

# Effect of ferrous on the adsorption of As(V) from aqueous solution on activated carbons

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**KEYWORD:** Activated carbon; arsenate; isotherm; ferrous

**ABSTRACT:** Arsenic is a toxic substance. The adsorption by activated carbon is generally considered to be one of the most efficient methods to remove As(V). In this paper, three kinds of commercial activated carbons (N1, N2 and N3) were used to adsorb As(V) from water. The result showed that the adsorption capacity of As(V) on N1, N2 and N3 were 2.539 mg / g, 1.014 mg / g and 0.581 mg / g, respectively. N1 had an advantage of adsorption capacity for arsenic. Besides, the effect of ferrous( $\text{Fe}^{2+}$ ) and chloride( $\text{Cl}^-$ ) ion on the adsorption of arsenate on N1 was investigated. Due to more activated sites being contributed by the adsorptive iron,  $\text{Fe}^{2+}$  promoted the adsorption of As(V) on N1.  $\text{Cl}^-$  occupied activated sites to declining the adsorption of As(V) on N1.

## introduction

Arsenic in drinking water is a great concern because long-term exposure to arsenic-contaminated drinking water can cause skin, kidney, lung, and bladder cancers (Jain et al. 2000). The adsorption by activated carbon is generally considered to be one of the most efficient methods to control organic and inorganic contaminants in water. Surface modification and impregnation of activated carbon, including Zr-loaded (Sandoval et al. 2011), Fe-loaded (Lodeiro et al. 2013), Ni-loaded (Dobrowolski et al. 2013), are identified as key methods for promoting adsorption affinity, selectivity and effectiveness for As. These materials represent a good adsorption efficiency, however, the cost is decline of surface area, pore structure and uptake of organics from water. There is also a problem that leaching of the ligand to the solution has directly influenced the application (Li et al. 2014). So it is possibly an effective way to promote adsorption of As by using dissolved  $\text{Fe}^{2+}$  directly. In addition, the other coexisting ions(example  $\text{Cl}^-$ ) in water also have an effect on the adsorption of arsenic.

Three commercial activated carbons were used to adsorb As(V) from water. Objectives of this work were the following: (i) to evaluate the adsorption equilibrium isotherms of As(V); (ii) to optimize activated carbon through experimental data; (iii) to explore the enhanced capacity of co-existing  $\text{Fe}^{2+}$  and  $\text{Cl}^-$  for As adsorption on the optimal activated carbon.

## Materials and methods

### Material and reagent

Activated carbons were obtained from Norit Netherlands Inc. and were available in  $8 \times 30$  US mesh size,  $12 \times 20$  US mesh size and  $12 \times 40$  US mesh size, abbreviated N1, N2 and N3, respectively. Stocks solutions of As(V) (1000 mg / L) were prepared by dissolving  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma,

USA) in deionized water, respectively. Solutions used for experiment were prepared by diluting the stock solutions. Other chemicals were analytical grades. All water samples used in the adsorption experiment were diluted from stock solution with deionized water.

### Adsorption Experiments

The adsorption isotherms were conducted at an initial pH of 7, a series of activated carbon of N1, N2 and N3 (15~250 mg) were placed in contacted with 50 mL As(V) solutions (pH=7), respectively. Then sealed and continuously stirred at 25°C, 150 rpm. The concentrations were measured after 48 h. The effects of ferrous ion were investigated by changing one factor but others remaining. The experimental results were average values at twice.

