Fabrication of bimetallic Ag/Fe immobilized on modified biochar for removal of carbon tetrachloride

Hongwei Wu1,2, Qiyan Feng1,⁎

1. School of Environmental Science and Spatial Informatics, China University of Mining and Technology, Xuzhou 221116, China. E-mail: whw_1982@126.com
2. Department of Chemistry, Zaozhuang University, Zaozhuang 277160, China

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ABSTRACT

As an effective conventional absorbent, biochar exhibited limited adsorption ability toward small hydrophobic molecules. To enhance the adsorption capacity, a novel adsorbent was prepared by immobilizing nanoscale zero-valent iron onto modified biochar (MB) and then the elemental silver was attached to the surface of iron (Ag/Fe/MB). It’s noted that spherical Ag/Fe nanoparticles with diameter of 51 nm were highly dispersed on the surface of MB. As the typical hydrophobic contaminant, carbon tetrachloride was selected for examining the removal efficiency of the adsorbent. The removal efficiencies of carbon tetrachloride by original biochar (OB), Ag/Fe, Ag/Fe/OB and Ag/Fe/MB were fully investigated. It’s found that Ag/Fe/MB showed higher carbon tetrachloride removal efficiency, which is about 5.5 times higher than that of the OB sample due to utilizing the merits of high adsorption and reduction. Thermodynamic parameters revealed that the removal of carbon tetrachloride by Ag/Fe/MB was a spontaneous and exothermic process, which was affected by solution pH, initial carbon tetrachloride concentration and temperature. The novel Ag/Fe/MB composites provided a promising material for carbon tetrachloride removal from effluent.

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Introduction

Carbon tetrachloride, a hydrophobic organic matter, has been widely used in many industries such as petrochemical, pharmaceutical, and allied industries (Saleh et al., 2015). Carbon tetrachloride is a priority pollutant listed by United States Environmental Protection Agency (EPA), because of its toxicity (Poursaberi et al., 2014), persistence, and relative hydrophobicity (Maithreepala and Doong, 2004). However, the disclosure and emission of carbon tetrachloride has caused serious contamination of environmental matrices in many regions (Beatriz et al., 2012; Penny et al., 2010). For example, Qiligou water source (Xuzhou, East China) was contaminated by the leakage of carbon tetrachloride, the peak concentration up to 3909 μg/L, which led to the water source closure from November 2000 (Han et al., 2006). Carbon tetrachloride can also contribute to smog formation, ozone destruction and harmful odor generation which can result in chronic toxicity for humans, animals and vegetation (Saleh et al., 2015). Many techniques such as advanced oxidation technology (Lee et al., 2012), thermal oxidation (Xu et al., 2015), biodegradation (Kwon et al., 2016), adsorption (Liu et al., 2010) and reduction (Huang et al., 2009) are adopted to solve the environmental issues caused by carbon tetrachloride. Among them, adsorption strategy provides a cost-effective and efficient approach to remove carbon tetrachloride.

Biochar can be derived from many kinds of agricultural by-products, sludge and animal wastes under lower temperature
(<700°C) compared to activated carbon (AC) (Chen et al., 2011; Jiang et al., 2016). With large surface area, good porosity and abundant surface functional groups, biochar reveals a higher adsorption capacity than other carbon adsorbents (Luo et al., 2011). It was reported that biochar is a cost-effective and high-efficient adsorbent for heavy metals (Chen et al., 2011), anions (Jung et al., 2015) and organic compounds (Feng et al., 2013). However, biochar usually possesses lower aromaticity and hydrophobicity than AC since it contains more noncarbonized organic matter (Chen et al., 2008). There is a limited chance to contact with carbon tetrachloride by biochar in aqueous solution due to that carbon tetrachloride is a hydrophobic and dense substance. The hydrophobicity, pore volume and varieties of functional groups of biochar can be changed by physicochemical modifying, such as steam activation, chemical modification, impregnation and heat treatment (Ahmed et al., 2016; Liu et al., 2012). Therefore, it is expected that the adsorption capability of hydrophobic pollutants on biochar can be enhanced by suitable modification.

