

The Adsorption of Arsenic on Magnetic Iron-Manganese Oxide in Aqueous Medium

Guiqiu Liu, Hefei Zhang

Abstract—The iron oxide and manganese oxide were widely used to remove pollutants for their excellent surface activities and adsorption capabilities. Given that the solid-liquid separation of powdered adsorption materials from water was difficult, the characteristics of arsenic adsorption with the magnetism ferromanganese oxide compound (MFO) were studied here. The results showed that the arsenic was adsorbed effectively by the test material, which could be separated easily from water because of its magnetism nature. The obtained adsorption isotherm data fitted the Freundlich well and the adsorption kinetics followed Lagergren pseudo-second order rate equation well. The arsenic adsorption proceeded very fast, and within 5 min the amount of adsorbed arsenic approached 60-80% of the maximal uptake potential under the equilibrium conditions. The desorption of arsenic was fairly efficient, and the rate of which afforded a comparable value with the rate of adsorption. The extent of adsorption depended on the surface loading and pH. The optimal adsorption of arsenic occurred at pH 6-9.4 for As(III) and pH<5 for As(V). The adsorbed arsenic can be effectively desorbed by the use of 10% NaOH solution while the desorption of As(V) was observed relatively easier than that of As(III).

Index Terms—Arsenic, Adsorption isotherm, Adsorption kinetics, Influencing factors, MFO.

I. INTRODUCTION

Arsenic is one of the priority pollutants in waste discharges. In some countries, the maximum concentration level (MCL) of arsenic in drinking water is regulated with the value of 0.05 mg/L[1], while the United States Environmental Protection Agency (USEPA) lowered the drinking water limit for arsenic to 10 µg/L with a compliance deadline of January 2006. Advanced water treatment process is necessary to remove arsenic from various types of wastewaters in order to reduce its concentration to a permitted level. The common strategies used for the arsenic removal included coagulation-precipitation, adsorption, ion exchange, sand filtration, membrane technology and so on. Adsorption is widely used with the merit such as high effectiveness and relatively easy operation. Iron oxide and manganese oxide are extensively used to remove arsenic due

to its unusual surface activity and high adsorption affinity towards arsenic. Although somewhat good results have been obtained, some deficiencies, such as poor performance for As(III) and difficulty with regeneration of spent adsorbents, still plagued the practice of arsenic removal from aqueous systems by the use of iron oxide and manganese oxide. Furthermore, typically powdered form of the adsorbents makes the separation of iron oxide and manganese oxide from treated water inefficient[1]-[3]. In this paper, the characteristics of As(III) and As(V) adsorption by the magnetism ferromanganese oxide compound (MFO) which were studied. This adsorption material may be separated from water easily due to its magnetism nature and then be recycled after the regeneration with NaOH solution.

II. EXPERIMENTAL

A. Preparation of MFO[4]

MFO was synthesized through reaction between $MnCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ in an alkali medium (Wang et al., 2004). The synthesized material was washed with deionized water, and subsequently dried at $100 \pm 5^\circ C$, then was ground and sieved through a 100 mesh sieve. The samples were characterized by XRD.

B. Preparation of Solutions

Solutions were prepared from $NaAsO_2$ for As(III) and Na_3AsO_4 for As(V). All chemicals used were of analytical reagent grade.

C. Arsenic Adsorption Isotherm Tests

Sodium arsenate and sodium arsenite were used as arsenic sources. To a series of 250 mL conical flasks were added 50 mL of 1-60 mg/L arsenic solutions and 50 mg of MFO. The pH was adjusted to 7.0 using 0.1 mol/L HCl or NaOH solutions. All samples were shaken at 250 rpm and room temperature ($20^\circ C$) in a mechanical shaker for 1h, then were balanced 24h. The solution pH was initially adjusted to determined pH and readjusted to the same value several times till the supernatant pH kept constant at desired pH during the experiment with diluted HCl or NaOH solutions. The suspension in each flask was filtered through a 0.45-µm membrane filter and the filtrate was analyzed for As(III) and As(V) after 24h. The quantity of As(III) and As(V) uptake by MFO was calculated from the decrease of its concentration in solution. The duplicate experiments demonstrated the high repeatability of this batch procedure and the experimental error for most cases could be controlled within 5%.

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pH effect experiments were carried out with the same procedure as described above to determine the effects of pH on arsenic adsorption except that different solutions conditions were controlled. The initial arsenic concentration was 20 mg/L, and the pH was in the range of 3-12. The samples were adjusted for several times till the desired pH was reached and stable.

D. Adsorption Kinetics Tests

In a 1000-ml two-neck distilling flask, 250mg of MFO and 500ml of solution were added. The initial solution contained 20mg/L of As(III) and As(V), respectively. The flask was placed in a water bath and mechanically stirred at 250rpm. The pH of the solution was adjusted to 7.0 with few drops of diluted HCl or NaOH solutions and the temperature was maintained at 20 °C. Two millilitres of supernatant were withdrawn with a 2ml pipette at various time intervals between 0 and 2h.

