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Simple synthesis of NH_2 -functionalized Fe_2O_3 and its activated carbon composites for removing heavy metal ions

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Abstract. The novel recyclable and biodegradable adsorbents $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{oxidation-activated carbon (NH}_2\text{-Fe}_2\text{O}_3/\text{OAC)}$ with great physical properties and high adsorption for uptake heavy metal ions were synthesized in this work. The $\text{NH}_2\text{-Fe}_2\text{O}_3$ samples were prepared via one-pot hydrothermal methods, typically, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ethylene glycol and sodium acetate anhydrous were directly dissolved under stirring, followed by x mL of DETA and 0.1 g of SDS at room temperature ($x=0.5, 1, 2, 3, 4$ and 5 mL). The as-prepared $\text{NH}_2\text{-Fe}_2\text{O}_3$ were added into the mixture of oxidation-activated carbon, followed by the cation surfactant CTAB. After reflux condensation, the composites were washed, dried and labeled name $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$. Systematically characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectra (FTIR) and X-ray diffraction (XRD), physicochemical properties were all indicated obviously in this paper. The high adsorption rates of the adsorbents achieved over 88.11 % and 98.25 % towards Pb(II). In the ternary solution, the studied heavy metals revealed selective removal sequence: $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)}$.

1. Introduction

Environmental and human threats posed in the environment by highly toxic heavy metal ions are a serious problem [1-5]. It is urgent to remove toxic heavy metal ions from the environment before their discharge into the environment. Adsorption and chemical inactivation are regarded as the promising approach considering that they are the cost-effective methods remediation of metal contaminated environment [6]. Therefore, scholars face the challenges of the preparation technics of the new type material for the remediation of heavy metals.

Researchers found that newly functionalized adsorbents prepared in various methods revealed better adsorption capacity in uptake heavy metal ions. Hai et al. used spray dryer to obtain Chitosan microspheres, then graft amino groups to MA on it, followed by a substitution reaction to graft DETA



[1]. Nana Wang et al. took a one-pot approach to prepare a xanthate-modified thiourea chitosan sponge costing two days or more [2]. Xin Li et al. attempted hydrothermal method to prepare Fe_3O_4 -GS after fabricating GO via an improved method [4]. Ke Wang et al. chose microwave to assist the formation of NH_2 -functionalized Zr-MOFs which can remove both Pb(II) and Cd(II) [5]. Xitong Sun et al. fabricated amino-functionalized magnetic cellulose composite by means of the deposition of silica from the hydrolysis of sodium silicate onto Fe_3O_4 which was formed by co-precipitation of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ [7]. Maria et al. fabricated $\gamma\text{-Fe}_2\text{O}_3$ /Carbon Hybrids by a two-step process [8]. Jun et al. used an aerosol spray pyrolysis technology to synthesis three-dimensional (3D) porous $\gamma\text{-Fe}_2\text{O}_3$ @C nanocomposite [9].

However, the above methods are often time-consuming, with the prepared adsorbents expensive, a simple synthesis method for effective adsorbents needs to be proposed to deal with heavy metal ions. In order to obtain better environmentally, recyclable nano-composites, the novel simple synthesis NH_2 -functionalized $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3$ /OAC for removing heavy metal were presented in this study.

2. Experimental

2.1. Synthesis of $\text{NH}_2\text{-Fe}_2\text{O}_3$

The $\text{NH}_2\text{-Fe}_2\text{O}_3$ samples were prepared via one-pot hydrothermal methods, typically, 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 40mL ethylene glycol and sodium acetate anhydrous were directly dissolved under stirring, followed by x mL of DETA and y g of SDS at room temperature (x=0.5, 1, 2, 3, 4 and 5 mL). Then, the mixture was transferred to a Teflon-lined autoclave and heated at 160 °C for 8 hours. After it cooled off, the deionized water and ethanol were used to wash. Finally, the samples were put into the air dry oven under 60 °C.

2.2. Preparation of oxidation-activated carbon (OAC)

Oxidation-activated carbon was prepared from natural activated carbon according to modified Hummers method. In a typical reaction, natural activated carbon and HNO_3 were added into flask in a water bath, the mixture was kept at 80 °C for about 4 hours. Finally, the resulting solution was filtered and washed with anhydrous ethanol and deionized water many times. Finally, the samples were put into the air dry oven under 80 °C.

