In situ formation of nanoscale zero-value iron on fish-scale-based porous carbon for Cr(VI) adsorption

Chengming Li, Bicheng Huang, Chengxian Li, Xiao Chen and Yaqin Huang

ABSTRACT

Magnetic carbon materials that have nanoscale zero-valent iron (nZVI) supported on fish scale based hierarchical lamellar porous carbon (FHLC) is reported in this study. The nZVI on FHLC was in the form of body-centered-cubic iron (Fe) crystal. Although it was demonstrated that the specific surface area ($S_{ BET}$), total pore volume ($V_t$) and micropore volume ($V_m$) of the FHLC decreased with the increase of Fe contents, a certain amount of addition of iron nanoparticles on FHLC enhances the Cr(VI) adsorption properties. The as-prepared material shows faster adsorption rate and higher maximum adsorption capacity (357.14 mg/g) compared to bare FHLC (344.83 mg/g). In addition, this magnetic carbon material exhibits a high saturated magnetization (16.49 emu/g). It is indicated that the as-prepared carbon material not only can be used to remove Cr(VI) efficiently but also shows excellent magnetic separation performance from wastewater.

Key words | adsorption, fish scale, hexavalent chromium, zero-value iron

INTRODUCTION

Chromium (Cr) produced from industrial water discharge is a major toxic element found in the environment (Li et al. 2013). The most common oxidation states of chromium range from $+3$ to $+6$. However, Cr(VI) is the most hazardous, as it can diffuse through cell membranes in the form of CrO$_4^{2-}$ or HCrO$_4^-$, and subsequently oxidizes biological molecules (Krishna et al. 2004). Therefore, hexavalent chromium (Cr(VI)) has to be removed before being discharged into the aquatic system.

Of various removal processes, adsorption technology attracts the most attention in both fundamental studies and industrial applications, due to its easy operation and capability to adsorb a wide range of materials (Zhao et al. 2011). Among a variety of adsorbent materials, activated carbon with high efficiency stands out for its extensive pore surface area, interconnected pore structure and unique surface chemistry (Li et al. 2013). Activated carbon possesses three types of oxygen-containing surface groups such as acidic, neutral and basic. The presence of acidic surface oxides renders the carbon surface hydrophilic and polar in character which, in turn, gives rise to adsorption of polar and ionic species such as heavy metals (Kirk-Othmer 2007). Despite the demand of activated carbon for Cr(VI) adsorption is high, its high cost hinders its wide application. Another problem of the industrial removal processes is the separation of the Cr-absorbed carbon materials. Traditional separation methods involved filtration or centrifugation, which is tedious, laborious, energy intensive and expensive (Zhang et al. 2014). Although the addition of magnetic particles may help (Zhu et al. 2008; Zhang et al. 2010; Lv et al. 2011; Chen et al. 2013; Zhu et al. 2011), such materials usually result in low adsorption capacity and saturated magnetization, thus they are not good for industrialization. Therefore, our research group focuses on fish scale to develop a cost-effective activated carbon with high adsorption capacity, (Chen et al. 2010; Huang et al. 2014) and also designs a novel strategy.

Fish scale is a byproduct of fisheries, and approximately 50,000 tons of fish scale is discarded as waste every year in China (Huang et al. 2014). Moreover, we have demonstrated that fish scale, which is composed of collagen fiber and inorganic calcium-deficient hydroxyapatite, can be employed to prepare porous carbon materials. Here, collagen could provide affluent carbon resource, and hydroxyapatite acts as a natural template for the formation of a porous structure (Chen et al. 2010). The potential benefits of fish scale based hierarchical lamellar porous carbon (FHLC) are: (1) FHLC has high surface area and hierarchical porous structure, which could enhance the dispersibility of nanoscale
zero-valent iron (nZVI) particles and promote more adsorption sites for Cr(VI); and (2) abundant functional groups existing on the carbon surface are favorable to interact with Cr(VI) under acidic conditions.