Desorption kinetics experiments were carried out with the same procedure as described above except that the adsorbent was replaced by MFO saturated adsorption arsenic, and carried out in 10% NaOH solution instead of 20mg/L arsenic solution.

E. Methods of Analysis

The solutions were spectrophotometrically analyzed for arsenic by the silver diethyldithiocarbamate method.

III. RESULTS AND DISCUSSION

A. Effect of pH on As(III) and As(V) adsorption on MFO

To determine the optimum pH for adsorption of arsenic over MFO, the uptake of arsenic as a function of pH was studied. The adsorption of arsenic in the range of pH3-11.5 is shown in Fig.1. The optimal pH for As(III) adsorption was observed in the range of 6-9.4. Beyond the optimal pH range, As(III) uptake significantly decreased. The optimal As(V) adsorption occurred acidic conditions, As(V) uptake significantly decreased as pH rise in pH4-10.5. Compared As(III) and As(V) adsorption, it was found the extent of As(V) uptake by MFO was significantly lower than As(III) as the pH over 5, and its more than As(III) as the pH below 5.

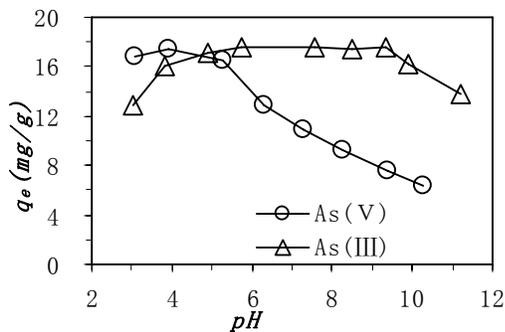
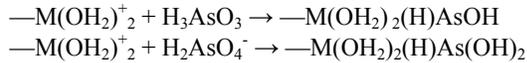


Fig 1 Effects of pH on As adsorbed

Regardless arsenic adsorbed in electrostatic attraction, or ionic exchange or the coordinate complexing, it is most advantageous for arsenic adsorbed when the form of arsenic be in anion and the absorbent with positive charge. pH affects significantly the speciation of arsenic in solution and the

surface charge of the solid particles. Arsenate species and their corresponding stability pH values are H₃AsO₄ (pH<2), H₂AsO₄⁻ (pH 2-7), HAsO₄²⁻ (pH 7-11), and AsO₄³⁻ (pH>12). Trivalent arsenic is stable as neutral H₃AsO₃ at pH < 9, while H₂AsO₃⁻, HAsO₃²⁻, and AsO₃³⁻ are stable species in the pH ranges of 9-12, 12-13, and >13, respectively. On the other hand, to interpret the experimental data using amphoteric dissociation theory, the value of pH_{PZC} is needed where the surface charge is zero. The surface of solid adsorbent is positively charged when the equilibrium pH values are below pH_{PZC}, and it will be negatively charged when the equilibrium pH above pH_{PZC}. The adsorption reactions between arsenic species and metal oxides with pH_{PZC} > 7 in acidic environment are as follows[5]:



In neutral and alkaline environment, they are expressed as:
 $\text{—M(OH)}_2^- + \text{H}_2\text{AsO}_3^- (+ \text{H}_3\text{AsO}_3) \rightarrow \text{—MO}_2\text{AsOH}^-$
 $\text{—M(OH)}_2^- + \text{HAsO}_4^{2-} \rightarrow \text{—MO}_2\text{As(O)OH}^-$

The pH_{zpc} of MFO detected was pH8.5. As the equilibrium pH increased from lower pH to pH8.5, the decreased adsorption arsenate was attributed to the decreasing electrostatic attraction between the surface of MFO and anionic arsenate species. The lower adsorption of arsenate at pH > 8.5 could be due to an increased repulsion between the negatively charged arsenate species and negatively charged surface sites. Since arsenite species have less negative charge character as compared to arsenate species at pH < 9, they do not exhibit as much repulsion, and as a result, arsenite was preferably adsorbed by MFO in a wide pH range. The decrease in the adsorption yield above pH9.4 may be attributed to an increase of negatively charged arsenite species and negatively charged surface sites.

Tests shows that the adsorption of As(III) at acidic pH is a hydrogen-release process, in contrast to a hydrogen-consuming process at alkaline pH. Thus, under separate acidic and alkaline conditions, further increase in acid and alkali strength will shift the adsorption reaction from the right side to the left side and lead to the reduction of As(III) adsorption with increasing intensity of acidity and alkalinity. The favored As(III) adsorption at nearly neutral pH is a result of insignificant release(or consumption) of hydrogen during the reaction of H₃AsO₃ and MFO.

