Removal of Cs\(^+\) from water and soil by ammonium-pillared montmorillonite/Fe\(_3\)O\(_4\) composite

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ABSTRACT

To remove cesium ions from water and soil, a novel adsorbent was synthesized by following a one-step co-precipitation method and using non-toxic raw materials. By combining ammonium-pillared montmorillonite (MMT) and magnetic nanoparticles (Fe\(_3\)O\(_4\)), an MMT/Fe\(_3\)O\(_4\) composite was prepared and characterized. The adsorbent exhibited high selectivity of Cs\(^+\) and could be rapidly separated from the mixed solution under an external magnetic field. Above all, the adsorbent had high removal efficiency in cesium-contaminated samples (water and soil) and also showed good recycling performance, indicating that the MMT/Fe\(_3\)O\(_4\) composite could be widely applied to the remediation of cesium-contaminated environments. It was observed that the pH, solid/liquid ratio and initial concentration affected adsorption capacity. In the presence of coexisting ions, the adsorption capacity decreased in the order of Ca\(^{2+}\) > Mg\(^{2+}\) > K\(^+\) > Na\(^+\), which is consistent with our theoretical prediction. The adsorption behavior of this new adsorbent could be expressed by the pseudo-second-order model and Freundlich isotherm. In addition, the adsorption mechanism of Cs\(^+\) was NH\(_4\)\(^+\) ion exchange and surface hydroxyl group coordination, with the former being more predominant.

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Introduction

In order to solve the problems of energy demand and environmental pollution, many countries are seeking new clean energy alternatives to fossil fuels. Nuclear power, which has provided approximately 18.93% of the world’s electricity (International Atomic Energy Agency, 2015), is one of the most promising methods. However, nuclear power plants emit approximately 200 to 300 tons of radioactive waste globally each year (Yang et al., 2014b). In addition, when nuclear power accidents occur, radioactive pollutants leak into the environment. For example, in Japan’s 2011 Fukushima nuclear accident, approximately 630,000–770,000 TBq radionuclides were released into the environment, including thousands of tons of radioactive waste (Yang et al., 2014c; Yasunari et al., 2011), which threatened human health and the ecosystems. Meanwhile, the Chinese government decided to build 6 to 8 nuclear power plants each year starting in 2016, which drew more attention to radioactive wastewater (Zhang et al., 2015). Radioactive isotopes of cesium (\(^{134}\)Cs and \(^{137}\)Cs) are the primary concerns among radioactive wastes, because of their abundant content and a long half-life (with 2.06 and 30 years, respectively) (Zhang et al., 2015). At present, there are many ways to decontaminate radionuclide from wastewater. Precipitation, solvent extraction, membrane dialysis, and adsorption are the most commonly used methods (Long et al., 2013; Wu...
Among these methods, adsorption is a simple operation, economical and feasible.

Clay minerals such as bentonite, illite, kaolinite, montmorillonites, sepiolite, and zeolite which are natural and low cost adsorption materials have been widely used for the removal of cesium ions from the solution (Bayülken et al., 2011; Nakano et al., 2003; Poinssot et al., 1999). Montmorillonite (MMT) belongs to the 2:1 clay family and its layered structure consists of two silica tetrahedral sheets fused to one alumina octahedral sheet. The isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral layer and Mg$^{2+}$ or Fe$^{2+}$ for Al$^{3+}$ in the octahedral layer results in a negative surface charge on the clay, and these negative sites can adsorb cations such as Ca$^{2+}$, K$^+$ and Na$^+$ between the layers through electrostatic attraction (Wu et al., 2009; Yang et al., 2016). Compared with other clay minerals, MMT has a higher adsorption capacity of cesium because of its high cation exchange capacity (CEC), large surface area, stable chemical properties and large reserves in China (Wang et al., 2010b; Westrich et al., 1995).

Natural MMT primarily occurs in the form of Ca-MMT or Na-MMT, which has low selective adsorption to Cs$^+$. MMT pillared with ethylamine (Karamanis and Assimakopoulos, 2007; Long et al., 2013) and aluminum (Karamanis and Assimakopoulos, 2007) has been investigated, but the performance of selective adsorption of Cs$^+$ was not high. The hydration radius of NH$_4^+$ is similar to that of Cs$. Ca$-MMT pillared by NH$_4^+$ would preferentially exchange Cs$^+$ under other coexisting ions. In addition, MMT is usually powder-suspended in the solution, which is difficult to be separated and reused after Cs$^+$ sorption. Magnetic separation, which has been used to remove cesium ions from the solution, is convenient to separate the adsorbent from wastewater (Cao et al., 2008; Fan et al., 2011; Hashemian et al., 2015; Oliveira et al., 2004; Pan et al., 2011; Sheha, 2012; Yantasee et al., 2007). MMT/Fe$_3$O$_4$ has been used to remove heavy metals (Cu$^{2+}$, Pb$^{2+}$, and Ni$^{2+}$) from aqueous solutions (Kalantari et al., 2015). However, the capture of Cs$^+$ in water and soil systems with the use of ammonium-pillared MMT/Fe$_3$O$_4$ magnetic composites, and its adsorption mechanism have not been investigated.