2.3. Synthesis of $\text{NH}_2\text{-Fe}_2\text{O}_3$ /oxidation-activated carbon ($\text{NH}_2\text{-Fe}_2\text{O}_3$ /OAC)

The as-prepared OAC was added into anhydrous ethanol and the mixture was kept at ultrasonic pretreatment for about 10 minutes. Next, $\text{NH}_2\text{-Fe}_2\text{O}_3$ and CTAB were added into the mixture in a water bath and kept at 70 °C for about 6 hours, and the composites were washed, dried and labeled as $\text{NH}_2\text{-Fe}_2\text{O}_3$ /OAC.

2.4. Characterization

The materials were characterized by scanning electron microscopy (SEM, JSM-7001F), transmission electron microscopy (TEM, JEM-2010), Fourier transform infrared spectra (FTIR) and X-ray diffraction (XRD, Bruker D8 ADVANCE) for more information about their shapes, compositions, functional groups, crystallization, surface area, and porous condition.

2.5. Adsorption

According to the previous study, 0.05 g $\text{NH}_2\text{-Fe}_2\text{O}_3$ and 0.05 g $\text{NH}_2\text{-Fe}_2\text{O}_3$ /OAC were suspended in 10 mg/L multiple system of Pb(II), Cd(II), and Cu(II). Adjusting pH to 5, then shake the mixture at 35 °C for 2 hours, afterwards, measured the concentration with Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

3. Results discussion

3.1. Morphology of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$

SEM was used to confirm the morphology of as-obtained $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$. Figure 1 a-f is the $\text{NH}_2\text{-Fe}_2\text{O}_3$ based on the various DETA values and the same condition of $\text{SDS}=0.1$ g under 160°C for 8 hours. The following composites $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ were sketched out in Figure 2 a-f. More detailed structural information was obtained from TEM, which is presented in Figure 3 a-d.

From the high magnification of SEM, the one-pot hydrothermal product $\text{NH}_2\text{-Fe}_2\text{O}_3$ shaped granulated and had relatively small size. With the amounts of DETA increase, the diameter of the particles decrease gradually (Figure 1).

Compared with previous images, $\text{NH}_2\text{-Fe}_2\text{O}_3$ were dispersed into the OAC under the action of anion surfactant CTAB in Figure 2. CTAB played a role as dispersing agent and enhanced the intercalation because of its hydrophobicity.

As is shown in TEM images (Figure 3), both $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ appeared single dispersed, as well as good crystallization. The porous particle can also apparently observed in Figure 3-(c).

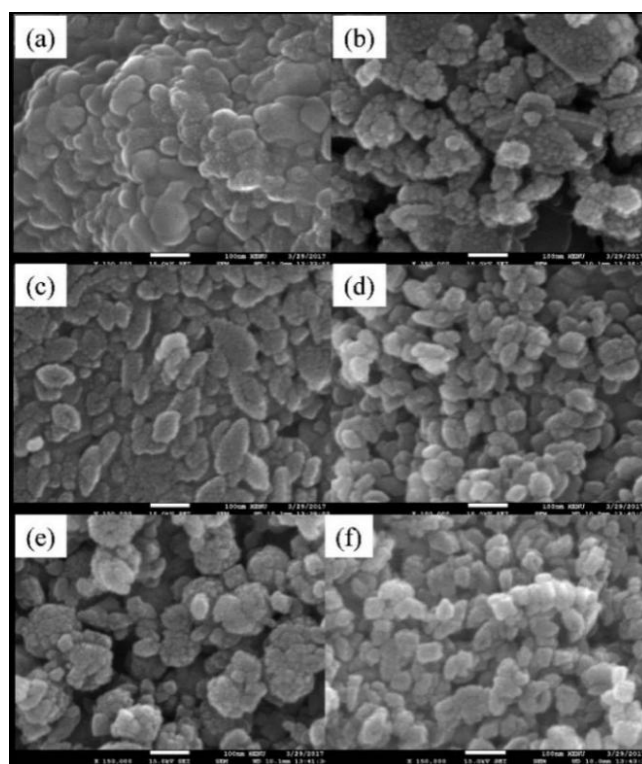


Figure 1. SEM images of $\text{NH}_2\text{-Fe}_2\text{O}_3$ under various DETA addition (a-f stands for DETA=0.5, 1, 2, 3, 4, 5 mL, respectively) .