B. Adsorption isotherms

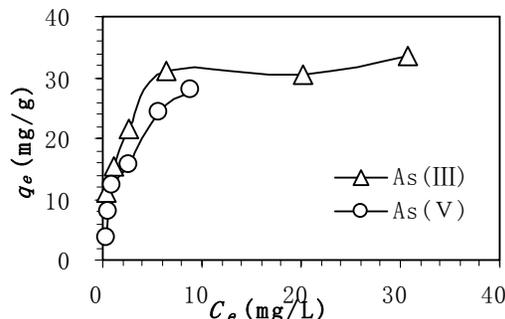


Fig. 2 Adsorption isotherm

Fig.2 shows the adsorption isotherm curve of arsenic. The amounts of arsenic adsorbed increased with the increasing equilibrium arsenic concentration in solution. The adsorption of As(V) with increasing equilibrium arsenic concentration can be divided into two stages, including a rapid enhancement in arsenic adsorption as equilibrium concentration of arsenic was low, and a slow increase of that as equilibrium concentration of arsenic was high. This was possibly related to the degree of surface coverage of MFO by arsenic adsorbate; the potential of arsenic adsorption was relatively greater as the surface coverage was low because more activated adsorption sites were readily accessible, while the situations conversed as the surface coverage was high because at this time few unoccupied adsorption sites were retained. Therefore, the amounts of arsenic adsorbed increased little as the equilibrium concentration of arsenic increased, and finally the equilibrium approached. Fig.3 shows that the adsorption data fitted Freundlich isotherm equation well. As a result of super activity and hydrolysis ability of As(V) relative to As(III), As(V) should be better adsorbed iron oxides. However, our results showed the difference between the amounts of As(III) adsorption and As(V) adsorption were no significant. This might be because that the affinity of Mn with As(III) were stronger than As(V). Alternatively, the specific structure of spinel compound oxides might be the second reason contributable to the equal adsorption of As(III) and As(V)[6].

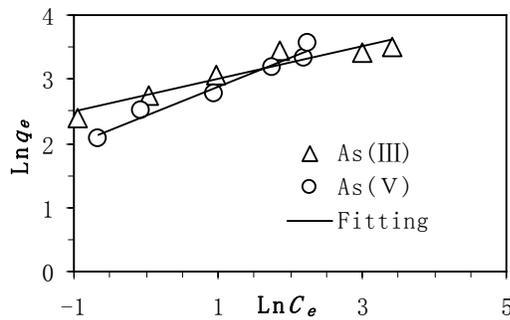


Fig.3 Freundlich fitting curve

C. Adsorption and desorption kinetics

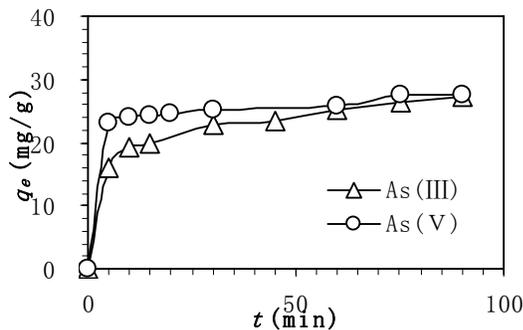


Fig. 4 Adsorption kinetics of arsenic

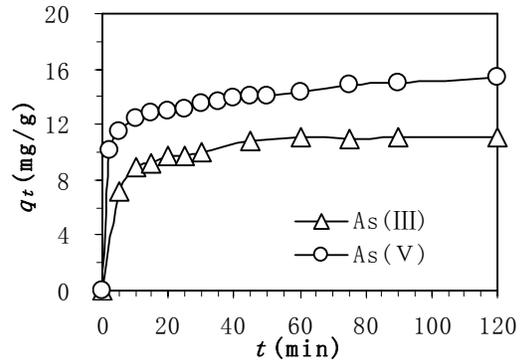


Fig.5 Desorption kinetics of arsenic

Fig.4- Fig.5 shows kinetics curve of arsenic adsorption and desorption. As seen in Fig.4- Fig.5, the adsorption and desorption of As(III) and As(V) on MFO was found to be time dependent. The speed of arsenic adsorption and desorption was quick firstly, and then dropped off, and finally approached the equilibrium. The amount of arsenic adsorbed or desorbed was 60-80% of the overall uptake or overall desorption within 5 minutes. The kinetics of adsorption and desorption process of particle solid materials in aqueous medium can be usually described with the modes such as Lagergren first order rate equation, Lagergren pseudo-second order rate equation, Parabolic diffusion equation, Elovich equation and Power function equation. The models of various adsorption kinetics are listed in table 1[7]-[9]. It was demonstrated that our data of adsorption kinetics and desorption kinetics followed the Lagergren pseudo-second order rate equation well.