Over the past decades, nanoscale zero-valent iron (nZVI) and bimetallic systems (Ni/Fe, Pd/Fe, Ni/Sl and Ag/Fe) have been proved to be valid ways for the removal of chlorinated hydrocarbons from water (Devi and Saroha, 2015; Lu et al., 2014; Wu et al., 2013; Xu et al., 2013). Noble metals or transition metals are usually used as the second metal and catalyst to enhance the dechlorination rate as well as alter the dechlorination mechanism (Parshetti and Doong, 2012). However, due to van der Waals attraction and high energy level of surface state, nanoparticles are apt to aggregate together to be more stable state but less reactivity (Xu et al., 2013). Generally, there are two approaches to solve the above issues: (1) adding surfactants such as starch (He and Zhao, 2005), carboxymethyl cellulose (He et al., 2009), guar gum (Xin et al., 2015) and PVP (Vijayakumar et al., 2012) during the preparation process; (2) stabilizing nanoparticles on the matrix with lots of functional groups (amino, hydroxyl and sulfonic group), such as polymeric resins (Jiang et al., 2011), active carbon (Choi et al., 2008; Wu et al., 2013) and biochar (Devi and Saroha, 2015; Han et al., 2015; Yan et al., 2014). Wu et al. (2013) found that the removal efficiency of bromate by nZVI supported on modified AC was 95.66% (after 5 min), while the efficiency of nZVI/AC was just 54.12%. Han et al. (2015) and Quan et al. (2014) stabilized nZVI on acid modified biochar (MB) for methyl orange dye degradation. Ag is relatively cheaper (compared with conventional catalysts Au, Pd and Pt) and possesses a higher standard potential (0.799 V), indicating that Fe (E_{Fe}^{0} = −0.44 V) and Ag can form a galvanic couple with higher potential and faster electron transfer rate (Denis et al., 2013). Luo et al. (2010) described that the removal efficiency of tetrabromobisphenol A by Ag/Fe nanoparticles was much higher than that of nZVI, owing to the existence of Ag as the catalyst. However, there is still limited study about Ag/Fe nanoparticles loading on MB for carbon tetrachloride removal. The primary objective of the work is to utilize the high adsorption and reduction by loading Ag/Fe nanoparticles on MB (Ag/Fe/MB) to enhance carbon tetrachloride removal efficiency.

In this study, a novel adsorbent Ag/Fe/MB has been successfully prepared and investigated in carbon tetrachloride removal in water. The surface morphology, porosity, distribution patterns and surface functional groups of immobilized Ag/Fe nanoparticles were characterized by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The recyclability and leaching studies were implemented to evaluate the stability of Ag/Fe/MB. The stabilized Ag/Fe nanoparticles were then used as an adsorbent for the removal of carbon tetrachloride. The effects of initial concentration and pH value on the removal efficiency were investigated. In addition, the reaction kinetics and thermodynamics were also investigated to uncover the adsorption and dechlorination mechanisms.

1. Materials and methods

1.1. Chemicals

Carbon tetrachloride (1 mg/mL), chloroform (1 mg/mL), and dichloromethane (1 mg/mL) were all purchased from China Ministry of Environmental Protection Institute of the Standard Sample. The biochar was purchased from Anhui Yineng Bioenergy Co., Ltd., China. It was prepared by fast pyrolysis of sawdust at about 773 K in the presence of N2. All other reagents were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd., China.

1.2. Synthesis of Ag/Fe/MB

Original biochar (OB) was first ground into a size of 200-mesh, followed by immersing in 3 mol/L NaOH solution (1:10, W/V) at 65°C for 2 hr under stirring at 300 r/min. Then the solution was washed with plenty of distilled water until the pH value of elution liquid was close to neutral, and dried at 353 K for 12 hr (Liu et al., 2012). The resultant biochar was stored in desiccators for the preparation of Ag/Fe/MB by liquid phase reduction method. The sample of Ag/Fe/MB was prepared by three steps: metal ion impregnation, sodium borohydride reduction and displacement reactions (Ahmed et al., 2016; Chun et al., 2010). Firstly, 2.0 g MB was dipped into a 50 mL coating solution (20 mL absolute ethanol and 30 mL distilled water) containing 0.05 g Polyethylene glycol (PEG) (4000) and 2.1 g FeSO₄·7H₂O. The solution was mixed intensively through stirring at 1000 r/min and ultrasound for 2 hr. Then nZVI/MB was fabricated by dropwise addition of 50 mL 0.6 mol/L NaBH₄ solution (25 mL absolute ethanol and 25 mL distilled water) to flask at 0°C for about 2 hr under severe stirring (Eq. (1)) (Wu et al., 2013; Xu et al., 2013).