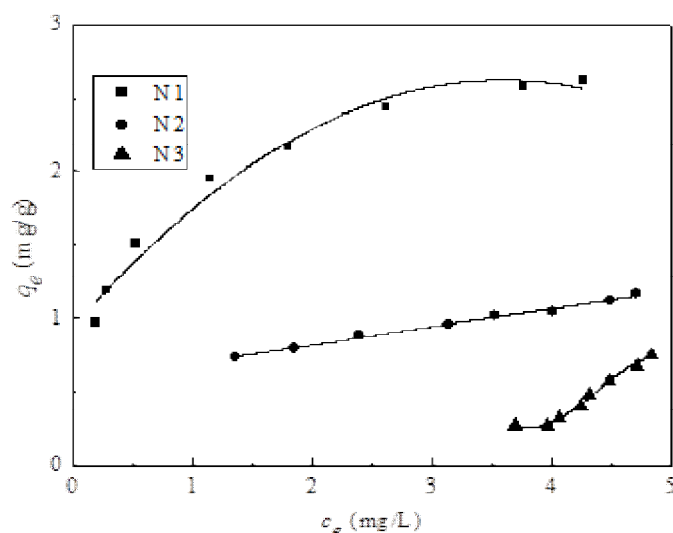
### Analytical Methods

All the water samples in the experiment were filtered through 0.45 μm glass fiber filters to separate the carbon particles, and the filtrate was analyzed for arsenic. The dissolved arsenic concentrations in solutions were measured by molybdenum blue method (Dhar et al. 2004).

## Results and discussion

### Adsorption isotherms

The adsorption capacity is an important factor because it demonstrates how much adsorbate is required when adsorption saturation. In this study, arsenic adsorption isotherms of three kinds of activated carbons were shown in Figure 1.



$c_0=5\text{mg/L}$ ;  $\text{AC}=0.3\sim 0.5\text{g/L}$ ;  $\text{pH}=7.0$ ;  $T=25\pm 0.2^\circ\text{C}$

Figure 1. Adsorption isotherms of As(V) on N1, N2 and N3.

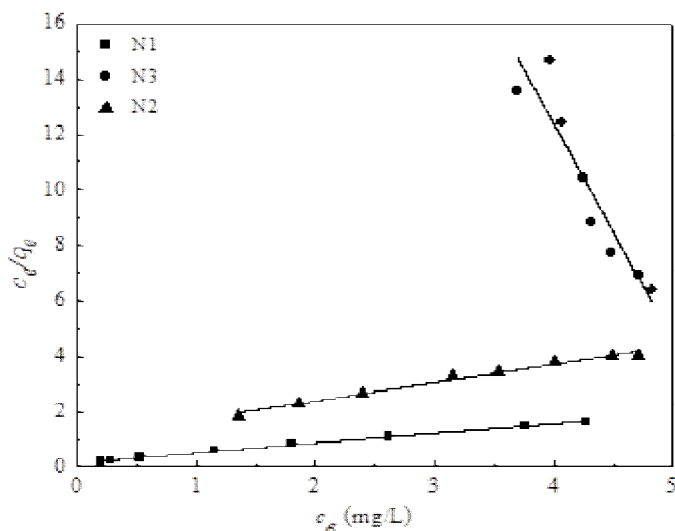
To understand the adsorption patterns better, the Langmuir and Freundlich equations were employed to analysis the adsorption isotherms. The adsorption capacity of the activated carbons was calculated by using the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (1)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (2)$$

where  $C_e$  = concentration of the adsorbate in solution at equilibrium;  $q_m$  = maximum equilibrium concentration of the adsorbate adsorbed on the adsorbent;  $K_L$  = constants associated with the heat of adsorption;  $K_F$  = adsorption capacity of adsorbent.

The linear Freundlich and Langmuir isotherm plots for the sorption of arsenic on carbons in Figure 2 and Figure 3. The isotherm parameters for As(V) for this research are reported in table 1.



$c_0=5\text{mg/L}$ ;  $AC=0.3\sim 0.5\text{g/L}$ ;  $\text{pH}=7.0$ ;  $T=25\pm 0.2^\circ\text{C}$

Figure 2. Langmuir isotherms of As(V) on carbons.

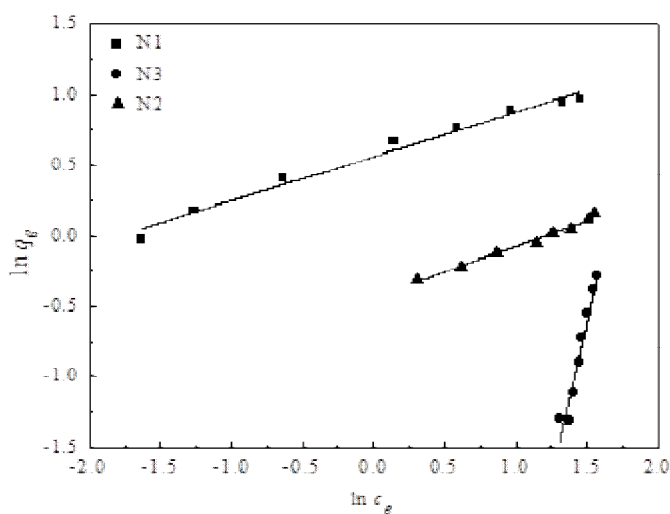


Figure 3. Freundlich isotherms of As(V) on carbons.

