

## Synthesis of Novel pH-Responsive Magnetic Nanocomposites as Highly Efficient Heterogeneous Fenton Catalysts

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Intelligent polymer was extendedly applied to fabricate a novel environmentally responsive Fenton catalyst in this study. The obtained magnetite/sodium carboxymethyl cellulose-*graft*-poly(acrylic acid) ( $\text{Fe}_3\text{O}_4/\text{CMC-g-PAA}$ ) nanocomposites showed perfect superparamagnetism, pH response, and superior catalytic activity. In a wide range of pH (3–9), the highly swollen polymer coating not only favored the dispersion of  $\text{Fe}_3\text{O}_4$  nanoparticles and protected them from leaching but also promoted interface mass transfer with large amounts of hydrophilic ingredients.

Fenton oxidation is one of the principal technologies in environmental remediation. However, when the Fenton process is used in practical wastewater treatment, it has several drawbacks, such as narrow working pH range and Fe sludge disposal problem.<sup>1</sup> As an active heterogeneous Fenton catalyst, magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles have attracted significant interest due to their advantages such as facile separation and recovery.<sup>2,3</sup> However, they have a strong tendency of aggregation because of their high surface energies and intrinsic magnetic interactions, which may result in obviously reduction of their reactivity. Many attempts have been made to increase the stability and activity of  $\text{Fe}_3\text{O}_4$  nanoparticles, such as the use of surfactants and chelating agents<sup>4,5</sup> and immobilization of  $\text{Fe}_3\text{O}_4$  in or on supports.<sup>6–9</sup> Although effective particle stabilization has been achieved through strong interparticle electrostatic and/or steric repulsions, stabilizers bring a surface diffusion barrier, which inhibits interactions between the highly reactive surface of nanoparticles and the target contaminants. Among all these studies, little attention was paid to the selectivity of the stabilizer on the reaction conditions.

Considering that the optimum pH of Fenton oxidation is around pH 3, an ideal stabilizer should respond rapidly to an acidic pH stimulus and consequently release the catalyst under this condition. Compared to the existing references, the purpose of the current study is to design a special intelligent polymer stabilizing coating that cannot only enhance nanoparticle dispersion and stabilization and decrease internal diffusion resistance but also undergo reversible swelling–deswelling transition in response to the environmental pH stimuli.

Herein, a nanocomposite with a semi-interpenetrating organic/inorganic network was synthesized based on linear sodium carboxymethyl cellulose (CMC), crosslinked poly(acrylic acid) (PAA), and  $\text{Fe}_3\text{O}_4$ . CMC is a water-soluble polysaccharide possessing both carboxylate and hydroxy groups that allow this “green” and inexpensive polysaccharide to exert strong interactions with metal particles. However, the intrinsic viscosity, strength, and heat-resistance of CMC are limited by its low molecular weight.<sup>10,11</sup> In the mean time, PAA is a polyanion composed of many carboxy side groups and is generally known to swell due to the deprotonation of the carboxylic acids to form carboxylate

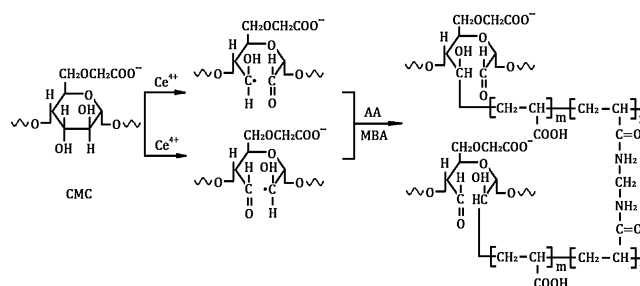


Figure 1. Grafting and crosslinking reaction of CMC and AA.

