# Original Paper

# Synthesis of Magnetic Ferrites by the Dosing Mode of Fe<sub>2</sub>SO<sub>4</sub> and Their Application for Cd(II) Removal from Aqueous

# Environment

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#### Abstract

At 25°C and pH value of 9.0, magnetic ferrite  $(F_1)$ was coated with ferrous sulfate  $(FeSO_4\cdot 7H_2O)$  to synthesize the  $F_2$  by co-precipitation, which  $F_1$  was prepared by ferrous sulfate. Then  $F_1$  and  $F_2$  were applied to remove Cd(II) from aqueous solutions. As-synthesized  $F_1$  and  $F_2$  were characterized by the settlement ratio, the  $Fe^{2+}/Fe^{3+}$  ratio, XRD, SEM and VSM. The results were represented by the settlement rate of 10%, the  $Fe^{2+}/Fe^{3+}$  ratio of 0.5. Several factors effecting the adsorption of Cd(II) ions were studied, including pH, contact time, the initial Cd(II) ions concentration and ammonia nitrogen concentration. Discussed on the adsorption kinetics and isotherm models of Cd(II) ions adsorption. The results revealed that the process of Cd(II) adsorption obeyed the pseudo-second order kinetic model and followed the Freundlich isotherm, indicating the Cd(II) adsorption was a chemical sorption, and the maximum adsorption capacity was 223.71mg/g. The Cd(II) ions adsorption increased with the increase of pH value, ferrite dosage and adsorption time, but ammonia nitrogen could restrain Cd(II) ions adsorption.

# **Keywords**

Synthesis, magnetic ferrites, Cd(II) removal, adsorption kinetics, adsorption isotherms

# 1. Introduction

In recent years, environmental contamination caused by toxic heavy metals has become a worldwide epidemic, especially in some areas where a significant threat to human health and the ecological system (Sharma et al., 2019). Among the heavy metals, cadmium is one of the most hazardous metals affecting

the environment due to its high toxicity, difficult degradability, high stability in water. The cadmium-contained wastewater from effluent discharge of different industries like metal fabrications, fertilizers, batteries, paints, pigments, metal plating, mining and so on (Hu et al., 2011; Narayanan et al., 2022; Niu et al., 2010). Cd(II) ions tend to accumulate in aqueous system and cause several diseases and health disorders in living organisms (Hu et al., 2011; Ozay et al., 2009; Kubra et al., 2021). For humans, cadmium can cause renal disturbances, lung issues, bone lesions, cancer and hypertension (Awual et al., 2018; Awual, 2019). The Environmental Protection Organization in China has established 0.005mg/l as the maximum contaminant level in domestic water supplies and 0.1mg/l as the maximum permissible discharge concentration into the natural environment.

At present, several technologies have been proposed for Cd(II) removal from aqueous solution, such as precipitation (Matlock et al., 2002), floatation (Kefala et al., 1999), ion exchange (Rengaraj et al., 2003), membrane process (Blöcher et al., 2003), electrochemical operation (Purkayastha et al., 2014) and adsorption (Babarindea et al., 2009). However, these methods have their own drawbacks that result in high operating cost, incomplete heavy metal removal, energy requirements, laborious techniques, and sludge generation involving disposal and further treatment (Chakravarty et al., 2010). Among them, adsorption is widely applied to the Cd(II) removal for its high efficiency, convenience and simple physicochemical treatment, especially for low-concentration heavy metal in aqueous solutions (Wang & Chen, 2009).