\[
\text{MB} + \text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} = \text{MB} - \text{Fe} + 2\text{B(OH)}_3^- + 7\text{H}_2\uparrow
\]

The synthesized nZVI/MB was washed with distilled water and absolute ethanol three times respectively. Subsequently, Ag/Fe/MB was synthesized by dropwise addition of 30 mL 2.6 mmol/L AgNO₃ solution to the nZVI/MB solution for about 2 hr under severe stirring. Reduction and deposition of Ag occurred on the surface of nZVI according with the reaction of Eq. (2) (Wang et al., 2015), then a thin discontinuous layer of Ag was formed on top of the nZVI.

\[
2\text{Ag}^+ + \text{Fe} = \text{Fe}^{2+} + 2\text{Ag}
\]
The resulting composites were washed with copious amount of distilled water and ethanol to remove excess inorganic ions, and the solid residue was dried in vacuum oven at 60°C for 24 hr and stored in anaerobic chamber for further use.

Ag/Fe/OB particles were synthesized by a similar procedure, except for that OB was mixed with PEG and FeSO₄·7H₂O instead of MB. However, Ag/Fe nanoparticles were synthesized without biochar addition during the similar procedure. To prevent synthesized nanoparticles from oxidation, the preparation process was operated under an anaerobic atmosphere.

1.3. Characterization of Ag/Fe/MB

The elemental compositions of biochars were measured using an elemental analyzer (1406SD1043, Elementar, Germany). The change of surface functional groups was analyzed using FT-IR (VERTEX 80v, Bruker, Germany) where the dried sample was mixed with KBr (1:30, W/W) and the spectra were recorded from 4000 to 400 cm⁻¹. Porosity, Brunner–Emmet–Teller (BET) surface area and total pore volume of composites were determined by N₂ adsorption–desorption isotherm (ASAP2460, Micromeritics, USA). High resolution transmission electron microscopy (HRTEM, G2F20, FEI, USA) and field emission SEM (SIGMA, Carl Zeiss Jena, Germany) were used to characterize the surface morphology of the particles. X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, Thermo Fisher, USA) was used to characterize elements state. The X-ray source was Al K Alpha and its spot size was 900 μm.

1.4. Carbon tetrachloride adsorption experiments

Batch experiments were performed in a 100 mL sealed serum bottle to investigate the adsorption of carbon tetrachloride by Ag/Fe/MB. 50 mg adsorbents were added followed by the addition of 100 mL of carbon tetrachloride solution (20 mg/L), and then the mixture was agitated at the rate of 180 r/min in a constant temperature oscillator (25 ± 1°C) for 240 min. The 100 μL of sample was withdrawn at given time intervals using a syringe to mensurate the residual concentration of carbon tetrachloride in the solution. The effects of initial solution pH (3–9), carbon tetrachloride concentration (5–40 mg/L) and temperature on carbon tetrachloride removal by particles were studied. In addition, each experiment was carried out in duplicate and the average values were reported.

1.5. Analytical method

Quantitative analyses of carbon tetrachloride, chloroform and dichloromethane were quantified by Agilent 6890 gas chromatograph (GC, USA) equipped with Electron capture detector (ECD) detector and a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The temperature of injector and detector was preset at 250°C, respectively. The temperature of oven was initially at 30°C (1 min), ramped from 30 to 80°C (10°C/min), then maintained at 80°C for 1 min. N₂ (99.999%) was used as the carrier gas (2.0 mL/min) and the split ratio was 20:1.

The carbon tetrachloride removal from the synthetic effluent was analyzed in the light of the adsorption capacity and removal efficiency (r, %), which have been calculated as Eqs. (3) and (4) (Devi and Saroha, 2015).

\[
q_t = \frac{C_0 - C_t}{m} \times V
\]

\[
r = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where, \(q_t\) (mg/g) is the amount of carbon tetrachloride adsorbed per unit weight of the adsorbent, while \(m\) (g) is the weight of particles and \(V\) (L) is the volume of solution. \(C_0\) (mg/L) is the initial concentration of carbon tetrachloride in the solution and \(C_t\) (mg/L) is the concentration of carbon tetrachloride at time \(t\) (min).