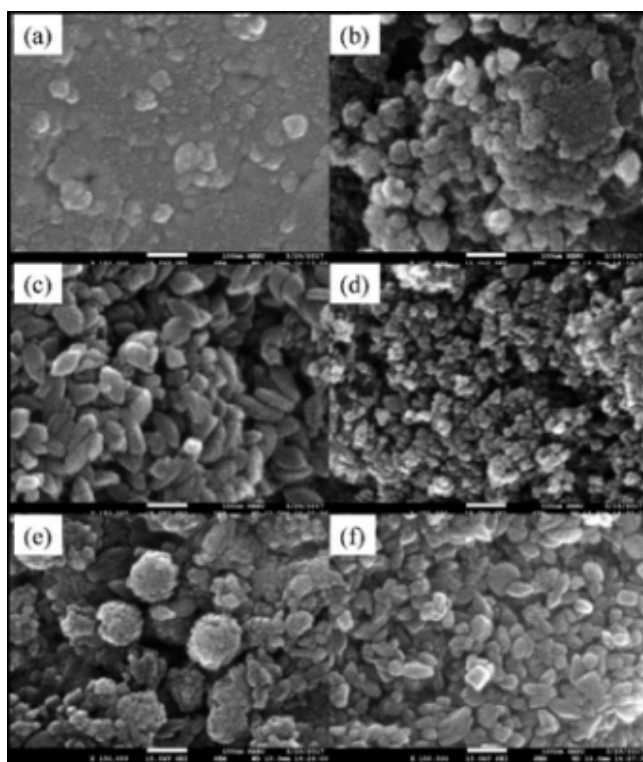


Figure 2. SEM images of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ under various DETA addition (a-f stands for DETA=0.5, 1, 2, 3, 4, 5 mL, respectively) .

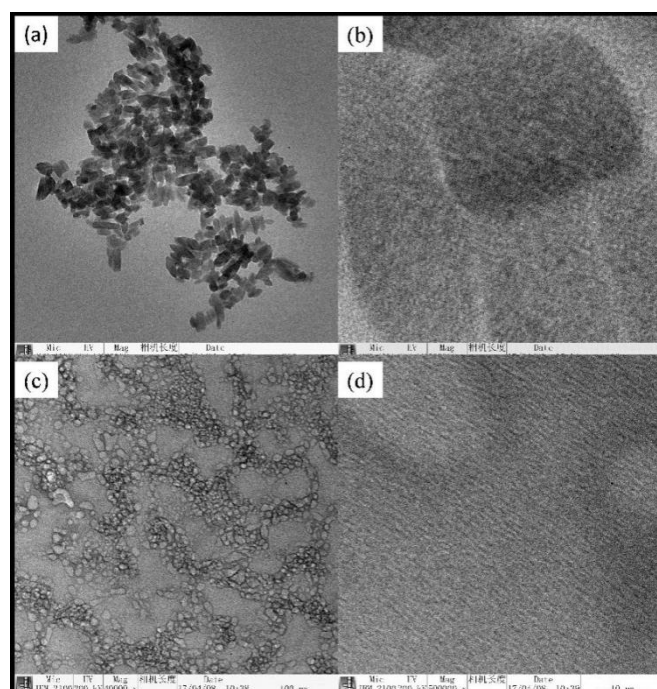


Figure 3. TEM of $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ (a and b represent for $\text{NH}_2\text{-Fe}_2\text{O}_3$; c and d represent for $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$).

3.2. FTIR Analysis

The FTIR spectra of the samples are shown in Figure 4. Figure 4a and b show the FTIR spectra of $\text{NH}_2\text{-Fe}_2\text{O}_3$, $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ and OAC, respectively. Figure 4c shows the FTIR spectra of $\text{NH}_2\text{-Fe}_2\text{O}_3$ with various DETA.

The characteristic peak at 560 cm^{-1} belongs to the lattice vibrations of the FeO_6 octahedral, that's the Fe-O stretching vibration [10]. The bands at 1443 cm^{-1} and 1578 cm^{-1} depicted in Figure 4 are assigned to Fe^{3+} and COO^- symmetric and asymmetric stretching. According to Jishi et al. [11], several infrared active modes may have a wavenumber near 1580 cm^{-1} , while the wavenumbers depend on the eometry of the OAC.