Based on these considerations above, we developed an economic in situ synthetic strategy to prepare nZVI supported on FHLC. FHLC could reduce iron chloride to zero-valent iron without any other additive due to its high reducibility under 850°C. The abundant groups in FHLC provide quantity sites to complex with Fe(III), and extensive pore surface area enhanced the dispersibility of nanoscale zero-valent iron formed in situ. We hope as-prepared materials could have excellent Cr(VI) adsorption properties and high saturated magnetization which make the sorbent easily separated. More interestingly, we found that a certain amount of addition of iron nanoparticles on FHLC can enhance the Cr(VI) adsorption capacity. The effects of pH value, initial Cr(VI) concentration and time on Cr(VI) adsorption capacity for magnetic fish-scale carbon were studied in this study.

MATERIALS AND METHODS

The stock solution of Cr(VI) in deionized water was prepared at a concentration of 1,000 mg/L from water-soluble metallic salts (K2Cr2O7). Solutions containing 0.1 mol/L NaOH and 0.1 mol/L HNO3 were used to adjust the pH of the water samples. Fish scales from tilapia were collected from Dali in Yunnan province. All reagents were of analytical grade and were commercially available from Beijing Chemical Works and were used without further purification.

Materials preparation

Tilapia fish scale was used to fabricate FHLC via pre-carbonization at 330°C followed by activation at 900°C with potassium hydroxide (KOH) as an activator. 0.2 g FHLC was mixed with iron chloride solution by milling in an agate mortar until forming a thick paste. Fe content was controlled by using a different mole number of iron chloride (0.5 mmol, 1.0 mmol, and 1.5 mmol). The paste was then calcinated at 850°C for 2 h under pure N2 environment (with purity of 99.99%). These products are denoted as FHLC-nZVI-0.5, FHLC-nZVI-1.0, FHLC-nZVI-1.5, respectively, in this article.

Characterization

The products were characterized by X-ray diffraction (XRD) using a Rigaku D/max-2500VB2 + /pC diffractometer. The scanning electron microscopy (SEM) images were taken on a HITACHI S-4700 electron microscope. Transmission electron microscopy (TEM) measurements were carried out on an H-800 microscopy at 200 kV. N2 adsorption-desorption isotherms at 77 K were measured using an adsorption instrument (Micromeritics ASAP 2020) to evaluate the surface area and pore-structure of adsorbents. Magnetic measurements were carried out on a magnetometer (Lake Shore 7410 VSM) at room temperature.

Adsorption experiments

Adsorption equilibrium experiments were carried out in a temperature-controlled thermostatic shaker operated at 130 rpm. For the adsorption isotherm experiments, 3 mg adsorbent was added into 5 mL of Cr(VI) solutions (50–400 mg/L, pH 2 at 30°C). For the kinetic experiments, 5 mL of 100 mg/L Cr(VI) solutions at pH 2 and 3 mg adsorbent were contacted in a weigh bottle. Samples were withdrawn at appropriate time intervals. The effect of pH on Cr(VI) adsorption was studied at different pH values (2–6) with 3 mg adsorbent and an initial Cr(VI) concentration 100 mg/L at 30°C. The concentrations of Cr(VI) in the supernatant were determined by UV-vis adsorption spectroscopy. And the amount of Cr(VI) adsorbed on the adsorbents was calculated using the following equation:

\[ Q_e = (C_0 - C_e)V/m \]  

where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of Cr(VI) (mg/g), respectively, \( V \) is the volume of solution (L) and \( m \) is the mass of adsorbents used (g).