In this study, ammonium-pillared MMT/Fe$_3$O$_4$ was synthesized by the in situ co-precipitation technique. The sorption of Cs$^+$ on MMT, Fe$_3$O$_4$ and MMT/Fe$_3$O$_4$ composite was measured, and the adsorption equilibrium, kinetics, thermodynamics and their applicability in real samples were also discussed. In addition, the adsorption mechanism was investigated by means of batch experiments, adsorption model and characterization techniques.

1. Experimental section

1.1. Materials

The chemicals FeCl$_3$·4H$_2$O, FeCl$_3$·6H$_2$O, NaCl, KCl, MgCl$_2$, and CaCl$_2$ of analytically pure (A.R.) grade were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Ethanol, NH$_3$·H$_2$O (25 wt.%) and hydrochloric acid of A.R. grade were purchased from Beijing Beihua Fine Chemicals Co., Ltd., China. Nonradioactive cesium chloride (CsCl) of extra-pure grade was purchased from Amresco, USA. Pure water generated by a Synergy Ultraviolet (UV) ultra-pure water system (Millipore, USA) was used to prepare the solution and synthesize the novel adsorbent.

1.2. Preparation of MMT/Fe$_3$O$_4$ composite

Fe$_3$O$_4$ was synthesized by the co-precipitation method as reported previously (Jolivet et al., 2004) with a slight modification. The synthetic process of the MMT/Fe$_3$O$_4$ magnetic particles was similar to that of Fe$_3$O$_4$. The composite mechanism is in situ aggregation (Zhao et al., 2011). First, 3.1736 g of FeCl$_3$·4H$_2$O (0.016 mol) was dissolved in 300 mL of deionized water; 3.00 g of MMT was added into the mixture to ultrasonic bath for 15 min, and the mixture was stirred for 30 min. Next, 7.5684 g of FeCl$_3$·6H$_2$O (0.028 mol) was dissolved in the suspension by stirring the mixture solution for 30 min at 80°C under nitrogen atmosphere. Then, 40 mL of NH$_3$·H$_2$O was injected into the mixture rapidly, and stirred under nitrogen for another hour, and cooled at room temperature. The obtained black precipitates were magnetically separated and washed repeatedly with distilled water and ethanol. Finally, the MMT/Fe$_3$O$_4$ magnetic fluid underwent vacuum freeze-drying for 12 hr.

1.3. Characterization

Fourier transform infrared (FT-IR) spectrum was recorded with KBr over the spectral range from 4000 to 400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ (Affinity-1, Shimadzu, Japan). Thermal gravimetric analysis (TGA) curves were measured using a TG-DSC instrument from 25 to 800°C under N$_2$ at a heating rate of 20°C/min (TGA/DSC1, Mettler-Toledo, Switzerland). Powder X-ray diffraction (XRD) patterns were recorded on a powder XRD (X Pert Pro MPD, Panalytical, Holland) with Cu Kα radiation over the 2θ range of 5°–80° at a scanning rate of 0.033°/sec. X-ray photoelectron spectrometry (XPS) was performed on a Scanning X-ray Microprobe (ESCSLAB 250Xi, ThermoFisher, USA), and the binding energy (BE) was calibrated using the C (1s) peak at 284.6 eV. The surface micromorphology was analyzed by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (S-4800/EX-350, Hitachi, Japan).

1.4. Adsorption experiments

The adsorption behaviors of inactive cesium (cesium-133) were determined by using a batch mode of operations. A certain amount of sorbents were ground into the powdered material and then dispersed in the aqueous cesium chloride solution. After the predetermined time of shaking at 200 r/min on a rotatory shaker, the adsorbent suspended in aqueous solution was separated with a 0.22 μm cellulose acetate filter membrane. The residual concentrations of metal ions remaining in the solution were measured using an atomic absorption spectrophotometer (ICP3500, ThermoFisher, USA), and the concentration of ammonium ion was determined by UV spectrophotometer (UV-2600, Shimadzu, USA).
2. Results and discussion

2.1. Materials characteristics

The microstructures and morphologies of the samples were characterized by SEM. The Fe₃O₄ (Fig. 1a) was agglomerated together and had a rough surface. Fig. 1b reveals that the MMT has a layered structure with irregular edges and a relatively smooth surface. Fig. 1c shows that the Fe₃O₄ is closely combined with the surface of MMT, the structure of which has not changed significantly. The above results show that MMT/Fe₃O₄ composite was successfully synthesized.

Particle size distribution of MMT/Fe₃O₄ composite (Fig. 1d) was measured using a laser particle size analyzer (Malvern 2000, Malvern Instruments Ltd., UK). Two different sizes of peaks are observed at different locations (near 1 and 10 μm), which may be assigned to Fe₃O₄ and MMT. The average particle size of MMT/Fe₃O₄ composite is 7.338 μm.