A variety of natural and industrial adsorbents have been used for Cd(II) removal, like activated carbon and activated alumina (Ku & Peters, 1987; Mahmoud et al., 2011), agricultural waste biomass and slag (Alemayehu & Lennartz, 2009; Gupta et al., 2003; Matheickal et al., 1999; Rouibah et al., 2010), carbon nanotubes, zeolites, sepiolite, etc (Pacheco et al., 2006; Su et al., 2010). These materials possess their own shortcomings of low sorption capacities and expensive. Therefore, the identification of the new adsorbent possessing high adsorption capacity, non-toxic, stable and economic is still the core content of the study in practical applications. The nanosized magnetic materials have a great potential to adsorb Cd(II) ions due to their high surface area, cost-effective, high removal efficiency, good purifying effect and unique advantage of easy separation under external magnetic field. Considering these characteristics, magnetic particles have attracted much attention to Cd(II) ions removal in aqueous environment. In recent years, the bare magnetic ferrite was prepared and applied to remove heavy metals from wastewater, which has been discussed in previous literatures. However, little information is available on the as-synthesized magnetic ferrite coated by ferrous sulfate and applied to the Cd(II) removal from wastewater. Meanwhile, the effect of ammonia nitrogen on the Cd(II) ions adsorption by the as-synthesized magnetic ferrite was also rarely studied.

In the present work, ferrous sulfate has been used as the raw material to prepare the magnetic ferrite. The magnetite nanoparticles  $(F_1)$  were coated ferrous sulfate and prepared the  $F_2$  successfully. Then applied them to remove Cd(II) and compared Cd(II) adsorption capacities of  $F_1$  and  $F_2$ . During the preparation of the magnetic ferrite, the following characteristics were investigated: the variation of

sedimentation ratio,  $Fe^{2+}/Fe^{3+}$  ratio, XRD and SEM photographs. Specifically, the effects of influential factors, including pH values, contact time, Cd(II) initial concentration and ammonia nitrogen concentration, on the adsorption process of Cd(II) ions were explored. Furthermore, the adsorption kinetics and isotherms investigation on Cd(II) adsorption by the  $F_1$  and  $F_2$  were also conducted to study the adsorption mechanisms.

#### 2. Materials and Methods

#### 2.1 Materials

All chemicals and reagents used were of analytical grade without any further purification, which were purchased from Hunan Chemical Reagent Company (Hunan, China). Ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O), high-strength aqua ammonia, sodium hydroxide (NaOH), hydrochloride (HCl), cadmium sulfate (CdSO<sub>4</sub>), EDTA standard solution, Zn powder (99.99%), sulfosalicylic acid, hexamethylenetetramine, dimethyl phenol orange indicator. Deionized water was used for the whole experiment.

# 2.2 Synthesis of Magnetic Ferrite

At 25°C, 1.51 distilled water was placed into a 21 flat-bottom flask. The flask was purged with nitrogen for 8 min to maintain the dissolved oxygen for the experiment, then plugged with the rubbers toppers. Subsequently, 7.5g of FeSO<sub>4</sub>·7H<sub>2</sub>O was dissolved in distilled water and stirred with a magnetic mixer, then NaOH (1mol/l) and HCl (1mol/l) were added into the flask to adjust the pH value of the solution to 9.0. On the basis of F<sub>1</sub>, F<sub>2</sub> was synthesized according to the preparation steps of F<sub>1</sub>. Once the reactions were finished, the black precipitates were collected on centrifugation at 3000 rpm. The precipitates were washed repeatedly with ethanol and water, and part of them were dried in a vacuum oven at 60°Cfor the subsequent analysis. The preparation flow of F<sub>1</sub> and F<sub>2</sub> are shown in Figure 1.

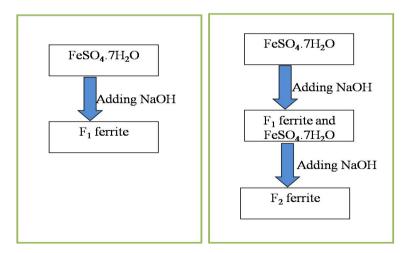


Figure 1. The Preparations Flow of F<sub>1</sub> and F<sub>2</sub> Ferrites

#### 2.3 Characterization

The physical and chemical characteristics of the magnetic ferrites used in this study were elucidated

using standard procedures. The crystal phases were examined by a MSAL-XD2X-ray diffractometer (XRD), using a Cu K $\alpha$  radiation ( $\lambda$ = 0.1541 nm) in the range of 10-80°(20) at 30 kV and 30 mA. The morphology and size of the as-synthesized particles were carried out using a scanning electron microscopy (SEM,JSM-6330,Japan) at an electron acceleration voltage of 20kV. The magnetic intensity of the ferrite was determined by the magnet and a vibration sample magnetic (VSM). The settling ability was determined by the settlement ratio, and the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio of the as-synthesized particles was measured by the complexometry method.