RESULTS AND DISCUSSION

Characterization of modified FHLC

The XRD patterns of synthesized samples are shown in Figure 1. Compared with the broad peak of amorphous FHLC (Figure 1(a)), the XRD patterns of the modified FHLC (Figure 1(b)–1(d)) show sharp peaks at 44.7°, 65.0° and 82.0°, corresponding to the (110), (200) and (211) diffraction planes of the body-centered-cubic Fe, respectively (JCPDS 06-0696). Using Scherrer equation, the Fe crystal sizes are estimated to be 26.4 nm, 27.7 nm, and 30.8 nm for FHLC-nZVI-0.5, FHLC-nZVI-1.0, FHLC-nZVI-1.5, respectively. This indicates that Fe has been crystallized on FHLC after calcination. The small peak at 55.4° may
come from ferriferous oxide or ferric oxide due to the oxidation of Fe surfaces. XRD results confirmed that all modified FHLC consisted of amorphous carbon and crystallized Fe.

Figure 2 shows SEM and TEM images of the fish scale carbon with and without nZVI. SEM images show that the porous structures of FHLC-nZVI-0.5 are kept. Rich hierarchical and interconnected porous structures can also be clearly observed, thus creating high surface area for facile diffusion of Cr(VI) during adsorption (Li et al. 2015). After nZVI was loaded on, some spherical plots were visible in Figure 2(d). These particles were proved to be nZVI by previous XRD analysis. TEM image suggests that these nZVI particles are spread on the surface or inside the network of FHLC. The average particle size is 28 nm which is close to the result measured by XRD.

Figure 3 shows the nitrogen adsorption–desorption isotherms and Table 1 lists the textual characteristics of the samples. All the nitrogen adsorption–desorption isotherms had a type IV shape with obvious hysteresis loop and the final climbing tail at the relative pressure from 0.9 to 1.0 (Huang et al. 2011). It was demonstrated that the specific surface area ($S_{BET}$), total pore volume ($V_t$) and micropore volume ($V_m$) of the FHLC decreased with the increase of Fe contents, while the mean pore diameter ($D_{mean}$) increased. The nZVI particles could block the micropore of FHLC, leading to the decrease of the specific surface area and the growth of the mean pore diameter. It was well known that the adsorption properties of an adsorbent for Cr(VI) depend on its high specific surface area, the pore properties, functional groups and so on. Adsorption properties of FHLC and modified FHLC will be discussed in the following section.
Adsorption properties

We now focus on the pH of a solution, which is an important factor affecting the adsorption because it involves both the aqueous charge distribution and the surface binding site of the adsorbent (Wei et al. 2016). Previous work showed that Cr(VI) exists as H2CrO4 for pH < 1.0, HCrO4/-Cr2O72- for 2.0 < pH < 6.0, and CrO42- species for pH > 6.0 in aqueous solutions (Hamadi et al. 2013; Levankumar et al. 2009). It can be seen from Figure 4 that the Cr(VI) adsorption onto FHLC and FHLC-nZVI-0.5 decreased as the pH increased from 2 to 6. As the pH of the Cr(VI) aqueous was lowered, more protons could easily coordinate with functional groups present on the sorbent surface (Wei et al. 2016). Therefore, Cr(VI) is more easily adsorbed on FHLC and FHLC-nZVI-0.5 when the pH is low. The higher adsorption capacity of FHLC-nZVI-0.5 than that of FHLC can be explained by the increasing respective adsorption sites after supporting nZVI. It is obvious to find that the adsorption of FHLC-nZVI-0.5 is much higher at high pH. This reason may be inferred that the surface of Fe0 (Fe2O3) is hydroxylated and the negatively charged surface can exchange chromate anions (Hu et al. 2005).