The FT-IR spectrums of Fe₃O₄, MMT, and MMT/Fe₃O₄ composite are presented in Fig. 2a. The 566 cm⁻¹ band of Fe₃O₄ is assigned to the vibration of Fe–O, which is also observed in the MMT/Fe₃O₄ composite (Wang et al., 2010a). The bonds at 3626 and 795 cm⁻¹ of the MMT and MMT/Fe₃O₄ composite correspond to stretching vibrations of the structure for the Al–OH and Si–O groups (Wu et al., 2012). The strong bonds at 1086 and 1034 cm⁻¹ of the MMT and MMT/Fe₃O₄ composite are related to the Si–O vibrations of amorphous silica and the tetrahedral sheet (Madejová, 2003). The bond positions at 914, 844, 520, and 463 cm⁻¹ for the MMT and MMT/Fe₃O₄ composite are attributed to the deformation vibrations of the Al–Al–OH, Al–Mg–OH, Si–O–Al and Si–O–Fe structure. The bonds near 3433 and 1643 cm⁻¹ are due to the OH stretching and deformation of water. The new bond near 1404 cm⁻¹ of MMT/Fe₃O₄ composite is attributed to vibration of N–H. Compared with MMT, most bonds of MMT/Fe₃O₄ composite are in the same position, meaning that the basic crystal structure of the MMT/Fe₃O₄ composite remains unchanged after loading Fe₃O₄. However, the relative intensity of bonds from 1000 to 600 cm⁻¹, especially at 623 cm⁻¹ compared with the MMT, imply that Fe₃O₄ and MMT may form a new chemical bond to combine together.

The crystal structures of the Fe₃O₄, MMT and MMT/Fe₃O₄ composites were investigated using XRD and the patterns are shown in Fig. 2b. A series of characteristic peaks of Fe₃O₄ MNPs at 2θ = 30.2°, 35.5°, 43.2°, 57.2°, 62.7° were assigned to the (220), (311), (400), (422), (511), (440), and (533) planes of cubic structure, respectively, with cell constant \(a = 0.8397\) nm (JCPDS card NO. 99-0073). The main characteristic peaks of MMT (Montmorillonite-15A) can be indexed to 5.8° (001), 17.7° (003), 19.8° (100), 29.5° (005), 34.9° (110), 36.0° (006), 54.0° (210), and 61.9° (010) planes of the hexagonal structure with cell constant \(a = b = 0.5169\) nm, and \(c = 1.502\) nm (JCPDS card NO. 13-0135). Quartz is also present in MMT according to this XRD pattern at 2θ = 20.8° and 26.6°. The characteristic peaks of Fe₃O₄ and MMT are shown in the pattern of MMT/Fe₃O₄ composites, suggesting that the crystal structure of Fe₃O₄ and MMT do not change noticeably. The (001) reflection and the basic spacing of MMT and MMT/Fe₃O₄ composite is 5.81° (\(d_{001} = 1.52\) nm) and 6.93° (\(d_{001} = 1.27\) nm), indicating that the structure of MMT interlayer has changed after loading Fe₃O₄ MNPs. In addition, the (001) reflection relative intensity of MMT/Fe₃O₄ is significantly lower than that of MMT, implying that (010) planes of MMT/Fe₃O₄ become more disordered than

![Fig. 1 – SEM images of (a) Fe₃O₄, (b) MMT, (c) MMT/Fe₃O₄ composite, and particle size distribution of (d) MMT/Fe₃O₄ composite. SEM: scanning electron microscopy; MMT: montmorillonite.](image-url)
MMT. The relative intensity of characteristic peaks of Fe₃O₄ is higher than that of MMT in MMT/Fe₃O₄ composite pattern, meaning that Fe₃O₄ has a higher proportion in MMT/Fe₃O₄ composites, and a more accurate assessment of MMT/Fe₃O₄ composite component ratio by TGA.

As shown in Fig. 3, the weight loss from Fe₃O₄ (2%) and MMT/Fe₃O₄ composite (3.5%) below 200°C is ascribed to the evaporation of adsorbed water, which is reflected by a strong endothermic peak at 82°C (Joshi et al., 2009; Tan et al., 2014). The weight loss from Fe₃O₄ (2%) and MMT/Fe₃O₄ composite (1.5%) from 200 to 400°C is assigned to the desorption of crystal water. The weight of Fe₃O₄ increased by approximately 0.4% from 400 to 800°C and may be oxidized to Fe₂O₃, resulting in a strong exothermic peak at 504 and 544°C. The first weight loss of MMT corresponds to the dehydration of water molecules absorbed in pores and between the silicate layers, which appear the endothermic valleys at 96 and 154°C (Zhuang et al., 2015). However, the endothermic valley of MMT/Fe₃O₄ composite at 154°C did not appear, suggesting that water molecules adsorbed the MMT layers were replaced by new ions. The last weight loss of the MMT and MMT/Fe₃O₄ composite seen from 550 to 750°C is caused by the loss of structural hydroxyl groups (Bajaj and Jasra, 2007). According to the weight loss of each sample, the contents of Fe₃O₄ and MMT in MMT/Fe₃O₄ composites are calculated to be approximately 68.14 wt.% and 31.14 wt.%, respectively.