2. Results and discussion

2.1. Characterization of Ag/Fe/MB

The FT-IR plots of OB, MB and Ag/Fe/MB are shown in Fig. 1. The spectrum peak of OB and MB is approximately the same, such as 3649 cm⁻¹ (phenolic hydroxyl stretching vibration) and 2872 cm⁻¹ (C–H symmetric stretching vibration). However, alteration of the intensity and position of some peaks occurred, indicating that the chemical state of the surface functional groups significantly changed after alkali treatment. The intensity of the peak at 783 cm⁻¹ (Si–O–Si vibration) weakened after alkali treatment, because alkali can react with the Si–O–Si groups to form silicate anions (Liu et al., 2012). The peak of aromatic C=C vibration shifted from 1540 (OB) to 1560 cm⁻¹ (MB) and the intensity also increased after alkali modification, illustrating that the aromaticity of biochar is enhanced, which is in accordance with elemental analyses (Table 1). Some new peaks appeared in the plot of Ag/Fe/MB compared with that of OB and MB. The new broad band at around 3426 cm⁻¹ is associated with the vibration of...
intramolecular hydrogen bond, indicating that the surface structure of biochar is rearranged during the preparation process of Ag/Fe/MB (especially excessive NaBH₄ was added to the solution). The peak at 613 cm⁻¹ is associated with the Fe–O adsorption peak, explaining that iron is stabilized on the biochar (Liu et al., 2015). The enhanced peak at about 1135 cm⁻¹ is attributed to the band of phenolic C–O stretching vibration, due to dipole moment is increased after loading of Fe. The peak at 1337 cm⁻¹ is indicative of borate, produced during synthesis (Xia et al., 1995).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>H/C</th>
<th>(O + N)/C</th>
<th>Brunner–Emmet–Teller (BET) surface area (m²/g)</th>
<th>Pore size (Å)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OB</td>
<td>87.35</td>
<td>2.17</td>
<td>0.78</td>
<td>9.52</td>
<td>0.0248</td>
<td>0.1179</td>
<td>94.4251</td>
<td>50.5664</td>
<td>0.1194</td>
</tr>
<tr>
<td>MB</td>
<td>91.48</td>
<td>1.23</td>
<td>0.74</td>
<td>6.36</td>
<td>0.0134</td>
<td>0.0776</td>
<td>313.8487</td>
<td>48.1540</td>
<td>0.3778</td>
</tr>
</tbody>
</table>

OB: original biochar; MB: modified biochar.

Table 1 – Elemental composition and general characteristics of the biochar samples.

Fig. 2 – Scanning electron microscopy images of OB (a), MB (b), Ag/Fe/OB (c), Ag/Fe/MB (d), exhausted Ag/Fe/OB (e) and exhausted Ag/Fe/MB (f).
The SEM images of OB, MB, fresh and exhausted Ag/Fe/OB (MB) are shown in Fig. 2. It can be observed that the MB (Fig. 2b) has rougher surface than the raw biochar (Fig. 2a), with more abundant micropore on the surface, which is in line with the results of the determination of surface areas. As illustrated in Table 1, the surface area and pore volume of MB are much higher than those of raw biochar. Elemental analyses indicated that the ratio of H/C and (O + N)/C for MB is much less than that of OB. This observation suggests that the polarity of MB is reduced while the aromaticity is increased, which is beneficial to the reaction with hydrophobic contaminants (Chen et al., 2005). The impregnation of particles on the biochar results in the formation of small globular structures on the biochar surface (Fig. 2c, d). The MB allows more proper dispersion and smaller diameter of nanoparticles, which will increase the reactivity of Ag/Fe/MB. The diameters of Ag/Fe nanoparticles, as estimated by TEM images, are 51 and 169 nm on MB and OB respectively. Moreover, smaller spherical particles are also observed on the surface of globular structures (Fig. 2c), illustrating that discontinuous Ag particles formed on the surface of nZVI which has been stabilized on the surface of OB. However, the HRTEM image indicates that Ag particles have formed a relatively constant layer, thickness of 3–4 nm, surrounding the nZVI on the surface of MB (Fig. 3a, b). Energy dispersive x-ray spectrometry (EDX) spectrum confirms the existence of silver on nZVI surface (Fig. 3c). Moreover, the presence of zero-valent silver and iron can be further confirmed by X-ray photoelectron spectrum (discussed in Section 2.4). As illustrated in Fig. 2e and f, the diameter of the Ag/Fe sphere greatly increased after carbon tetrachloride adsorption owing to the formation of iron oxides layer on Ag/Fe/OB (MB) surfaces.