Figure 4a showed the sharp bands at these two position, whereas they declined after combining with OAC. The phenomenon is accounted to the highly reactive NH_2 of OAC. As limited DETA is provided, COO^- didn't react with Fe^{3+} properly (Figure 4b), as the DETA augments, the band gradually declined and disappeared at 1578 cm^{-1} when $\text{DETA}=2\text{ mL}$. The peaks centered at 2857 cm^{-1} and 2927 cm^{-1} are associated with hydrophobic alkyl group from both DETA and SDS. The strong adsorption at near 2900 cm^{-1} is due to the stretching of N-H bond and O-H bond [12-13]. With the existence of the peak at 1600 cm^{-1} , these two peaks indicated that the amino group are integral parts of the composite.

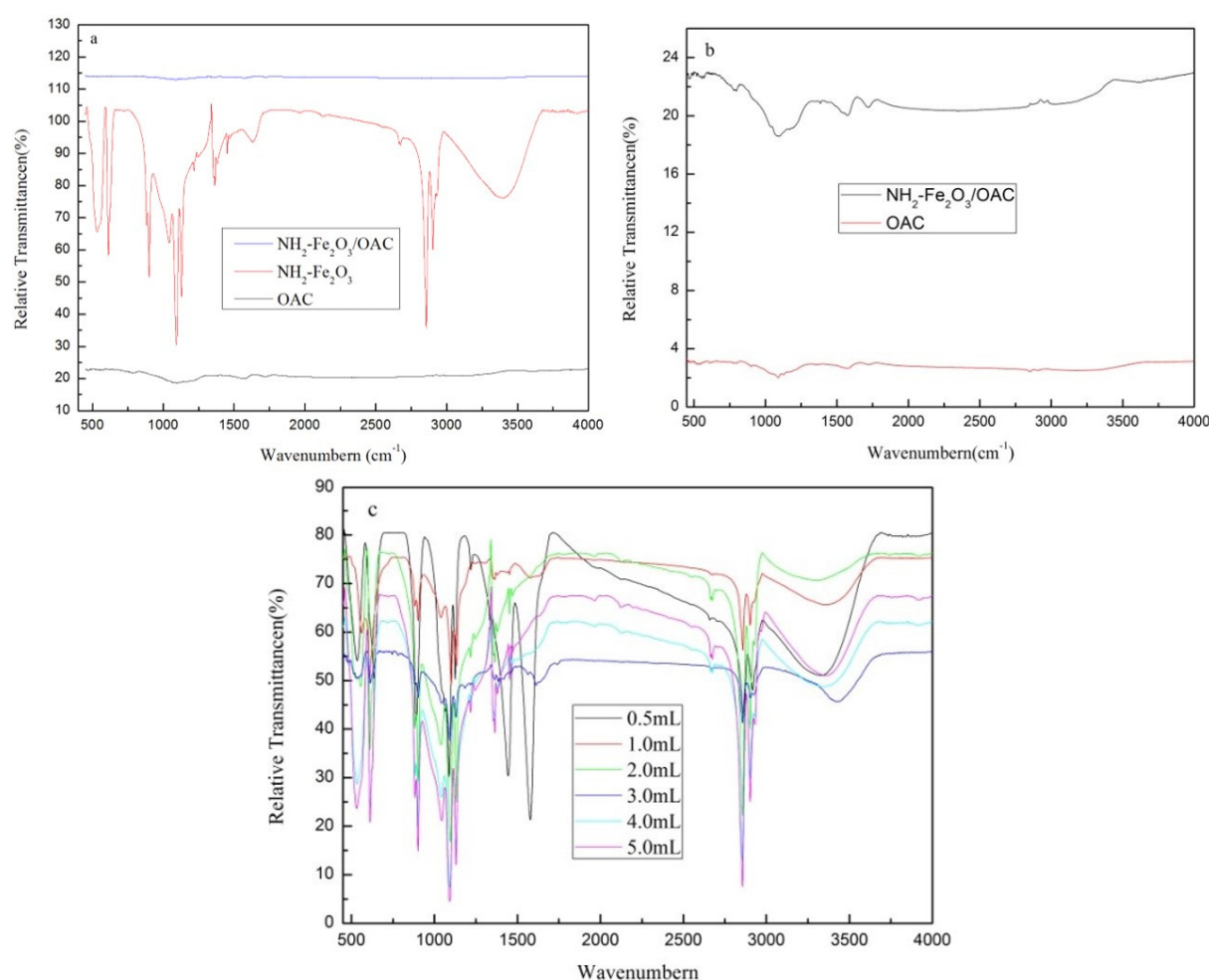


Figure 4. FTIR of various DETA (a: $\text{NH}_2\text{-Fe}_2\text{O}_3$, OAC and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$; b: $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ and OAC; c: $\text{NH}_2\text{-Fe}_2\text{O}_3$ with various DETA) .

3.3. X-ray Diffraction and electron dispersive spectroscopy analysis