2.2. Effect of solid/liquid ratio and initial concentration

The effect of solid/liquid (S/L) ratio on Cs⁺ adsorption by Fe₃O₄, MMT and MMT/Fe₃O₄ composite is shown in Fig. 4a. The adsorption capacity of MMT and MMT/Fe₃O₄ composite is significantly higher than that of Fe₃O₄. The adsorption capacity of Fe₃O₄ and MMT/Fe₃O₄ composite do not change significantly with increasing solid/liquid ratio, whereas that of MMT which decreases noticeably. Fig. 4b shows the effect of initial concentration on Cs⁺ adsorption by Fe₃O₄, MMT, and MMT/Fe₃O₄ composite. The adsorption capacity of Fe₃O₄, MMT and MMT/Fe₃O₄ composite increases with the increase of the initial concentration. The adsorption capacity of Fe₃O₄ and MMT is nearly linear in relation to initial concentration. However, when the initial concentration of Cs⁺ is higher than 15 mg/L, increasing rate of MMT/Fe₃O₄ composite decreases obviously, which implies that it may reach saturation adsorption capacity.

There are two reasons that can explain the effect of solid/liquid ratio and initial concentration. Firstly, the collision probability of Cs⁺ on the material surface increases with the
increase of the solution volume and initial concentration. Secondly, adsorption of cesium on the surface of the adsorbent has different behaviors at different stages. At a relatively low concentration, most of the Cs\(^+\) can be adsorbed and increase proportionately with the rising concentration. However, when the adsorbent is about to reach saturation adsorption capacity, the adsorption behavior can be seen as a reversible reaction, resulting in only part of the cesium being adsorbed by the adsorbent. Furthermore, the adsorption becomes more difficult with the increase of concentration.

Fig. 4 – Effect of (a) solid/liquid ratio (pH 6.7, [Cs\(^+\)]\(_{\text{initial}}\): 20 mg/L, temperature: 25°C, contact time: 2 hr) and (b) initial concentration study of Cs\(^+\) adsorption by Fe\(_3\)O\(_4\), MMT and MMT/Fe\(_3\)O\(_4\) composite (pH 6.7, temperature: 25°C, contact time: 2 hr, S/L: 0.5 g/L).

Fig. 5 – Effect of pH and temperature (T) study of Cs\(^+\) adsorption by (a) Fe\(_3\)O\(_4\), (b) MMT and (c) MMT/Fe\(_3\)O\(_4\) composite ([Cs\(^+\)]\(_{\text{initial}}\): 20 mg/L, temperature: 25°C, contact time: 2 hr, S/L: 0.5 g/L), (d) ions concentration in the initial solution.
2.3. Effect of pH and temperature

Usually, pH plays an important role in the adsorption process. To investigate the effect of pH on the adsorption capacity of Fe₃O₄, MMT and MMT/Fe₃O₄ composite, experiments were conducted at pH levels from 2 (HCl) to 12 (NaOH). Fig. 5a–c shows that the adsorption capacity for Cs⁺ onto Fe₃O₄, MMT, and MMT/Fe₃O₄ composite gradually increases as pH increases from 2 to 4. The increasing rate slows down in the pH range from 4 to 10, reaches its maximum at pH 11, and then decreases rapidly. This phenomenon could be explained by the change of different ion concentrations in the initial solution in Fig. 5d. H₂O⁺ is preferentially adsorbed by Fe₃O₄, MMT, and MMT/Fe₃O₄ composites, leading to fewer surface adsorption sites available for Cs⁺ at low pH (Yang et al., 2016). As shown in Fig. 5d, with the increase of pH (2–4), the H₂O⁺ of the solution is neutralized by the OH⁻, and thus reducing competition with Cs⁺, which leads to a rapid increase in the adsorption capacity of the adsorbent. As the pH (4) increases further, H₂O⁺ in the solution decreased slightly and more adsorption sites are released slowly. However, when the pH exceeds 11, the concentration of Na⁺ increases rapidly, resulting in competition with Cs⁺ again, which takes over the reactive surface adsorption sites and also restrains the bonding of Cs⁺.

The effect of different temperatures (15, 25, and 35°C) on the adsorption capacity of Fe₃O₄, MMT, and MMT/Fe₃O₄ composite is shown in Fig. 5a–c. The adsorption capacity for Cs⁺ onto Fe₃O₄ increases with an increase in temperature, indicating that the adsorption process is endothermic, contrary to MMT. However, the adsorption capacity of Cs⁺ onto the MMT/Fe₃O₄ composite is nearly constant with the change of temperature, indicating that Fe₃O₄ and MMT are both involved in the adsorption process.

