted to the adsorption behavior of ROX. Notably, the larger differences in ROX adsorption were observed among the various iron-salt-derived MCs compared to

<table>
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<th>Table 4 Fe content analysis during the acid leaching experiments for various MC samples.</th>
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<tr>
<td>Sample</td>
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<tr>
<td>pH 2</td>
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<tr>
<td>MC-Cl-0.02</td>
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<tr>
<td>MC-N-0.02</td>
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<tr>
<td>MC-Ox-0.02</td>
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<td>MC-Cl-0.02</td>
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<td>MC-S-0.02</td>
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**Fig. 8.** Effect of iron salt type on the hysteresis loop of the as-prepared magnetic carbon composites
the various FeCl₃-content-derived MCs. The maximum adsorption capacities \(q_m\) were 416.7, 400.0, 370.4, 322.6, and 270.3 mg/g for the MC-Cl-0.02, MC-N-0.02, MC-Ox-0.02, MC-Ci-0.02, and MC-S-0.02 samples, respectively. Compared to other reported adsorbents [39–44], the MC-Cl-0.02 and MC-N-0.02 samples exhibited larger adsorption capacities for ROX removal, suggesting that they are the most promising candidates for adsorptive ROX removal.

It is well documented that the adsorption of organic pollutants onto a porous carbonaceous material is mainly driven by the pore-filling effect [45,46]. As shown in Fig. 10, strong positive correlations \(R^2 \geq 0.96\) were observed between the porosities of various iron-salt-derived MCs and their ROX adsorption capacity \(q_m\), further confirming the pore-filling mechanism of the porous carbonaceous material. In parallel, ROX adsorption likely occurred onto iron oxides through a surface complexation between the As(V) moiety of the ROX molecule and iron oxide surface [39,40]. As shown in Fig. S17, the weak adsorptions between 890 and 760 cm⁻¹ in FT-IR spectra were assigned to the As–OH and As–OFe vibration, confirming the occurrence of the complexation reaction. However, the Fe content on the MC surface (concluded from the XPS analysis, Fig. S11) was relatively low. In addition, the activated carbon sample (without iron oxide, MC-Cl-0) also had high ROX adsorption capacity (Fig. S15 b), with insignificant peaks in the 890–760 cm⁻¹ range (Fig. S17). Thus, the ROX adsorption onto the synthesized MCs was mainly controlled by the porosity of the MCs with a small contribution from the complexation reaction.

4. Conclusions

In this work, simultaneous activation and magnetization is realized via a facile and high-efficiency method for the preparation of high-porosity and acid-resistant magnetic carbon materials. Due to the fact that the role of iron salt during synthesis has been overlooked for a long time, we systematically studied various types of iron sources in terms of their effects on porosity, acid resistance, and the adsorption capacity for the magnetic carbon materials. It was found that FeCl₃ is a valuable iron salt for use in the preparation of high-porosity and acid-resistant MCs. Our results demonstrated that the selection of iron salt is an important strategy. These findings have significant implications for the controlled synthesis of efficient MCs for maximizing their performance during the treatment of organic pollutants in waste water.
Future work will focus on the development of magnetic carbon synthesis by using multiple activators (such as K$_2$CO$_3$ and KOH) through a combination of currently successful FeCl$_3$ ratios along with other iron salts [47,48].

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2015.12.044.

Fig. 10. - Correlations between the maximum adsorption capacity ($q_{\text{m}}$, obtained from the Langmuir equation) and the porosity of the magnetic carbon composites derived from various iron salts: BET surface areas (a), micropore surface areas (b), total pore volumes (c) and micropore volumes (d). (A color version of this figure can be viewed online.)

![Graphs showing correlations between maximum adsorption capacity and porosity](image_url)

References