Table 1. Adsorption isotherm parameters of As(V).

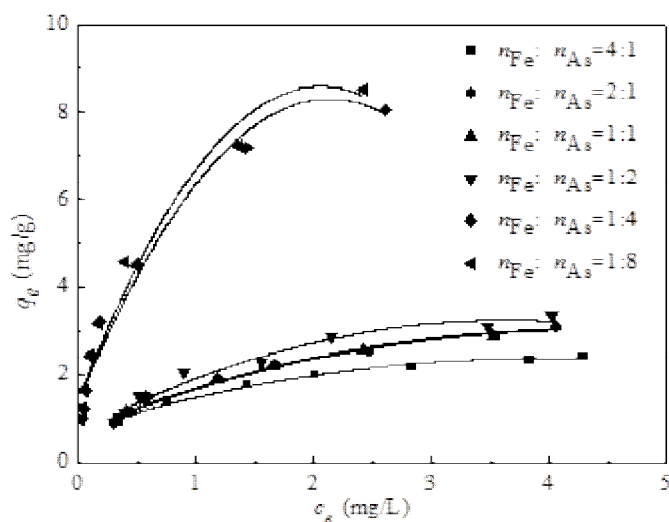
carbons	Langmuir model		Letter size paper		1/n	$R^2$
	$q_m$	$K_L$	$R^2$	$K_F$		
N1	3.69	4.549	0.9819	2.59	0.021	0.8885
N2	1.97	2.807	0.9911	1.38	0.192	0.9464
N3	0.54	0.112	0.6716	1.88	0.244	0.9094

The correlation coefficient values ( $R^2$ ) suggested that the adsorption of As(V) on N1 and N2 were better simulated with Langmuir model. Thus, the adsorptions of arsenic were mainly monolayer adsorption on N1 and N2. The adsorption capacity of As(V) on N1 and N2 were 3.69 mg / g and 1.97 mg / g, respectively. It was obvious that on N1 had a relative higher adsorption capacity than on N2. Moreover, N1 had a higher adsorption affinity to As(V), which can be known from the values of  $K_L$ . The correlation coefficient values ( $R^2$ ) suggested that the adsorption of As(V) on N3 were better simulated with Freundlich model. Thus, the adsorption of arsenic were

mainly multilayer adsorption on N3, however adsorption capacity was little. In summary, N1 has a greater saturation adsorption capacity for arsenic.

### Effect of $\text{Fe}^{2+}$ on N1

The effects of  $\text{Fe}^{2+}$  on the removal of As(V) were illustrated in Figure 4, Figure 5 and Table 2. As is shown in above figures, with the increase of molar mass ratio of Fe and As ( $n_{\text{As}}:n_{\text{Fe}}$ ) from 0.25 to 2, the adsorption capacity of As(V) on N1 was slowly increased from 2.794 mg / g to 4.074 mg / g, and rapidly increased to 8.834 mg / g ( $n_{\text{As}}:n_{\text{Fe}} = 4:1$ ), then slowly increased with the growth of  $n_{\text{As}}:n_{\text{Fe}}$ .