Table 1 – The bare and hydrated radii of cations (Volkov et al., 1997).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (nm)</th>
<th>Hydrated radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O⁺</td>
<td>0.115</td>
<td>0.28</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.117</td>
<td>0.358</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.149</td>
<td>0.331</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.072</td>
<td>0.428</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.100</td>
<td>0.412</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.148</td>
<td>0.331</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>0.186</td>
<td>0.329</td>
</tr>
</tbody>
</table>
2.4. Effect of coexisting ions

The phenomenon of competitive adsorption of H\(^+\), Na\(^+\), and Cs\(^+\) has been observed. To further investigate the effects of coexisting cation ions on the adsorption of Cs\(^+\), monovalent Group I and divalent Group II cations (Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)) were selected owing to their abundance in natural environment. In Fig. 6a–c, the adsorption capacity of Fe\(_3\)O\(_4\), MMT, and MMT/Fe\(_3\)O\(_4\) composite with added cations is lower than that of the blank. MMT plays a major role in the adsorption process of cesium in MMT/Fe\(_3\)O\(_4\) composite by comparing the adsorption capacity. The adsorption capacity decreases with increasing coexisting cation ion concentration. When Na\(^+\) or K\(^+\) coexist, the adsorption capacity of MMT and MMT/Fe\(_3\)O\(_4\) composite is almost 2 times that of Mg\(^{2+}\) and Ca\(^{2+}\), and it decreases in the order of Ca\(^{2+}\) > Mg\(^{2+}\) > K\(^+\) > Na\(^+\). The results indicate that adsorption of Cs\(^+\) is a significant inhibition in the presence of coexisting cation ions. The effect of coexisting ions can be explained by cation exchange (Karamanis and Assimakopoulos, 2007), but the internal mechanism remains unclear. Recently, some studies have explained the influence of different ions on competitive adsorption by comparing the ionic radii (Yang et al., 2014a, 2016). The cation ion is hydrated and it represents the effective form in the water solution, with greater size than the ionic radius. As shown in Table 1, the hydrated radii of cations decrease in the order of Mg\(^{2+}\) > Ca\(^{2+}\) > Na\(^+\) > K\(^+\) > NH\(_4\)\(^+\) > Cs\(^+\) > H\(_3\)O\(^+\). The adsorption capacity and the hydrated radii of the cations are in the reverse sequence under the same charge number condition. However, according to previous studies, the different effects of Na\(^+\), K\(^+\) between Ca\(^{2+}\), and Mg\(^{2+}\) on the adsorption capacity could not be explained only by comparing the ion hydration radius. Therefore, it could be speculated that cation binding on the adsorbent surface involves multiple factors not only related to the ionic radius, but also to the charge number of the ions. That is to say, we could compare the adsorption affinity \((F, N)\) of the coexisting cation ions on adsorbent (MMT or MMT/Fe\(_3\)O\(_4\) composite) by the following equation, which is similar to Coulomb electrostatic law:

\[
F = \frac{k |q_1q_2|}{r^2}
\]

where, \(k ((N\cdot m^2)/C^2)\) is constant, \(q_1 (C)\) and \(q_2 (C)\) are the charge of the ion and the adsorbent, the scalar \(r (m)\) is the distance between the charges. The higher the \(F\) value of the coexisting ions, the stronger the binding affinity, and the more obvious the inhibitory effect on the adsorption of Cs\(^+\). The hypothesis is that adsorption affinity decreases in the order of \(F_{Ca^{2+}} > F_{Mg^{2+}} > F_{H_3O^+} > F_{Cs^+} > F_{Na^+},\) in accordance with the experimental adsorption capacity increase. The results may provide guidance in the process of finding and modifying an adsorbent for selective adsorption of cesium.

2.5. Adsorption kinetics and isotherms

Fig. 7a shows the kinetics for the adsorption of Cs\(^+\) by Fe\(_3\)O\(_4\), MMT, and MMT/Fe\(_3\)O\(_4\) composite at different time intervals. For Fe\(_3\)O\(_4\), MMT, and MMT/Fe\(_3\)O\(_4\) composite, the adsorption capacity reached approximately 1.82, 18.58 and 26.79 mg/g, respectively. It was observed that Fe\(_3\)O\(_4\) has little absorbance for Cs\(^+\), and the adsorption of MMT/Fe\(_3\)O\(_4\) composite should be mainly attributed to the composition of MMT. The reason for the higher adsorption capacity of MMT/Fe\(_3\)O\(_4\) composite than

![Graph](image_url)

**Table 2 – Adsorption kinetic constants and their correlation coefficients.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_e (mg/g))</td>
<td>(k_1/hr)</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>1.70035</td>
<td>59.23102</td>
</tr>
<tr>
<td>MMT</td>
<td>18.51148</td>
<td>783.11756</td>
</tr>
<tr>
<td>MMT/Fe(_3)O(_4)</td>
<td>24.57756</td>
<td>213.01996</td>
</tr>
</tbody>
</table>
that of MMT is that the cations (Ca²⁺) between the layers of MMT may be exchanged by other ions (NH₄⁺) in the process of synthesizing the composite material. It is also shown that the adsorption process is very rapid within 5 min and then gradually reaches adsorption equilibrium in 1 hr. Therefore, the connect time of adsorbent was determined as 2 hr in the following experiments.