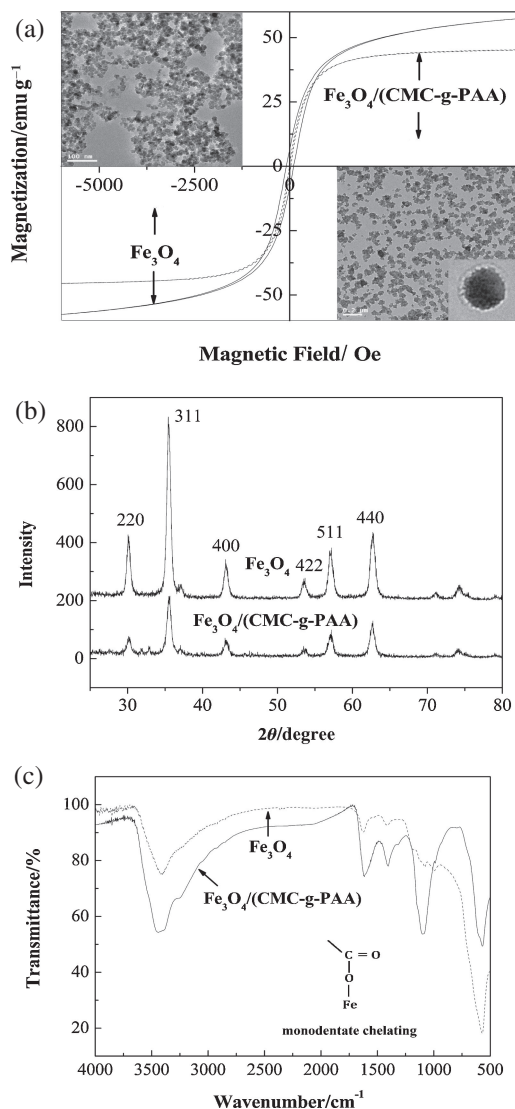
ions.<sup>12,13</sup> Therefore, the CMC polymer matrix was modified in this study with PAA by chain extension (Figure 1) to introduce the pH-responsive function and increase swelling ability. The pH-sensitivity and swelling behavior of the  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  nanocomposites were evaluated using phenol as typical organic pollutant to examine the catalytic performance of these nanocomposites for Fenton reaction.

Iron(III) chloride hexahydrate (1.623 g) and iron(II) sulfate heptahydrate (1.668 g) were dissolved in 150 mL of CMC solution ( $3.6 \text{ g L}^{-1}$ ), and then 40 mL of ammonia (2.5%) was added to it. After aging for 40 min, the resulting suspension was mixed with 167.2 mg of acrylic acid (AA) (partially neutralized by 10 mL of  $0.15 \text{ mol L}^{-1}$  NaOH solution), 2.7 mg of methyl-enebisacrylamide (MBA), and 10 mL of aqueous solution of cerium(IV) ammonium nitrate ( $1.06 \text{ g L}^{-1}$ ). The mixture was maintained at  $70^\circ\text{C}$  for 3 h. The whole reaction process was carried out in a nitrogen atmosphere. The obtained products,  $\text{Fe}_3\text{O}_4/\text{CMC-g-PAA}$  nanocomposites, were washed and vacuum-dried. Uncoated  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesized by coprecipitating  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions with ammonia.<sup>2</sup>

The catalyst ( $1 \text{ g L}^{-1}$ ) was dispersed in 100 mL of phenol solution (chemical oxygen demand (COD):  $500 \text{ mg L}^{-1}$ ). Degradation of phenol was initiated by rapidly adding  $\text{H}_2\text{O}_2$  ( $0.4 \text{ mL}$ , 30 wt %). The reaction mixture was vibrated at  $25^\circ\text{C}$  in the absence of light. At selected time intervals, aliquots (2 mL) were withdrawn and filtered for analysis. COD for the samples was measured using a COD measurement kit (Hach, U.S.).

The saturation magnetization value of  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  was found to be  $45.39 \text{ emu g}^{-1}$  (Figure 2a), which was lower than that of the  $\text{Fe}_3\text{O}_4$  ( $55.41 \text{ emu g}^{-1}$ ) but was high enough to be magnetically separated from solution.<sup>14</sup> The absence of coercivity and remanence indicated that the nanocomposites had a superparamagnetic property, which enabled them to redisperse rapidly when the magnetic field was removed.<sup>15</sup>

The individual particles of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  appeared quasi-spherical and had a diameter of about 10–20 and 40–100 nm, respectively (Figure 2a). Compared with the  $\text{Fe}_3\text{O}_4$  nanoparticles, the  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  nanocomposites exhib-

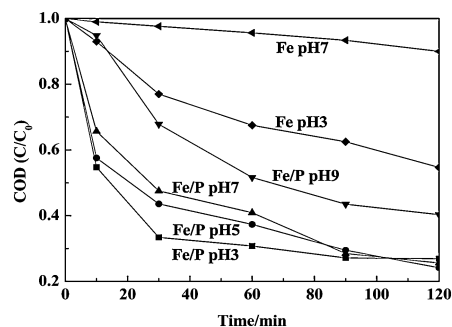


**Figure 2.** Vibrating sample magnetometer (VSM) spectra and transmission electron microscopy (TEM) images (scale bar: left 100 nm, right 0.2  $\mu\text{m}$ ) (a), XRD patterns (b), and FTIR spectra (c) of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$ .

ited excellent dispersion and had an undulant and coarse surface, which was due to the hydrophilic and swelling properties of polymer.