To quantify the adsorption properties of these new carbon materials, we used Langmuir and Freundlich isotherms to describe the equilibrium established between adsorbed metal ions on the adsorbent (Qe) and metal ions remaining in solution (Ce) at a constant temperature (Gupta & Ali 2004). The adsorption equilibrium curves of Cr(VI) on the samples are shown in Figure 5. The corresponding adsorption isotherm constants are given in Table 2. Both the Langmuir and Freundlich isotherm models fitted the adsorption data well and gave similar correlation coefficients. The maximum adsorption capacities of

Table 1 | The textural characteristics of the samples (Lu & Zhao 2004)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>S_BET (m^2/g)</th>
<th>V_t (cm^3/g)</th>
<th>V_mic (cm^3/g)</th>
<th>D_mean (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHLC</td>
<td>2671.74</td>
<td>1.80</td>
<td>0.79</td>
<td>2.69</td>
</tr>
<tr>
<td>FHLC-nZVI-0.5</td>
<td>2301.72</td>
<td>1.57</td>
<td>0.69</td>
<td>2.72</td>
</tr>
<tr>
<td>FHLC-nZVI-1.0</td>
<td>1662.27</td>
<td>1.18</td>
<td>0.49</td>
<td>2.84</td>
</tr>
<tr>
<td>FHLC-nZVI-1.5</td>
<td>1350.80</td>
<td>1.00</td>
<td>0.40</td>
<td>2.95</td>
</tr>
</tbody>
</table>

*S_BET, BET (Brunauer-Emmett-Teller) surface area, S_BET was measured in relative pressure range of 0.04-0.20.

V_t, total pore volume, V_t was measured at P/P_0 = 0.99.

V_mic, micropore volume, V_mic was determined using the Dubinin-Radushkevich equation.

D_mean, mean pore diameter, D_mean was estimated from Equation 4 V_t/S_BET.

Figure 3 | The nitrogen adsorption-desorption isotherm of the samples (a) FHLC, (b) FHLC-nZVI-0.5, (c) FHLC-nZVI-1.0 and (d) FHLC-nZVI-1.5

Figure 4 | Effect of pH on the Cr(VI) adsorption for (a) FHLC and (b) FHLC-nZVI-0.5.

Figure 5 | Adsorption amounts of Cr(VI) on the samples (a) FHLC, (b) FHLC-nZVI-0.5, (c) FHLC-nZVI-1.0, and (d) FHLC-nZVI-1.5 as a function of initial Cr(VI) concentration.
FHLC and FHLC-nZVI-0.5 based on the Langmuir model were as high as 344.83 mg/g and 357.14 mg/g, respectively, which could be attributed to the large surface area and high reactivity of nZVI. However, the maximum capacities decreased rapidly with the increased amount of nZVI. These results can be explained by the following: (1) according to the nitrogen adsorption–desorption isotherms, the specific surface area and total pore volume decreased with the increase of Fe contents; (2) although nZVI could provide adsorption sites for Cr(VI), functional groups in FHLC were covered by nZVI, especially in FHLC-nZVI-1.0 and FHLC-nZVI-1.5.

Figure 6(a) shows the time profile of Cr(VI) adsorption. Both adsorption curves exhibited the same trend: within 30 min, about 49% and 60% Cr(VI) were adsorbed onto FHLC and FHLC-nZVI-0.5, respectively. It is worth to note that the removal efficiency for Cr(VI) is much higher than other magnetic materials reported before this work. For example, nZVI particles supported on carbon nanotubes need 350 min to remove 60% of Cr(VI) with an initial Cr(VI) concentration of 60 mg/g, and chitosan/nZVI beads needed 100 min to removal 60% of Cr(VI) with a initial Cr(VI) concentration of 100 mg/g (Lv et al. 2011; Liu et al. 2012). In our case, Cr(VI) adsorption is rapid at first, and then slows down gradually until the equilibrium is reached. The adsorption process can be explained by the diffusion mechanisms, including external diffusion and intra-particle diffusion. To further understand the adsorption process, we applied the Weber-Morris equation:

$$Q_t = K_d t^{1/2} + L$$

where $L$ is the intercept (mg/g), $K_d$ is the diffusion rate constant (mg·g⁻¹·min⁻⁰.⁵) of the adsorption step, which is estimated from the straight line of $Q_t$ versus $t^{1/2}$. Plots of $Q_t$ versus $t^{1/2}$ for Cr(VI) adsorption on both FHLC and FHLC-nZVI-0.5 are shown on Figure 6(b). The values of $K_d$ and $L$ calculated from the slope and intercept are summarized in Table 3. As shown in Figure 6(b), both FHLC and FHLC-nZVI-0.5 have two distinct stages. According to the model, the first stage represented external mass transfer and the second stage represented intra-particle diffusion. At first, Cr(VI) diffused fast from the solution to the adsorbent exterior surface. Then Cr(VI) diffused from the adsorbent exterior surface to the pores or capillaries of adsorbent internal structure (Chen et al. 2013).

### Magnetic properties

Figure 7 shows the room temperature hysteresis loop of the FHLC-nZVI-0.5. The saturated magnetization ($M_s$) of the FHLC-nZVI-0.5 is calculated to be 16.49 emu/g. It is worth to note that the saturated magnetization is higher than that of

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$Q_m$ (mg/g)</th>
<th>$b$ (L/mg)</th>
<th>$R^2$</th>
<th>$K_f$ (mg/g)</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHLC</td>
<td>344.83</td>
<td>0.123</td>
<td>0.9956</td>
<td>86.54</td>
<td>0.2778</td>
<td>0.9823</td>
</tr>
<tr>
<td>FHLC-nZVI-0.5</td>
<td>357.14</td>
<td>0.170</td>
<td>0.9956</td>
<td>112.15</td>
<td>0.2338</td>
<td>0.9876</td>
</tr>
<tr>
<td>FHLC-nZVI-1.0</td>
<td>303.03</td>
<td>0.077</td>
<td>0.9900</td>
<td>70.11</td>
<td>0.2742</td>
<td>0.9883</td>
</tr>
<tr>
<td>FHLC-nZVI-1.5</td>
<td>270.27</td>
<td>0.084</td>
<td>0.9917</td>
<td>75.28</td>
<td>0.2328</td>
<td>0.9896</td>
</tr>
</tbody>
</table>

**Figure 6** | The adsorption kinetics (a) and corresponding Weber-Morris model (b) for Cr(VI) on FHLC and FHLC-nZVI-0.5.
of magnetic graphene nanocomposites (9.50 emu/g) and magnetic porous carbon microspheres (13.9 emu/g) (Zhu et al. 2013; Zhu et al. 2014). Although the saturated magnetization of FHLC-nZVI-0.5 is smaller in contrast with RHC-mag-CN (22 emu/g) (Li et al. 2016), the maximum Cr(VI) adsorption capacity of FHLC-nZVI-0.5 (357.14 mg/g) is much higher than that of RHC-mag-CN (16 mg/g). Furthermore, the added magnetic properties make the separation of adsorbent after Cr(VI) adsorption much easier compared to traditional labor-intensive filtration or centrifugation methods. These results revealed that the material can be considered as a promising, high-capacity and easily separated adsorbent for the adsorption of Cr(VI) from aqueous solution.

**CONCLUSIONS**

In summary, we have designed a new functional carbon material that has nZVI embedded in FHLC by a thermal reduction method. The as-prepared magnetic carbon material showed high saturated magnetization and enhanced adsorption properties for Cr(VI), a toxic element in the environment. The saturated magnetization and the maximum adsorption capacity of the as-prepared material were found to be as high as 16.49 emu/g and 357.14 mg/g, respectively. FHLC-nZVI-0.5 showed higher maximum adsorption capacity than FHLC (544.85 mg/g). These results revealed that the material can be considered as a promising, high-capacity and easily separated adsorbent for the adsorption of Cr(VI) from aqueous solution.

**ACKNOWLEDGEMENTS**

Financial support from the National Natural Science Foundation of China (nos 51272017 and 51432003) is gratefully appreciated.

**REFERENCES**


First received 25 September 2015; accepted in revised form 17 December 2015. Available online 9 February 2016