In order to explore the mechanism of the adsorption process, the pseudo-first-order (2) and pseudo-second-order (3) were used to analyze which model was more consistent

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_max (mg/g)</td>
<td>K_L (L/mg)</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>5.560000</td>
<td>0.01126</td>
</tr>
<tr>
<td>MMT</td>
<td>72.84806</td>
<td>0.03522</td>
</tr>
<tr>
<td>MMT/Fe₃O₄</td>
<td>27.52689</td>
<td>0.88005</td>
</tr>
</tbody>
</table>

**Table 3 – Adsorption isotherm constants and their correlation coefficients.**

![XPS spectra of wide scan (a), Fe 2p spectra (b), Si 2p spectra (c), Al 2p spectra (d), O 1s spectra (e) and Cs 3d spectra of MMT/Fe₃O₄ composite. XPS: X-ray photoelectron spectrometry;](image)
with the experimental data. These two models can be expressed by the following equations (Vipin et al., 2013):

$$\ln (q_e - q_t) = \ln q_{\text{max}} - k_1 t$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\text{max}}} + \frac{1}{q_{\text{max}}}$$

where, $q_e$ (mg/g) and $q_t$ (mg/g) are the sorption capacity at equilibrium and at time $t$ (hr); $k_1$/hr and $k_2$ (g/(mg·hr)) are the pseudo-first-order and pseudo-second-order adsorption rate constants, respectively. The fitted pseudo-first-order and the pseudo-second-order model parameters are summarized in Table 2. For Fe$_3$O$_4$, MMT and MMT/Fe$_3$O$_4$ composite, the correlation coefficient ($R^2$) of the pseudo-second-order all better that of the pseudo-first-order, suggesting that electron transfer or sharing occurred and chemical adsorption may be rate limiting step in the process of adsorption.

The relationship between the adsorption capacity of the adsorbent and the concentration of the adsorbate under equilibrium conditions at a given temperature could be described by the adsorption isotherm, which could provide the information of the adsorption process (Hamdaoui and Naffrechoux, 2007). Fig. 7b shows the adsorption of Cs$^+$ by Fe$_3$O$_4$, MMT, and MMT/Fe$_3$O$_4$ composite at different equilibrium concentrations, with an adsorption time of 2 hr, temperature of 25°C, S/L of 0.5 g/L, and pH of 6.7. In order to determine the adsorption mechanism, the Langmuir (4) and Freundlich (5) isotherm models were used to fit the experimental data, expressed as:

$$q_e = K_1 C_{\text{eq}}^{1/n}$$

where, $q_e$ (mg/g) and $q_{\text{max}}$ (mg/g) are the equilibrium and maximum sorption capacity; $K_1$ (L/mg) is the Langmuir adsorption constant; $C_e$ (mg/L) is the equilibrium concentration of the adsorbate; $K_2 (L/(mg·g^{n-1}))$ and $n$ are the Freundlich adsorption constants. The Langmuir and Freundlich parameters are listed in Table 3. The $q_{\text{max}}$ value of MMT is 72.848 mg/g, which is approximately 14.2 and 2.6 times higher, respectively, than that of Fe$_3$O$_4$ and the MMT/Fe$_3$O$_4$ composite. A possible reason is that partial surface of MMT is covered by Fe$_3$O$_4$, which eventually leads to a decrease of the maximum adsorption capacity of the MMT/Fe$_3$O$_4$ composite. For Fe$_3$O$_4$ and MMT, the correlation coefficient ($R^2$) of Langmuir is better than that of Freundlich, which belongs to monolayer adsorption. However, Freundlich is found to be a better fit for the MMT/Fe$_3$O$_4$ composite, suggesting that it belongs to multilayer adsorption. The $n$ value is larger than unity, indicating that the interaction force between Cs$^+$ and MMT/Fe$_3$O$_4$ composite is strong (Ngah et al., 2010).

### 2.6. Adsorption mechanism

The pH and coexisting cations have a great influence on the adsorption capacity of Cs$^+$ onto MMT/Fe$_3$O$_4$ composite. This indicates that H$^+$ and other cations play a very important role in the adsorption process, which affect the surface functional groups (hydroxyl groups) and the interlayer cations, respectively. The former is the coordination reaction between Cs$^+$ and the surface hydroxyl group (chemical binding process), and the latter is the ion exchange reaction between Cs$^+$ and the interlayer cation (electrostatic binding process). The
and NH4 and Ca2+ had insignificant changes, but both Cs+ adsorption amount of Cs+ adsorption was slightly higher than NH4. That is to say, the chemical bonding reaction between Cs+ and a portion of the surface hydroxyl groups are exchanged by deconvoluted into three peaks with metal oxide (M). Fe 2p is significantly reduced by 0.52 eV, indicating a strong hydroxyl bonded to metal (M).