### 2.4 Adsorption Cd(II) ions

The adsorption behaviors of  $F_1$  and  $F_2$  were examined through batch sorption experiments, the stock solution of Cd(II)(2000mg/l)was prepared using  $CdSO_4$  in distilled water to give a variety of concentrations. A certain quantity of the ferrites and varying concentrations of Cd(II) ions were placed in 250ml flasks with rubber stoppers, the flasks were put into a Thermostatic Magnetic Stirrer and stirred until the reaction finished, then the Cd(II)ions in the supernatant was measured by Flame Atomic Absorption Spectrometer as the residual concentration( $C_t$ ) in solution, their final pH were adjusted to a certain value using 0.1M HCl and 0.1M NaOH. The removal rate( $\eta$ ) and the adsorption capacity ( $Q_e$ ) were calculated by the following equations:

$$\eta = [(C_o - C_e)/C_o] \times 100\% \tag{1}$$

$$Q_e = [(C_o - C_e) \times V]/m \tag{2}$$

Where  $C_o$  is the initial concentration of Cd(II) ion(mg/l),  $C_e$  is the final concentration of Cd(II) ion(mg/l), V is the volume of Cd(II) ion solution (l) and m is the weight of the ferrite used,  $\eta$  is the removal rate of Cd(II) ion (%).

#### 3. Results and Discussion

# 3.1 Characterization of the Magnetic Ferrites

The settlement ratio reflects the sedimentation property of the particles in an aqueous environment. It is an important index because it can be used to tell whether the as-synthesized magnetic ferrite in solution had difficult to settle, it also provides information about the particle size and the degree of compaction of the prepared ferrite. The lower the sedimentation ratio, the better the sedimentation property of the magnetic ferrite is. The settlement ratio was determined every 5min during a period of 30min,the experimental data for the ferrites are given in Figure 2.

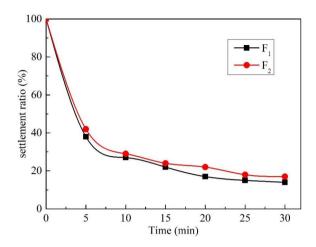


Figure 2. The Variation of Settlement Ratio of F1 and F2

From Figure 2, the both curves have a similar trend over time. A rapid decrease was exhibited in the settlement ratio for the first 1min, reaching 24% for  $F_1$  and 22% for  $F_2$ . Then had a mild decrease after that time and tended to maintain stable in the end and the final settlement ratios were 10% for  $F_1$  and 17% for  $F_2$ . Within 30min, the settlement ratio of  $F_2$  was slightly higher than that of  $F_1$ . This explained that the particles of  $F_2$  are bigger than that of  $F_1$ , the result showed that the sedimentation property of  $F_1$  was better than that of  $F_2$ .

The main composition of ferrite is  $Fe_3O_4$ , according to the theoretical calculation,  $Fe^{2^+}/Fe^{3^+}$  ratio is 0.5. According to the determination of the  $Fe^{2^+}/Fe^{3^+}$  ratios (0.5 for  $F_1$ , 0.63 for  $F_2$ ) the result illustrated that the  $F_1$  was in consistent with that in  $Fe_3O_4$  and formed completely, while  $F_2$  formed with impurities.

The ferrite nanoparticles have attracted attention because of the strong magnetic features, higher chemical resistance to oxidation (Jacob et al., 2013; Liu et al., 2012; Song & Zhang, 2006). In the present work, the black colored Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized in solutions and their magnetic property are shown in Figure 3.