The X-ray diffraction (XRD) patterns revealed that the two nanomaterials had similar diffraction peaks, which could be indexed to the cubic phase of  $\text{Fe}_3\text{O}_4$  (Figure 2b). This result indicated that the crystal structure of  $\text{Fe}_3\text{O}_4$  was not changed after modification. The intensity decrease of  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  peaks was due to amorphous polymer coating on the  $\text{Fe}_3\text{O}_4$  surfaces. The crystal sizes of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  were both about 15 nm by calculation using the Debye–Scherrer formula.

In the Fourier transform infrared (FTIR) spectrum of nano- $\text{Fe}_3\text{O}_4$ , the characteristic absorption band of  $\text{Fe}_3\text{O}_4$  appeared at  $573\text{ cm}^{-1}$ . The broad band around  $3406\text{ cm}^{-1}$  was assigned to the  $-\text{OH}$  group. In the spectrum of  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$ , the characteristic peak of  $\text{Fe}_3\text{O}_4$  was much weaker than that in the



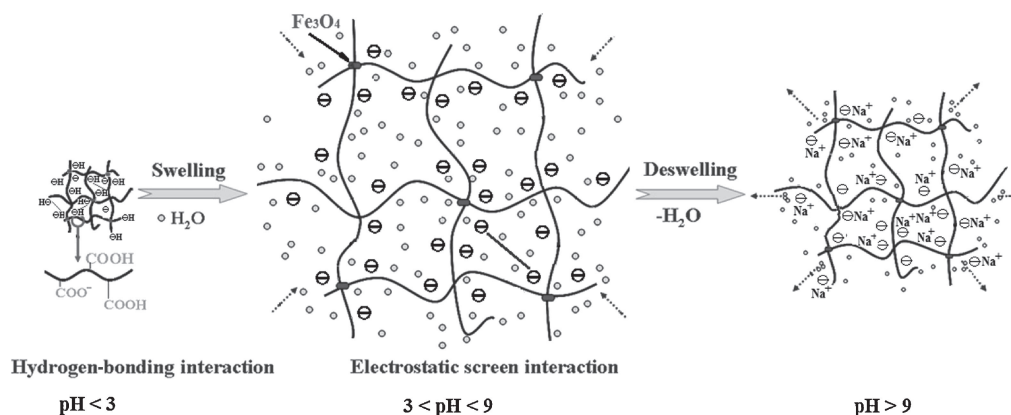
**Figure 3.** Effects of initial pH on COD abatement using  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  (Fe/P) and  $\text{Fe}_3\text{O}_4$  (Fe) catalysts.

spectrum of  $\text{Fe}_3\text{O}_4$ , and many absorption bands of CMC-g-PAA appeared. The peaks observed at  $3444$  and  $3246\text{ cm}^{-1}$  were due to  $-\text{OH}$  and  $-\text{CONH}_2$  stretching, the peak at  $1101\text{ cm}^{-1}$  was due to  $\text{CH}_2-\text{O}-\text{CH}_2$  stretching, while the peaks at  $1614$  and  $1404\text{ cm}^{-1}$  were due to  $-\text{COO}$  asymmetric and symmetric stretching, respectively. The separation of the symmetric and asymmetric stretches of the carboxylate group [ $\Delta\nu = \Delta(\text{asym}) - \Delta(\text{sym})$ ] was used to determine the bonding mechanism in many other reports.<sup>16,17</sup> In this work,  $\Delta\nu$  was  $210\text{ cm}^{-1}$ . Thus, monodentate interaction was the primary mechanism for binding CMC molecules to  $\text{Fe}_3\text{O}_4$  nanoparticles (Figure 2c).