The 1s spectra of the MMT/Fe3O4 composite before and after Cs+ analysis of XRD. The BE values of the Fe 2p, Si 2p, Al 2p, and O elements on the surface of MMT/Fe3O4 composite have changed 0.01 eV (MMT), respectively, implying that oxygen constitutes the existence of chemical binding and electrostatic binding. The importance of the two reactions is not clear.

To verify the presence of the chemical bonding reaction, the element characteristics of the samples before and after adsorption were analyzed by XPS. Fig. 8a shows that Al, Si, Ca, O, C, Mg, and Fe exist in the surface of MMT and MMT/Fe3O4 composite. The spectrum of the MMT/Fe3O4 composite appears new characteristic peak of N 1s and the peak area of Ca 2p reduces significantly, indicating that Ca2+ in MMT is replaced by NH4 in the process synthesizing the MMT/Fe3O4 composite. In addition, the characteristic peak of Cs 3d of MMT/Fe3O4 composite after Cs+ sorption (MMT/Fe3O4 – Cs) is also observed (Fig. 8f). As shown in Fig. 8b, the BE of Fe 2p peak demonstrates that iron oxides in the composite are Fe3O4 rather than Fe2O3 (Lu et al., 2009), which is consistent with the analysis of XRD. The BE values of the Fe 2p, Si 2p, Al 2p, and O 1s spectra of the MMT/Fe3O4 composite before and after Cs+ sorption are presented in Table 4. The changes of the BE values of Al 2p and Si 2p are not significant, which means that Al and Si atoms may not participate in Cs+ chemical bonding adsorption process. However, after Cs+ sorption, the BE value of Fe 2p is significantly reduced by 0.52 eV, indicating a strong interaction between Cs+ and Fe atoms. The O 1s spectra can be deconvoluted into three peaks with metal oxide (M – O), hydroxyl bonded to metal (M – OH), and adsorbed H2O (Bhowmick et al., 2014; Tang et al., 2013). The O 1s peak of MMT/Fe3O4 composite is both composed of O 1s peaks of Fe3O4 and MMT according to peak shape and BE position. After Cs+ sorption, the BE values of M – OH decrease by 0.25 (Fe3O4) and 0.01 eV (MMT), respectively, implying that oxygen constituents on the surface of MMT/Fe3O4 composite have changed and a portion of the surface hydroxyl groups are exchanged by Cs+. That is to say, the chemical bonding reaction between Cs+ and the surface of MMT/Fe3O4 composite exists.

Similarly, in order to verify the presence of an electrostatic binding reaction, experiments studied the concentration of cations in the solution before and after Cs+ adsorption (Table 5). With the increase of initial Cs+ concentration, Na+, K+, Mg2+, and Ca2+ had insignificant changes, but both Cs+ adsorption and NH4 release increased significantly, indicating that ion exchange occurred between Cs+ and NH4. Additionally, the amount of Cs+ adsorption was slightly higher than NH4 released, considering the effect of the blank, and pH decreased gradually, possibly due to the H+ released. This demonstrates that the electrostatic binding reaction (ion exchange) is more dominant than the chemical bonding reaction (surface hydroxyl group) in the process of Cs+ adsorption by the MMT/Fe3O4 composite. Adsorption reactions can be expressed by the following equations, where X and S stand for the surface of MMT and Fe3O4, respectively.

\[
X\text{NH}_4 + \text{Cs}^+ \rightarrow X\text{Cs} + \text{NH}_4^+ \quad (6)
\]

\[
\text{SOH} + \text{Cs}^+ \rightarrow \text{SOCs} + \text{H}^+ \quad (7)
\]

### 2.7. Regeneration, reuse and application of MMT/Fe3O4 composite

The magnetic field of Fe3O4 and MMT/Fe3O4 composite was measured at room temperature (Fig. 9c). The extrapolated saturation magnetization (\(M_s\)) and remnant magnetization (\(M_r\)) of Fe3O4 are 47.002 and 3.0241 emu/g. The \(M_s\) and \(M_r\) of MMT/Fe3O4 composite are 36.295 and 0.86416 emu/g, which showed that it is lower than that of Fe3O4. The result demonstrated that the MMT/Fe3O4 composite could be easily separated from the solution under an external magnetic field (Fig. 9d).