Table 1 Equation model of arsenic adsorption and desorption kinetics

Title of equation	Integral forms of equation
Lagergren first order equation	$\ln (q_{eq}-q_t) = A + k_1 t$
pseudo-second-order equation	$t/q_t = A + t/q_{eq}$
Parabolic diffusion equation	$(1-q_t/q_{eq}) = -kt^{1/2}+A$
Elovich equation	$q_t = A + k \ln t$
Power function equation	$\ln q_t = \ln A + k \ln t$

The form of Lagergren pseudo-second order rate equation can be expressed as:

$$\frac{dt}{dq_t} = k_2 (q_{eq} - q_t)^2 \quad (1)$$

Integral forms of the equation :

$$\frac{t}{q_t} = A + \frac{t}{q_{eq}} \quad (2)$$

$$v_0 = \frac{1}{A} \quad (3)$$

$$k_2 = \frac{v_0^2}{q_{eq}} \quad (4)$$

where t is the time (min), q_t is adsorption or desorbthe quantity at t time (mg/g), q_{eq} is the balance quantity of adsorption or desorb (mg/g), k_2 is the initial velocity constant [g/(mg·min)], v_0 is the initial velocity of adsorption or desorb [mg/(g·min)].

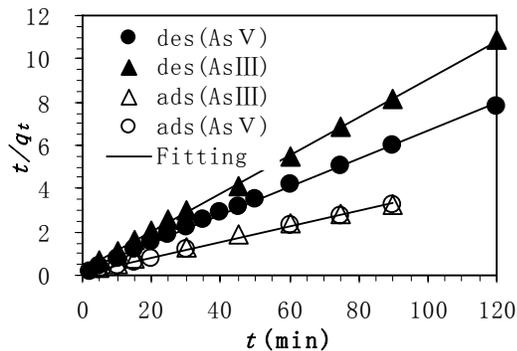


Fig.6 Lagergren Plots for As(III) and As(V) adsorption and desorption

The linear plot of t/q_t vs t shows the applicability of Lagergren equation for As(III) and As(V) [Fig.6]. The fitting parameter obtained were listed in table 2, including v_0 , q_{eq} and R^2 (correlation coefficient). As seen from table 2, the initial speed of As(III) adsorption was considerably smaller than As(V), but the amount of equilibrium As(III) adsorption was more than As(V). Concerning the initial

speed and the extent of equilibrium desorption, As(III) showed smaller values than As(V). The percentage of equilibrium As(III) desorption was 66.3% comparing the greater value of 86.2% for As(V).

The kinetics of arsenic adsorption was initially quick, and then dropped off. Arsenic was initially adsorbed by the exterior surface of the MFO. When the adsorption at the exterior surface reached the saturation level, the arsenic ions began to enter the MFO via the pores within the particles and were adsorbed by the interior surface of the particles. When the arsenic ion diffused into the pores of the MFO, the diffusion resistance was increased, which in turn led to a decrease in diffusion rate. With the decrease in arsenic concentration in the solution, the diffusion rate became constantly lower, and consequently, the diffusion processes reached equilibrium. The desorption of arsenic from the MFO may be the reversible process of adsorption, in which the arsenic adsorbed onto the exterior solid surface released from the solid surface into the aqueous phase with rapid speed, and then the arsenic species adsorbed in the internal solid phase began to be desorbed. Furthermore, with the increase in arsenic desorption and arsenic concentration in solution, the diffuse resistance of arsenic from the oxide surface to aqueous phase gradually increased, which also caused the decrease in the rate of arsenic desorption.

Table 2 Coefficients of a pseudo-second-order kinetic model fitting of arsenic adsorption and desorption kinetics

Type of reaction	As(III)				As(V)			
	v_0 [mg/(g·min)]	q_{eq} [mg/g]	k_2 [g/(mg·min)]	R^2	v_0 [mg/(g·min)]	q_{eq} [mg/g]	k_2 [g/(mg·min)]	R^2
Adsorption	4.68	28.33	0.058	0.996	12.67	27.86	0.016	0.998
Desorption	3.04	11.64	0.02	0.998	4.30	15.55	0.02	0.998

IV. CONCLUSIONS

As(III) and As(V) were effectively removed by MFO via adsorption, the difference of adsorption capacity between As(III) and As(V) was not significant. The extent of arsenic adsorption depended on surface loading and pH. The adsorption isotherm data obtained fitted the Freundlich well and the adsorption kinetics followed Lagergren pseudo-second order rate equation. Both adsorption and desorption proceeded very fast, and in 5 minutes the amount of arsenic adsorption or desorption reached up to 60-80% of those detected in equilibrium conditions. The adsorbed arsenic can be effectively washed out with 10% NaOH solution, while the desorption percentage of As(V) was considerably greater than As(III).

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