The chemical and phase composition of the prepared particles were established by the X-ray diffraction and electron dispersive spectroscopy analysis. The observed peak intensity and width in the XRD pattern exhibit well-defined peaks assigned to the crystal structures of γ - Fe_2O_3 according to the standard card JCPDS card No. 39-1346 [14,15], which is shown in Figure 5. The main characteristic peaks of $\text{NH}_2\text{-Fe}_2\text{O}_3$ appeared around $2\theta=15.069^\circ$, 30.38° , 33.917° , 44.484° , 63.86° , 64.875° , 69.074° , which correspond to (110), (220), (310), (410), (441), (530) and (611), respectively. And the peaks of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ around $2\theta=25.84^\circ$, 34.065° , 44.628° , 54.582° and 64.061° mapped (211), (310), (410), (430) and (441), respectively. These proved the composite is consisted of $\gamma\text{-Fe}_2\text{O}_3$.

Figure 6 stands for $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ with various DETA added in, the visible peaks at (310), (410), (430) and (441) are consistent.

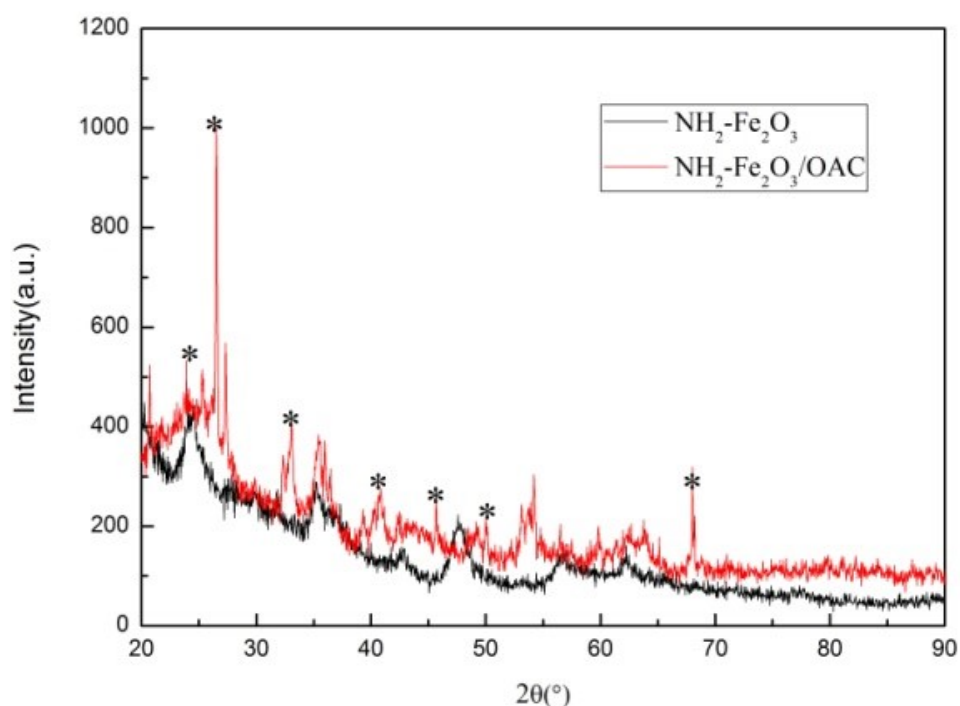


Figure 5. XRD of $\text{NH}_2\text{-Fe}_2\text{O}_3$ and $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$.