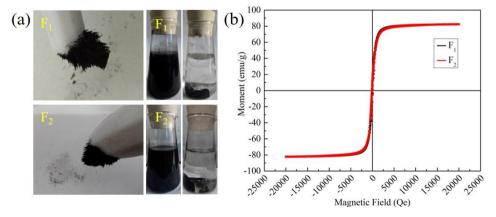


Figure 3. (a) Photograph of F<sub>1</sub> and F<sub>2</sub> Showing Spinel Ferrite Nanoparticles and Their Attraction towards a Magnetic Stir Bar, (b) Room-temperature Hysteresis Loop Curve of the Magnetic Ferrites

From Figure 3, the both magnetic ferries were essentially super-paramagnetic with the magnetization saturation values of 82.30 emu/g for F<sub>1</sub> and 82.16 emu/g for F<sub>2</sub>. Figure 3a showed that these magnetic particles could be separated toward the external magnetic within 2 min. Almost all the nanoparticles could be separated from solution by a strong external magnet, and they could be well dispersed again by physical shaking when the external magnetic field was removed.

The morphology and the crystal structure of the synthesized  $F_1$  and  $F_2$  were determined by using SEM and X-ray diffraction (XRD) analysis, as shown in Figure 4.

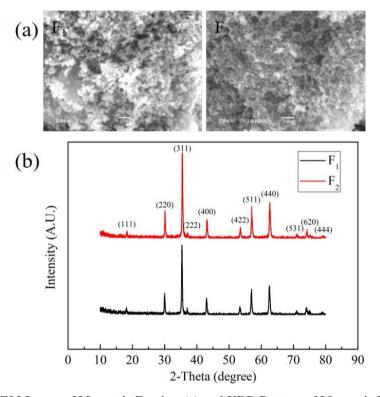


Figure 4. SEM Image of Magnetic Ferrites (a) and XRD Pattern of Magnetic Ferrites (b)

Figure 4a displays the SEM images of F<sub>1</sub> and F<sub>2</sub>, which reveals that the particles of the both magnetic ferrites are a narrow size distribution and in the range of nanometer. From Figure 4b, the XRD patterns of the both display eleven relatively strong reflection peaks in the 2θ region of 10-80°. All reflection peaks at (111), (220), (311), (222), (400), (422), (511), (440), (531), (620) and (444) can be well-indexed to a cubic inverse spinel structure of the Fe<sub>3</sub>O<sub>4</sub> (JCPDS cardno.79-0416) (Barakat & Schmidt, 2010). The result confirms that the coated F<sub>2</sub> does not cause the phase change of bare F<sub>1</sub> (Maity & Agrawal, 2007; Simeonidis et al., 2011).

# 3.2 Cd(II) Adsorption

# 3.2.1 Effect of pH

In the Cd(II)adsorption process, pH plays a key role to affect the interactions of adsorbent and adsorbate, it also determines the speciation of metal in solution (Deng & Ting, 2005; Eldridge et al.,

2015; Huang et al., 2012). At 25°C, the magnetic ferrite quantities were 0.2g, the initial Cd(II) ions concentration was 100mg/l, the reaction time was 1h.Cd(II) ions adsorption by the both magnetic ferrites at various pH(pH 6.0-9.0) are shown in Figure 5.

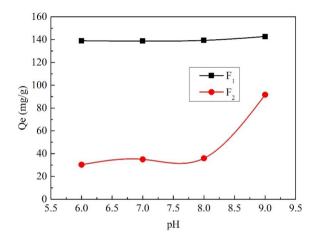


Figure 5. Effect of pH on the Adsorption of Cd(II) Ions

From the Figure 5, it was observed that the adsorption capacities of the magnetic ferrites changed over time. A little change was found in the F<sub>1</sub> curve in the initial pH from 6.0 to 8.0, the adsorption capacity increased from 138.9mg/g to 139.2mg/g. Then the adsorption capacity of F<sub>1</sub> has a slight increase in the pH from 8.0 to 9.0 and the final value of 142.6mg/g. From the F<sub>2</sub> curve, a little change was exhibited in the pH range of 6.0-7.0 and the adsorption capacity reached 35.0mg/g. While a clear increase was found in pH from 7.0 to 9.0, the adsorption capacity increased from 35.0mg/g to 91.6mg/g and showed an increasing trend. The result showed that the magnetic ferrites could adsorb Cd(II) ion from water and the Cd(II) adsorption property of F<sub>1</sub> was better than that of F<sub>2</sub>.