2.2. Adsorption/reduction of carbon tetrachloride by Ag/Fe/MB

2.2.1. Effect of Ag/Fe/MB on carbon tetrachloride removal

The removal efficiency of Ag/Fe/MB compared to that of OB, Ag/Fe and Ag/Fe/OB for the removal of carbon tetrachloride is shown in Fig. 4. It was found that OB exhibited the slowest initial reaction rate, due to the fact that there is only adsorption process during the removal of carbon tetrachloride. In comparison, Ag/Fe nanoparticles showed a higher efficiency of carbon tetrachloride removal (71.3%) within 15 min, while the reaction rate dropped severely at a later stage because of the metal oxidation (the color of the solution became yellow at about 30 min), indicating that the rate of reduction was...
faster than that of adsorption (Huang et al., 2009). The carbon tetrachloride removal efficiency obtained using Ag/Fe/MB was much higher than other three particles. A 93.3% carbon tetrachloride removal efficiency was obtained by Ag/Fe/MB for a 60 min contact time and the carbon tetrachloride was absolutely removed by 90 min. However, 91.1% carbon tetrachloride removal efficiency was acquired using Ag/Fe/OB during the same reaction time of 60 min and the entire removal needed 180 min. The higher carbon tetrachloride removal efficiency gained by Ag/Fe/MB was partly due to the higher aromaticity and hydrophobic pollutant. In conclusion, the enhanced adsorption capacity of MB promoted the mass transfer of carbon tetrachloride onto MB, enhancing the contact of carbon tetrachloride with Ag/Fe nanoparticles. The simultaneous reduction of adsorbed carbon tetrachloride made the earlier carbon tetrachloride occupied surface sites free and space for further adsorption, which resulted in increased removal efficiency. Similar results had also been reported on the nitrophenols removal by Ag/Fe nanoparticle that involved calcium alginate beads (Gupta et al., 2014).

2.2.2. Removal of carbon tetrachloride kinetic study
The kinetics of adsorption was investigated to examine the removal mechanism by using various kinetic models, such as pseudo-first-order (Eq. (5)), pseudo-second-order (Eq. (6)) and intraparticle diffusion model (Eq. (7)). The two previous models are adsorption reaction models, which are originated from chemical reaction kinetics. However, intraparticle diffusion model is a kind of adsorption diffusion model (Qiu et al., 2009). The linear form of models is expressed as follows (Sun et al., 2015):

\[
\ln \left( \frac{q_e}{q_t} - 1 \right) = -k_1 t + \ln q_e
\]  

(5)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]  

(6)

\[
q_t = k_2 q_e^{1/2}
\]  

(7)

\[
h = k_2 q_e^{2/1}
\]  

(8)

where, \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g/(mg·min)) and \( k_i \) (mg/(g·min\(^{0.5}\))) are the rate constants of the pseudo-first-order, pseudo-second-order and intraparticle diffusion models, respectively. The \( q_e \) (mg/g) is the amount of carbon tetrachloride adsorbed at equilibrium, while \( q_t \) (mg/g) is the amount of carbon tetrachloride adsorbed at time \( t \) (min). The initial adsorption rate \( h \) (mg/(g·min)) can be expressed as Eq. (8) (Saleh et al., 2015). These parameters of kinetic models can be calculated easily by analyzing the intercept and slope of linear plots.

The linearized plots of pseudo-second-order kinetic model and intraparticle diffusion model for carbon tetrachloride adsorption are shown in Fig. 5, and the fitted model parameters are given in Table 2. The results showed that the pseudo-second-order model expressed the best correlation coefficient (\( r \)) for all of the materials (Fig. 5a) (\( R^2 > 0.99 \)). The experimental
data \( (q_{e, \text{experiment}}) \) and the calculated data \( (q_e) \) from pseudo-second-order model were highly consistent with each other, indicating that the removal of carbon tetrachloride was well characterized by the kinetic model of pseudo-second-order. The experiment result was in accordance with that of other reports on the removal of carbon tetrachloride by AC/ZnO composite (Saleh et al., 2015). Ag/Fe nanoparticles expressed the highest reaction rate constant \( (k_2 = 16.9 \, \text{g/(mg·min)}) \), which was about 0.7–10.2 times higher than other materials, due to the strong reduction activity and sufficient contact with carbon tetrachloride through severe stirring in an oscillator. However, the higher reaction rate maintained only half an hour because of oxidation. The reaction rate constant and the initial reaction rate of Ag/Fe/MB \( (k_2 = 9.85 \, \text{g/(mg·min)}, \ h = 31.5 \, \text{mg/(g·min)}) \) were also much higher than those of OB and Ag/Fe/OB. The adsorbent possessed more sustained higher reactivity, indicating that Ag/Fe/MB had a better performance than unstabilized Ag/Fe nanoparticles in the removal of carbon tetrachloride.