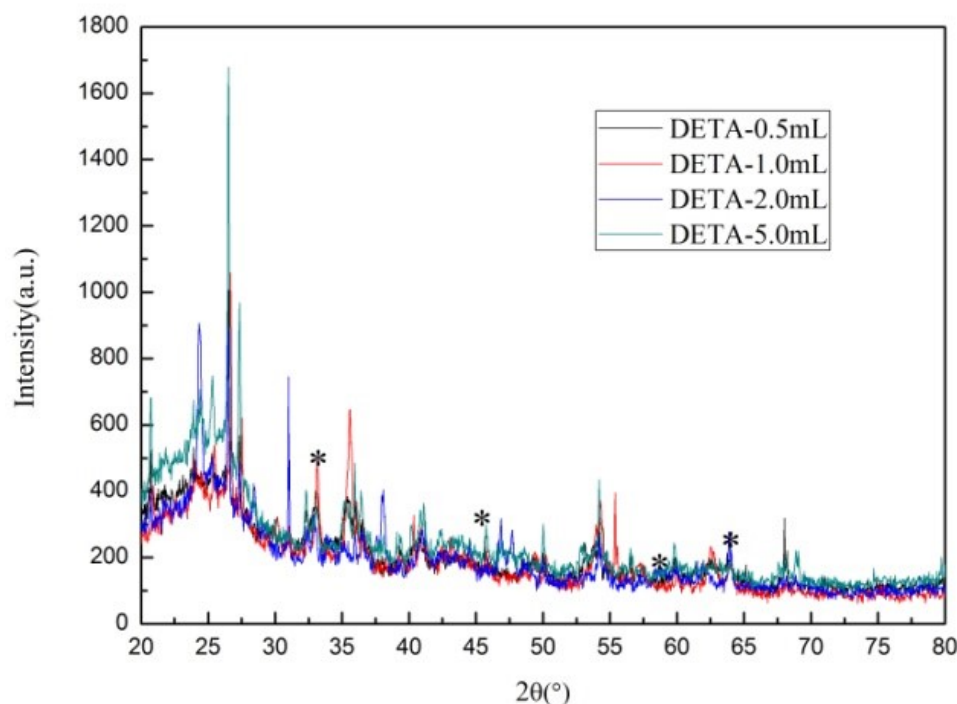


Figure 6. XRD of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ in various DETA levels.

3.4. Adsorption in Ternary Systems

The adsorption tests of the as-prepared composites, which were performed in wastewater treatment, is performed in this work. The experimental condition is a ternary liquid system including Pb(II) , Cd(II) , and Cu(II) , measured by ICP-MS. As is shown in the following Fig. 10, when $\text{DETA}=5\text{ mL}$, the $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ and $\text{NH}_2\text{-Fe}_2\text{O}_3$ achieved 88.11 % and 98.25 % adsorption rate toward Pb^{2+} . For the other two metal ions, they were restrained by the presence of Pb(II) . The high selective factor and physicochemical properties of these studied heavy metals revealed the selective adsorption sequence: $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)}$ [2]. The experimental results agree with other Yu's studying.

The adsorption capacity of $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ were 34.8 mg/g for Cu(II) and 13.4 mg/g for Cd(II) . And the adsorption capacity of $\text{NH}_2\text{-Fe}_2\text{O}_3$ 18.4 mg/g for Cu(II) and 10.8 mg/g for Cd(II) .

4. Conclusions

In summary, the recyclable, controllable, and easy prepared magnetic adsorbents used in heavy metal treatment are synthesized in this work. The adsorption rate towards Pb(II) of the composites $\text{NH}_2\text{-Fe}_2\text{O}_3/\text{OAC}$ and $\text{NH}_2\text{-Fe}_2\text{O}_3$ were up to 88.11 % and 98.25 %, respectively. The selective adsorption sequence is obvious in ternary systems: $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)}$. The SEM, EDS, TEM, FTIR and XRD techniques are used to characterize the good physical properties of the composites.

Overall, from outstanding performance of the prepared composites, they might serve as promising adsorbents applied to heavy metal treatment, and lay foundation for the successful application of NH_2 -functionalized Fe_2O_3 and oxidation-activated carbon in environmental pollution control.

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