The variation in the adsorption capacity with pH is explained by the adsorption mechanism. At low pH, the surface was surrounded by H<sup>+</sup>, which competed with Cd(II) ion and prevented it from approaching the binding sites on the ferrite (Wong et al., 2003). The adsorption capacity increases with the pH increasing, this increase might be accounted for the lower competition of H<sup>+</sup> with Cd(II) ions for the active site (Panuccio et al., 2009), and the higher competition of hydroxyl ions with the ferrite for the Cd(II) ions. If so, Cd(II) ions are not only absorbed by ferrite, but are also bound to the hydroxyl ions, which leads to the apparent adsorption capacity forCd(II) ions increasing as the pH increases. However, every heavy metal has the critical pH value, when the pH value is higher than the critical pH value, hydrolysis and precipitation were dominant in solution. The critical pH value of Cd(II) ion was 8.4 (Wang, 1993). Therefore, pH 8.0 was selected as the most suitable pH for Cd(II) adsorption by the both magnetic ferrites.

3.2.2 Effect of Contact Time on Adsorption of Cd(II) Ions

At 25°C and pH of 8.0, the initial concentrations of Cd(II) ions was 200mg/l and the magnetic ferrites were 0.2g.The Cd(II) ion adsorption capacity versus time is shown in Figure 6.

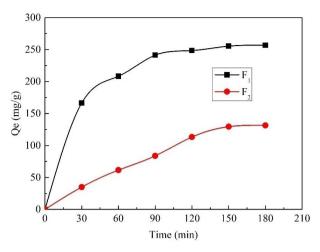


Figure 6. Effect of Contact Time on Adsorption Cd(II) Ions

From Figure 6, the Cd(II) ion was adsorbed rapidly by  $F_1$  at the first 30min and a small change was observed in  $F_1$ curve after that time, then gradually reached the equilibrium, that is due to the absence of internal diffusion resistance (Ahmaruzzaman & Gayatri, 2011; Chang & Chen, 2005). The final adsorption capacity of Cd(II) ion was 256.67mg/g. While the adsorption capacity of Cd(II) by  $F_2$  has a homogeneous variation, increasing from 0mg/g to 131.52mg/g in the whole process, then the curve displays a trend to equilibrium. However, the adsorption capacity of Cd(II) by  $F_1$ was higher than that of  $F_2$ , the phenomenon illustrates that the adsorption efficiency of the bare magnetic ferrite was better than that of the coated magnetic ferrite.

In adsorption process, the kinetic parameters are very important for determination of rate of adsorption. Then the pseudo-first order (Esen et al., 2014) and pseudo-second order (Ho & McKay, 1999) kinetic models were used to investigate the kinetics of the adsorption of Cd(II) ions by the magnetic ferrites. They are expressed in equations(3) and (4), respectively.

$$ln(Q_e - Q_t) = lnQ_e - K_1 t$$
(3)

$$t/Q_t = 1/(k_2Q_e^2) + t/Q_e$$
 (4)

Where  $Q_e$  (mg/g) and  $Q_t$ (mg/g) are the metal uptake per unit weight of adsorbent(mg/g) at equilibrium and metal uptake per unit weight of adsorbent(mg/g) at time t (min), respectively.  $K_1$ (min<sup>-1</sup>) and  $K_2$  (g/mg·min) are the rate constant of pseudo-first order and pseudo-second order kinetics respectively. The obtained values of slope and intercept were utilized for determination of  $K_1$  and  $K_2$ . The plots of  $ln(Q_e-Q_t)$  versus t and  $t/Q_t$  vs. t were given in Figure 7 and the calculated parameters are listed in Table 1.