The correlation coefficient of intraparticle diffusion model was very poor compared to pseudo-second-order model across the entire contact period. However, the data of carbon tetrachloride adsorption by OB well fitted the model of intraparticle diffusion within the initial 60 min \( (R^2 = 0.9992, \ \text{Fig. 5b}) \), indicating that the role of intraparticle diffusion was important for carbon tetrachloride adsorption onto OB at the early stage (Cui et al., 2016).

### 2.2.3. Effect of initial pH

The effect of initial solution pH on the removal of carbon tetrachloride by Ag/Fe/MB is shown in Fig. 6. The solution pH was adjusted from 5 to 9 by adding 0.1 mol/L NaOH or H₂SO₄. The lower pH values were not reflected in the figure, due to that the leaching potential of metals was severe under stronger acidic conditions. The result showed that the optimal solution pH value for carbon tetrachloride removal by Ag/Fe/MB was 6. There was a slight increase in the carbon tetrachloride removal efficiency with increase of pH value from 5 to 6. However, the carbon tetrachloride removal efficiency decreased with an increase of pH value from 6 to 9. This phenomenon is related to the fact that less hydrogen (indispensable for dechlorination of carbon tetrachloride) was produced and more passivation layers formed on the surface at higher pH values (James et al., 2000). Similar trend was also described in the chlorinated methane dechlorination by Pd/Fe nanoparticles (Wang et al., 2009).

#### 2.2.4. Effect of initial carbon tetrachloride concentration

The effect of initial concentrations of carbon tetrachloride (5–40 mg/L) on removal efficiency by Ag/Fe/MB was studied in Fig. 7a. The removal efficiency was declined with the increased concentration. It could be found that the data were in line with the pseudo-second-order kinetic model at different initial carbon tetrachloride concentrations \( (R^2 > 0.97, \ \text{Fig. 7b}) \). The \( k \) for carbon tetrachloride removal decreased from 0.014 g/(mg·min) at 5 mg/L to 0.001 g/(mg·min) at 40 mg/L, while the initial rate constant \( (h) \) for carbon tetrachloride removal increased from 1.62 mg/(g·min) at 5 mg/L to 7.63 mg/(g·min) at 40 mg/L. The removal process of carbon tetrachloride on Ag/Fe/MB involved the adsorption of carbon tetrachloride on the surface and the simultaneous reduction. The adsorption capacity was limited at a fixed adsorbent

### Table 2 – Kinetics parameters of carbon tetrachloride removal by adsorbents.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Parameter</th>
<th>OB</th>
<th>Ag/Fe</th>
<th>Ag/Fe/OB</th>
<th>Ag/Fe/MB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>( k_1 \times 10^9 , \text{(min}^{-1}) )</td>
<td>2.56</td>
<td>3.31</td>
<td>2.14</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>( q_e , (\text{mg/g}) )</td>
<td>41.3</td>
<td>33.4</td>
<td>14.3</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9889</td>
<td>0.9578</td>
<td>0.9827</td>
<td>0.8606</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>( q_e , (\text{mg/g}) )</td>
<td>53.5</td>
<td>140</td>
<td>54.5</td>
<td>56.5</td>
</tr>
<tr>
<td></td>
<td>( k_2 \times 10^3 , \text{(g/(mg·min))} )</td>
<td>1.51</td>
<td>16.9</td>
<td>5.1</td>
<td>9.85</td>
</tr>
<tr>
<td></td>
<td>( h , (\text{mg/(g·min)}) )</td>
<td>4.32</td>
<td>333.2</td>
<td>16.3</td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9948</td>
<td>0.9999</td>
<td>0.9988</td>
<td>0.9996</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>( q_{e, \text{experiment}} , (\text{mg/g}) )</td>
<td>50.4</td>
<td>138</td>
<td>53.2</td>
<td>56.1</td>
</tr>
<tr>
<td></td>
<td>( k_i , (\text{mg/(g·min}^{0.5})) )</td>
<td>25.7</td>
<td>2.71</td>
<td>9.86</td>
<td>8.07</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.7367</td>
<td>0.7535</td>
<td>0.8623</td>
<td>0.7232</td>
</tr>
</tbody>
</table>