Fenton oxidation experiments of phenol were conducted using the prepared  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  as catalyst, respectively. The reaction scheme on degradation of phenol has been frequently reported in the literature.<sup>2,3</sup> Control studies using either  $\text{H}_2\text{O}_2$  or catalyst alone showed that no phenol was degraded in the solution. As shown in Figure 3, only 10% of phenol was mineralized at neutral pH in the  $\text{Fe}_3\text{O}_4-\text{H}_2\text{O}_2$  system, while 75% of phenol was mineralized in 120 min (pH 3–7) in the  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})-\text{H}_2\text{O}_2$  system. Surprisingly, the mineralization rate of phenol catalyzed by  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  at pH 9 was even higher than that catalyzed by  $\text{Fe}_3\text{O}_4$  at pH 3. The superior catalytic performance of  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  can be explained as follows: (i) the polymer shell can prevent particle aggregation, providing highly effective surface area; (ii) the water absorbent polymer may allow a rapid diffusion of reactant molecules;<sup>18</sup> (iii) the binding between carboxy groups and iron oxide surfaces may lead to the rapid regeneration of Fe(II) species and production of  $\bullet\text{OH}$  radicals.<sup>19,20</sup>

It was noteworthy that the  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  nanocomposites exhibited high catalytic activity over a wide pH range, which could be associated with the pH-sensitive characteristic of the polymer shell. The responsive behaviors of nanocomposites in aqueous solutions with different pH values (pH 2–10) were investigated by dispersibility analysis.<sup>21</sup> Between pH 3 and 9, the nanocomposites were well dispersed in water and remained stable for more than a week. However, when the solution pH was lower than 3 or higher than 9, the nanocomposites rapidly flocculated and accumulated at the bottom of the centrifuge tube. This revealed that the polymer chains reached higher swelling ratio in the pH range from 3 to 9 but shrank when the pH is too low or too high and exhibited pH-sensitive “on–off” switching behavior, which made them suitable candidates for controlled nanoparticle-delivery systems.<sup>22</sup>

In  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$ , the polymer was not only bonded to the  $\text{Fe}_3\text{O}_4$  surface but also formed a crosslinked network, so



**Figure 4.** Schematic illustration of the swelling–deswelling mechanism of the  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  nanocomposites under various pH.

that it could not be dissolved but only swelled in solution.<sup>23,24</sup> The swelling/deswelling mechanism of nanocomposites is shown in Figure 4. At low pH, most of the carboxylate anions are protonated. The hydrogen-bonding interaction among  $-\text{OH}$  and  $-\text{COOH}$  groups is strengthened, and the additional physical crosslinking is generated. So the network tends to shrink. At higher pH, carboxy groups are ionized. The hydrogen-bonding interaction is broken, and the electrostatic repulsion between  $-\text{COO}^-$  groups increases. The network tends to swell. The reason for the deswelling in the highly basic solution is due to the “charge screening effect” of excess  $\text{Na}^+$  in the media, which shields the carboxylate anions and prevents effective anion–anion repulsion.<sup>12,25</sup>

Obviously, the polymer shell was maintained in a stretched state under a wide pH range of 3–9, which could provide steric stabilization to prevent aggregation. This loose surface coating did not obviously obstruct the contact of target substance with the active site of the inner catalyst. Instead, the hydrophilicity of polymer favored the interfacial reaction between the reactant and  $\text{Fe}_3\text{O}_4$ . The nanocomposites kept stable high catalytic activity (75%) at pH 3–7 because of the sufficient contact and reaction. However,  $\text{H}_2\text{O}_2$  is easily decomposed in basic solution. Therefore, despite the nanocomposites still being in the swelling state, the degradation rate decreased to 60% at pH 9. When the solution was under low (<3) or high pH (>9), the polymer would shrink to inhibit the transportation of solution through the coat and protect the inner  $\text{Fe}_3\text{O}_4$ .

After the Fenton reaction, the concentration of Fe ions in the solution was determined to be less than  $1 \text{ mg L}^{-1}$ . When  $1 \text{ mg L}^{-1}$   $\text{Fe}^{2+}$  was employed as a homogeneous Fenton catalyst under the same condition (pH 7), the COD removal was negligible. This result indicated that the degradation of phenol was mainly due to the catalytic heterogeneous reaction. The reusability of the catalyst was examined under identical oxidation conditions. COD (72%) was removed even the catalyst was reused for three times (pH 5), suggesting that the reused  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  may still maintain high reactivity. The excellent stability and reusability could significantly reduce the operation cost in practical applications.

In summary, this study employed pH-responsive polymer to encapsulate the magnetic nanoparticles. With advantages of high dispersion, sufficient iron supplement, and rapid diffusion, the prepared  $\text{Fe}_3\text{O}_4/(\text{CMC-g-PAA})$  nanocomposites exhibited outstanding Fenton catalytic activity and stability in a wide pH

range. These nanocomposites could be promising novel heterogeneous catalysts for the treatment of organic pollutants in wastewater.

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