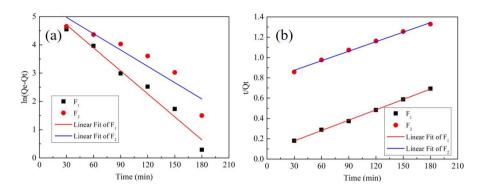


Figure 7. Graphical Representation of Linear fit of Kinetics Model (a) Pseudo-first Order and (b)

Pseudo-second Order for the Adsorption of Cd(II) Ions onto F<sub>1</sub> and F<sub>2</sub>

Table 1. Pseudo First and Second Order Kinetics Data of Cd(II) Ions Adsorption by F<sub>1</sub> and F<sub>2</sub>

| Adsorbent | Pseudo-first order                  |                       |                | Pseudo-second order       |                       |                |
|-----------|-------------------------------------|-----------------------|----------------|---------------------------|-----------------------|----------------|
|           | K <sub>1</sub> (min <sup>-1</sup> ) | Q <sub>e</sub> (mg/g) | $\mathbb{R}^2$ | K <sub>2</sub> (g/mg·min) | Q <sub>e</sub> (mg/g) | R <sup>2</sup> |
| $F_1$     | 0.027                               | 249.90                | 0.968          | 1.50×10 <sup>-4</sup>     | 294.10                | 0.998          |
| $F_2$     | 0.019                               | 257.24                | 0.857          | 1.26×10 <sup>-5</sup>     | 319.49                | 0.993          |

From Table 1, the correlation coefficient ( $R^2$ ) values of pseudo-first order were 0.968 for  $F_1$  and 0.857 for  $F_2$ . In the second-order kinetics, the correlation coefficient ( $R^2$ ) values are 0.998 for  $F_1$  and 0.993 for  $F_2$ , which are higher than that of pseudo-first order. This indicated that the pseudo-second order model yielded a better fitting than the pseudo-first order, also suggested that the adsorption process of Cd(II) was very fast. It is supported the assumption that the adsorption was the chemisorption process (Crini et al., 2007), Similar results were reported where better fitting of the pseudo-second order model compared to the pseudo-first order for Cd(II) adsorption on different adsorbents (Ahmaruzzaman & Gayatri, 2011; Chang & Chen, 2005).

# 3.2.3 Adsorption Isotherms

Adsorption isotherms, that the amount of adsorbate on the adsorbent (Q<sub>e</sub>) as a function of equilibrium concentration in bulk solution (C<sub>e</sub>) at constant temperature, were also studied. It is rather important for explaining the adsorption process at equilibrium conditions. At 25°C and pH of 8.0, the adsorptions by the both magnetic ferrites were carried out at different initial concentrations of Cd(II) ions, i.e., 15,25, 30, 50, 60, 75, 90, 100 and 125mg/l in aqueous solution, and the magnetic ferrite quantities were 0.2g. The parameters obtained from different models provide lots of important information, including adsorption mechanism, surface properties and affinities of the sorbent. In the study, two popularly used adsorption isotherms, Langmuir (Ho & McKay, 1999) and Freundlich (Crini et al., 2007)models, were commissioned to fit these experimental data. The Langmuir isotherm model is based on the assumption

of homogeneity on the surface of adsorbent with a finite number of identical sites and a constant adsorption potential. The Freundlich isotherm is an empirical equation based on a highly heterogeneity surface adsorption. These two models are represented in equations (5) and(6), as follows:

Langmuir equation:

$$C_e/Q_e = 1/bQ_m + C_e/Q_m$$
 (5)

Freundlich equation:

$$lnQ_e = lnK_f + 1/nlnC_e$$
 (6)

Where  $C_e$  is the equilibrium concentration of metal in aqueous phase in mg/l and  $Q_e$  is the amount of Cd(II) ions adsorbed on per unit weight of ferrite in mg/g at equilibrium, the  $Q_m$  is the maximum adsorption capacity (mg/g) reflected on a complete monolayer adsorption and b is the Langmuir constant (l/mg) related to adsorption energy, the plot of  $C_e/Q_e$  versus  $C_e$  is shown in Figure 8a. In the Freundlich equation,  $K_f$  and n are the Freundlich constants related to the maximum sorption capacity (mg/g) and the heterogeneity factor (1/mg), respectively. They can be obtained from the slope and intercept of linear plot of  $lnQ_e$  vs.  $lnC_e$  as shown in Figure 8b, and all the parameters of the two models are listed in Table 2.