*Ag/Fe/OB: Ag/Fe nanoparticles attached to the surface of original biochar; Ag/Fe/MB: Ag/Fe nanoparticles attached to the surface of modified biochar; \( q_{e, \text{experiment}} \) the amount of carbon tetrachloride adsorbed at equilibrium in experiment.*

Fig. 6 – Effect of solution pH on carbon tetrachloride (CT) reduction efficiency using Ag/Fe/MB (initial carbon tetrachloride concentration 20 mg/L; T 25°C; contact time 240 min).
concentration (Devi and Saroha, 2015), so increased carbon tetrachloride concentration would result in competitive adsorption among the carbon tetrachloride molecules. However, increased carbon tetrachloride concentration could provide more molecules around particles, indicating higher initial reaction rate.

2.2.5. Effect of solution temperature
The thermodynamic parameters (ΔG°, ΔS° and ΔH°) for the removal of carbon tetrachloride on adsorbents, defining the adsorption is exothermic or endothermic, are calculated on the basis of the following equations (Nandi et al., 2009):

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

\[
\log\frac{q_e}{c_e} = \frac{\Delta S^0}{2.303R} + \frac{-\Delta H^0}{2.303RT}
\]

where, \(q_e\) is the amount of carbon tetrachloride adsorbed on the adsorbent at equilibrium (mg/g), \(c_e\) (mg/L) is the equilibrium concentration of carbon tetrachloride. \(R\) is the gas constant (8.314 J/(mol·K)) and \(T\) (K) means the absolute temperature. Entropy change (ΔS°) and enthalpy change (ΔH°) are achieved from the intercept and slope of the linear plot of \(\log(q_e/c_e) - 1/T\) based on Eq. (10). Moreover, Gibbs free energy (ΔG°) is calculated using Eq. (9) at each temperature.

It could be found that with an increase of solution temperature, removal efficiency decreased as showed in Fig. 8, indicating the adsorption on Ag/Fe/MB was exothermic in nature. The values of thermodynamic parameters for carbon tetrachloride adsorption on OB and Ag/Fe/OB were also calculated, which were listed in Table 3.

The negative values of Gibbs free energy observed at the three temperatures for adsorbents were investigated in this study, indicating that carbon tetrachloride adsorption on these materials was feasible and spontaneous. The negative values of enthalpy in this work illustrated that the adsorption process was exothermic and the higher heat of reaction process indicated that chemisorptions were more prevalent than physical adsorption except for the OB (Nandi et al., 2009). The negative values of entropy denoted that the degree of freedom decreased and the adsorbed carbon tetrachloride on the adsorbents was more organized, while OB showed the opposite trend.

2.3. Recycling and leaching study
Reusability and the leaching potential of the adsorbents are important factors for practical applications of reaction

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (J/(mol·K))</th>
<th>ΔG° (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OB</td>
<td>-7.18</td>
<td>2.521</td>
<td>-7.91</td>
</tr>
<tr>
<td>Ag/Fe/OB</td>
<td>-26.44</td>
<td>-60.0592</td>
<td>-9.14</td>
</tr>
<tr>
<td>Ag/Fe/MB</td>
<td>-42.01</td>
<td>-113.823</td>
<td>-9.22</td>
</tr>
</tbody>
</table>

\(\Delta S^0\): entropy change; \(\Delta H^0\): enthalpy change; \(\Delta G^0\): Gibb’s free energy change.
After the completion of the first reduction cycle, the used adsorbents were regenerated by relay high speed centrifugation and washed with deoxidation water and methanol for the next cycle (Dong et al., 2014). The removal efficiency of the adsorbent during different cycles is shown in Fig. 9. In the first removal cycle, it emerged that 100% of carbon tetrachloride was removed at a concentration of 20 mg/L. The removal efficiency declined to 80%, when the experiment reached its third cycle. The sample of Ag/Fe/MB could be regenerated and reused better due to higher adsorption properties and resistance to oxidation and passivation (Denis et al., 2013).