Adsorbent recycled from magnetic separation should be regenerated and reused in order to lower the usage cost. In this study, HCl, NaCl and NaOH solutions were used to test the regeneration of the MMT/Fe3O4 composite. The used MMT/Fe3O4 composite was added to 0.5 mol/L different solutions (HCl, NaCl and NaOH), ultrasonic cleaning for 15 min, and then magnetic separation. The main regenerative chemical reaction is expressed by the following equation, where Y and Z stand for the surface of the MMT/Fe3O4 composite and the addition of cations (H+ and Na+).

\[
\text{YCs} + \text{Z}^{+} \rightarrow \text{YZ} + \text{Cs}^+ \quad (8)
\]

Fig. 9a shows that the removal of Cs+ by the MMT/Fe3O4 composite gradually decreases with the increase of cycling times. The HCl solution had the best regeneration effect, and the removal efficiency of Cs+ was still over 60% after reuse in four cycles. Some reasons can explain these results. Firstly, part of the quality was lost in the process of regeneration. Secondly, compared with Na+, hydrated radii of H+ is smaller than that of cesium ion, and it is easier to regenerate. Furthermore, the crystal structure of MMT may be destroyed by NaOH, which leads to the lowest regeneration efficiency.

In order to evaluate the application of the MMT/Fe3O4 composite, natural water samples without any further treatment, including seawater (the Pacific Ocean near Qingdao, China), river water (the Huangpu River near Shanghai and Zhuanhe River near Beijing, China), drinking water (Beijing, China), and water type (Table 6). The concentration of some selected major cation ions and pH value of the water type.

<table>
<thead>
<tr>
<th>Water type</th>
<th>Na+ (mmol/L)</th>
<th>K+ (mmol/L)</th>
<th>Mg2+ (mmol/L)</th>
<th>Ca2+ (mmol/L)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water</td>
<td>444.813</td>
<td>10.57711</td>
<td>47.15144</td>
<td>9.37455</td>
<td>7.60</td>
</tr>
<tr>
<td>Huangpu River water</td>
<td>0.246413</td>
<td>0.048677</td>
<td>0.178315</td>
<td>0.42003</td>
<td>7.35</td>
</tr>
<tr>
<td>Zhuanhe River water</td>
<td>0.456283</td>
<td>0.094081</td>
<td>0.47579</td>
<td>0.338198</td>
<td>7.58</td>
</tr>
<tr>
<td>Drinking water</td>
<td>0.436643</td>
<td>0.077845</td>
<td>0.430831</td>
<td>1.112518</td>
<td>7.61</td>
</tr>
<tr>
<td>Deionized water</td>
<td>0.001900</td>
<td>0.000485</td>
<td>0.000754</td>
<td>0.000561</td>
<td>6.70</td>
</tr>
</tbody>
</table>
China), and deionized water, all with the same added concentration of cesium ions, were treated. The removal efficiency of Cs⁺ by the MMT/Fe₃O₄ composite was all over 80% in all cases except seawater, because the coexisting cations in seawater were significantly higher than in other water samples (Table 6). The removal rate of Cs⁺ by the MMT/Fe₃O₄ composite decreased with the increase of coexisting cations, which has a great influence on the practical application of the adsorbent in real water environments.

Simulated cesium-contaminated soil was also prepared and then studied to research the elimination efficiency (Fig. 9e). For this part of the study, 1.0 g of cesium-contaminated soils was added to 50 mL plastic centrifuge tube, along with 40 mL solution (deionized water, HCl and NaCl). A certain mass of adsorbent was added to the plastic centrifuge tube while stirring. The tubes were shaken for 2 hr at 200 r/min at room temperature. Then the MMT/Fe₃O₄ composite was separated from the soil suspension under a magnetic field. Next, the rest of the suspension of soils was dried for 24 hr in a freeze dryer to ensure that the MMT/Fe₃O₄ composite could be widely used to treat cesium-contaminated soils in the future.

3. Conclusions

In this paper, a novel adsorbent was synthesized for removing cesium ions from water and soil. The process of synthesis was simple and environmentally friendly by using one-step co-precipitation method and non-toxic raw materials. By combining ammonium-pillared MMT and magnetic nanoparticles, the MMT/Fe₃O₄ composite showed a high adsorption capacity for cesium ions and can be rapidly separated from the mixed solution under an external magnetic field. It still had a high selectivity for cesium in the presence of coexisting ions and was not influenced by temperature. It was observed that the pH, solid/liquid ratio and initial concentration all affected the adsorption capacity. The adsorption capacity decreased in the order of Ca²⁺ > Mg²⁺ > K⁺ > Na⁺, which agreed with our theoretical prediction. The adsorption behavior could be expressed by the pseudo-second-order model and the Freundlich isotherm.

NH₄⁺ ion exchange was more dominant than hydroxyl groups in the cesium adsorption process. The adsorbent had high removal efficiency with regard to cesium-contaminated samples (water and soil) and also showed good recycling performance. It is safe to conclude that the MMT/Fe₃O₄ composite can be widely applied for the remediation of cesium-contaminated environments.

Acknowledgments

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REFERENCES


| Table 7—The elimination efficiency of MMT/Fe₃O₄ composite for cesium-contaminated soils. |
| Dosage (g) | 0.05 | 0.1 | 0.2 |
| E% (H₂O) | 61.72344 | 66.36458 | 73.82509 |
| E% (HCl) | 65.04147 | 71.07712 | 80.81003 |
| E% (NaCl) | 70.64363 | 78.94545 | 82.73073 |
| E: elimination efficiency. |