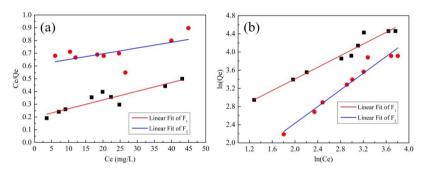


Figure 8. Langmuir Adsorption Isotherms (a) and Freundlich Adsorption Isotherms (b) of  $F_1$  and  $F_2$ 

Table 2. The Parameters of Adsorption Isotherms of Cd(II) Ions

| Adsorbent      | Langmuir adsorption isotherms |          |                | Freundlich adsorption isotherms |             |                |
|----------------|-------------------------------|----------|----------------|---------------------------------|-------------|----------------|
|                | $Q_m (mg/g)$                  | b (l/mg) | $\mathbb{R}^2$ | n                               | $K_f(mg/g)$ | $\mathbb{R}^2$ |
| F <sub>1</sub> | 223.71                        | 0.035    | 0.826          | 1.561                           | 8.381       | 0.955          |
| F <sub>2</sub> | 147.06                        | 7.36     | 0.287          | 1.090                           | 1.813       | 0.953          |

From Figure 8 and Table 2, both the Langmuir and Freundlich models could describe the adsorption of Cd(II) ions by  $F_1$  and  $F_2$ . For the Langmuir isotherm, their correlation coefficients ( $R^2$ )were 0.826for  $F_1$  and 0.287 for  $F_2$ . While the correlation coefficients ( $R^2$ ) of the both magnetic ferrites described by the Freundlich isotherm were 0.955for  $F_1$  and 0.953 for  $F_2$ . The results indicated that the Freundlich model

yielded a better fit than the Langmuir model and also showed that the Cd(II) adsorption by the magnetic ferrite was a multi-layer coverage. Their maximum adsorption capacities ( $Q_e$ ) were 223.71mg/g for  $F_1$  and 147.06mg/g for  $F_2$ , this suggested that the adsorption efficiency of Cd(II) ions by  $F_1$  was better than that of  $F_2$ .

In the Freundlich isotherm, n and  $K_f$  were used to reflect the adsorption properties between adsorbent and adsorbate.  $1 \le n \le 10$  represents a preferential adsorption, the n values 1.561 for  $F_1$  and 1.090 for  $F_2$  demonstrated that Cd(II) adsorption by the both magnetic ferrites were the preferential adsorption (Chen et al., 2009).  $K_f$  is adsorption coefficient, as the value of  $K_f$  increased, the adsorption capacity of Cd(II) ions by the magnetic ferrite strengthened. Therefore, the adsorption capacity of Cd(II) ions by  $F_1$  was better than that of  $F_2$ .

# 3.2.4 Effect of Ammonia Nitrogen

At the ambient temperature 25°C and pH of 8.0, the effect of ammonia nitrogen in wastewater on Cd(II) ions adsorption was investigated. The initial concentration of Cd(II) ions was 200mg/l, the magnetic ferrites were 0.2g and the initial concentrations of ammonia nitrogen were 50, 100 and 150mg/l, respectively. The two experimental groups were setted: the control group (contained Cd(II) ions) and the sample group (contained Cd(II) ions and ammonia nitrogen). The results are shown in Figure 9.

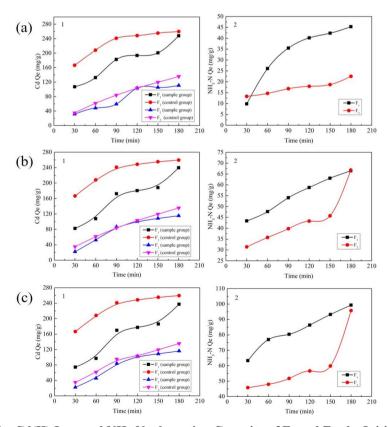


Figure 9. The Cd(II) Ions and NH<sub>3</sub>-N adsorption Capacity of F<sub>1</sub> and F<sub>2</sub>, the Initial Ammonia Nitrogen Concentrations:(a) 50mg/l, (b) 100 mg/l, and (c) 150 mg/l, Respectively