Containing different metals, the adsorbent was a potential threat to the environment when the metal dissolved in water. The leaching potential of Ag and Fe was investigated under different pH values, including pH 3, pH 6 and pH 9. The concentrations of metals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 8000, PerkinElmer, USA). The results showed that the leaching potential of Fe and Ag was more severe under acidic conditions compared to the near neutral and alkaline conditions. The leaching concentrations of Fe and Ag at pH 3 were 20.76 and 0.28 mg/L respectively, compared to 0.17 and 0.04 mg/L at solution pH 9. The concentrations of Fe and Ag in the leachate were the least (0.14 mg/L (Fe); 0.02 mg/L (Ag)) under pH 6, which were about half of water quality standard (0.3 mg/L (Fe); 0.05 mg/L (Ag)) (GB5749-2006). The rate of iron corrosion is faster at acidic solution, resulting in higher leaching potential. Conversely, the passivation layer is formed on the surface of the adsorbent.
surface of particles at alkaline solution pH, which can hinder the Fe dissolution (Devi and Saroha, 2015). The data indicated that adsorbents should be used in the near neutral and alkaline conditions with little environmental risk.

2.4. Mechanisms

The surface of the fresh and exhausted Ag/Fe/MB was analyzed by XPS for reaction mechanism investigation (Fig. 10). The peaks at 711.48, 719.75, and 724.94 eV were owing to the energies of Fe 2p$_{3/2}$, satellite Fe 2p$_{3/2}$, and Fe 2p$_{1/2}$ respectively (Fig. 10a), representing the existence of iron oxides (Li and Zhang, 2006b). It could be noticed that a smaller peak at 707.5 eV, suggesting the presence of Fe$^0$, disappeared completely in exhausted material due to the oxidation. The peaks located at 530.7, 531.4 and 532.9 eV were attributable to the binding energies of O 1s which could be constituted by the forms of O$_2^-$, OH and the adsorbed water (Fig. 10c). The area ratio of OH to O$_2^-$ on the material surface was approximately 2, indicating that the oxidized iron might be in the state of FeOOH and Fe(OH)$_3$ (Li and Zhang, 2006b). However, the peak of O 1s in Fig. 10d (fresh material) could be decomposed into only two separate peaks at around 530.5 and 532.3 eV, indicating that the surface oxide was mainly Fe$_2$O$_3$ (Li et al., 2006a).

Ag 3d region was described by a double peaks of 3d$_{5/2}$ and 3d$_{3/2}$ (368.51, 374.55 eV), corresponding the existence of Ag$^+$ (Fig. 10b) (Prieto et al., 2012). Characteristic spectral lines of exhausted Ag were near identical to that of fresh particles, indicating the silver basically remained unchanged as the catalyst. However, there was a fact that the area of Ag 3d region peaks declined from 1422 to 1251.2 (368.5 eV) and 1051.17 to 618.6 (374.55 eV), respectively, illustrating the concentration of Ag was decreased during the reaction process, which might be one reason for decrease of removal efficiency. It is believed that the hydrogen, produced by electrolysis of water, was adsorbed on the surface of Ag and then was dissociated into more active atomic hydrogen (Luo et al., 2010; Wang et al., 2015). The atomic hydrogen then attacked the bond of C–Cl and transformed it to C–H and Cl$^-$ by a surface-mediated process (Wang et al., 2015). With an outer nonuniform layer of Ag, the bare Fe$^0$ could also provide electron to break the C–Cl bond (Li et al., 2006a). Fe$^{2+}$ was oxidized by the dissolved oxygen in water to produce oxyhydroxide and hydroxides precipitate, which was conform to the variation of final solution pH (from the initial pH 6.0 to final pH 5.6) (Luo et al., 2010). On the basis of the study discussed above, the possible mechanism model for the removal of carbon tetrachloride by Ag/Fe/MB was described in Fig. 11 (Devi and Saroha, 2015; Li et al., 2006a).

3. Conclusions

In this paper, a novel adsorbent Ag/Fe/MB was successfully synthesized for the carbon tetrachloride removal. The result showed that the MB possessed more aromaticity, larger surface area and pore volume, which was contribute to adsorption of carbon tetrachloride and better dispersion of Ag/Fe nanoparticles. Carbon tetrachloride was adsorbed and simultaneously reduced by Ag/Fe/MB, which was fitted pseudo-second-order kinetic model well. The reaction rate constant was the highest at pH of 6 and the initial reaction rate increased with the carbon tetrachloride concentration.
Thermodynamic studies revealed that the removal of carbon tetrachloride was a spontaneous and exothermic process. Ag acted as a hydrogenation catalyst and activated molecular hydrogen to atoms, being responsible for the breakage of C–Cl bond. The leaching studies confirmed the lower environmental risk of Ag/Fe/MB in the neutral and alkaline conditions, predicting that Ag/Fe/MB could be a potential adsorbent to remove carbon tetrachloride.

Acknowledgments

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