From Figure 9a1, b1 and c1, the both magnetic ferrites not only adsorbed Cd(II) ions, but also adsorbed ammonia nitrogen. A comparison was showed between the control group and the sample group. When the ammonia nitrogen existed in solution, the adsorption capacities of Cd(II) ion by  $F_1$  and  $F_2$  decreased over time. There were a clear increase in adsorption capacity of Cd(II) ions by  $F_1$  inthe control and sample group, and the adsorption capacities of the sample group tended to increase. While compared to that of the control and sample groups by  $F_2$ , the both adsorption capacities hada little increase and tended to reach the equilibrium gradually. However, the adsorption capacity of the control group was higher than that of the sample group. The results illustrated that the ammonia nitrogen existed in solution could inhibited the adsorption of Cd(II) by the magnetic ferrite.

In addition, the ammonia nitrogen in solution also could be removed by the magnetic ferrites. From Figure 9a2, b2 and c2, the adsorption capacities of ammonia nitrogen increased over time with its concentration gradient. The phenomenon showed that Cd(II) ions and ammonia nitrogen were adhere to the surface of the magnetic ferrite simultaneously and competed with the active sites on the surface of the magnetic ferrite. Moreover, Cd(II) ion was easy to form the complex compound with ammonia nitrogen. When ammonia nitrogen existed in solution, part of Cd(II) ions were combined with ammonia nitrogen and adsorbed by the magnetic ferrite, the other Cd(II) ions and the free ammonia nitrogen were adsorbed directly by the magnetic ferrite in solution, the adsorption of ammonia nitrogen reduced the contact chances of Cd(II) ions and the magnetic ferrite. Therefore, the adsorption capacity of Cd(II) ions decreased over time. However, whatever the concentration of ammonia nitrogen was, the capacity of Cd(II) ions adsorption by  $F_1$  and  $F_2$  in control group was higher than that of the sample group. And the adsorption capacity of ammonia nitrogen by  $F_1$  was higher than that of  $F_2$ . The results revealed that the adsorption efficiency of  $F_1$  was better than that of  $F_2$ , and also suggested that the ammonia nitrogen restrained the adsorption of Cd(II) ions by magnetic ferrite in wastewater.

# 4. Conclusion

In this work, the  $F_1$  and coated  $F_2$  were successfully prepared by precipitation method and applied to Cd(II) ion adsorption from wastewater and studied the influencing factors on the adsorption of Cd(II) ions. Results discussed in the manuscript can be summarized as follows:

- (1) The  $F_1$  and  $F_2$ , prepared at the ambient temperature 25°Cand pH of 9.0, presented the settlement rate were 10% for  $F_1$  and 17% for  $F_2$ ,  $Fe^{2+}/Fe^{3+}$  ratios were 0.5 for  $F_1$  and 0.63 for  $F_2$ , the particle sizes were in the nanometer range and the as-synthesized products were the spinel structure of  $Fe_3O_4$ .
- (2) The adsorption capacities of Cd(II) ions by  $F_1$  and  $F_2$  increased with the increase of pH values, contact time and the initial concentrations of Cd(II) ion, and achieved an equilibrium.
- (3) The adsorption behavior of Cd(II) ion by  $F_1$  and  $F_2$  were in accord with the pseudo-second order model. The both models, Langmuir and Freundlich adsorption isotherms, were used to describe the Cd(II) ions adsorption by  $F_1$  and  $F_2$ , and Freundlich isotherm was best fitted for the linearity of Cd(II) ions concentration adsorption by the magnetic ferrites. This indicated that the adsorption of Cd(II) ions

by the magnetic ferrites were controlled by the chemical adsorption and were a multi-layer adsorption.

- (4) Ammonia nitrogen existed in the solutions hindered the Cd(II) ions adsorption by  $F_1$  and  $F_2$ , and leaded to the Cd(II) ions removal efficiency decreased.
- (5) These results revealed that the adsorption efficiency of the bare magnetic ferrite was better than that of the coated magnetic ferrite by ferrous sulfate.

# **Declaration of Conflicting Interests**

The authors declare no conflict of interest.

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