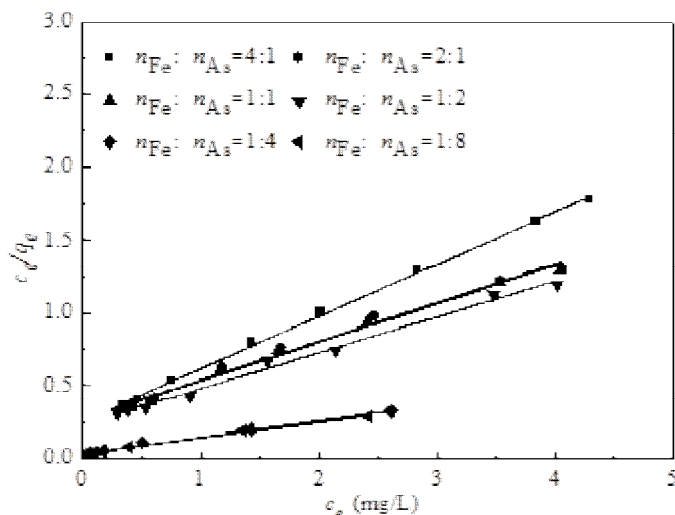


$c_0=5\text{mg/L}$ ;  $\text{AC}=0.3\sim 0.5\text{g/L}$ ;  $\text{pH}=7.0$ ;  $T=25\pm 0.2^\circ\text{C}$

Figure 4. Adsorption capacity of As(V) on N1 in different  $\text{Fe}^{2+}$  concentrations.

When the concentration of  $\text{Fe}^{2+}$  was low, the adsorption capacity of As(V) increased slightly. It may be due to the small amounts of  $\text{Fe}^{2+}$  which adsorbed on the activated carbons had certain complexing ability with As(V) ( Solozhenkin et al. 2003 ). The adsorption capacity of As(V) was affected by the ferrous amount on N1, due to arsenic adsorption on iron being site-specific chemisorption (Chang et al. 2010).

With  $n_{\text{As}}:n_{\text{Fe}}$  increased from 2 to 4, the ferrous combined on N1 rapidly enhance, and then largely increase the specific adsorption site, finally lead to a huge adsorption capacity of arsenate on N1. Further increase of the  $\text{Fe}^{2+}$  concentration resulted in the adsorption capacity of As(V) stabilized, and competitive adsorption may be the main reason. Overall, low concentration of  $\text{Fe}^{2+}$  was found to accelerate the adsorption of As(V). We considered that the binding ability between iron and As(V) mainly caused the phenomenon. It was said that As(V) was adsorbed onto iron oxides by inner-sphere surface complexes (Mondal et al. 2007).



$c_0=5\text{mg/L}$ ;  $\text{AC}=0.3\sim 0.5\text{g/L}$ ;  $\text{pH}=7.0$ ;  $T=25\pm 0.2^\circ\text{C}$

Figure 5. Adsorption capacity fitted with the Langmuir model on N1 in different  $\text{Fe}^{2+}$  concentrations.

Table 2. Adsorption capacity of As(V) on N1 in different  $\text{Fe}^{2+}$  concentrations.

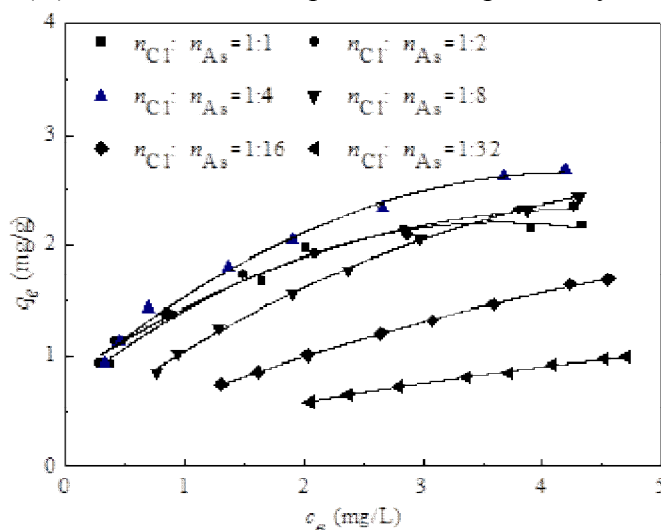
$n_{\text{As}}:n_{\text{Fe}}$	$q_m$	$n_{\text{As}}:n_{\text{Fe}}$	$q_m$	$n_{\text{As}}:n_{\text{Fe}}$	$q_m$
	$\text{mg/g}$		$\text{mg/g}$		$\text{mg/g}$
1:4	2.691	1:1	3.795	4:1	8.834
1:2	3.781	2:1	4.074	8:1	9.258

We were speculated that the ferrous ion had a stronger adsorption activity than As(V) and ferrous ion adsorbed on the carbon could provide more activated sites for As(V).

#### Effect of $\text{Cl}^-$ on N1

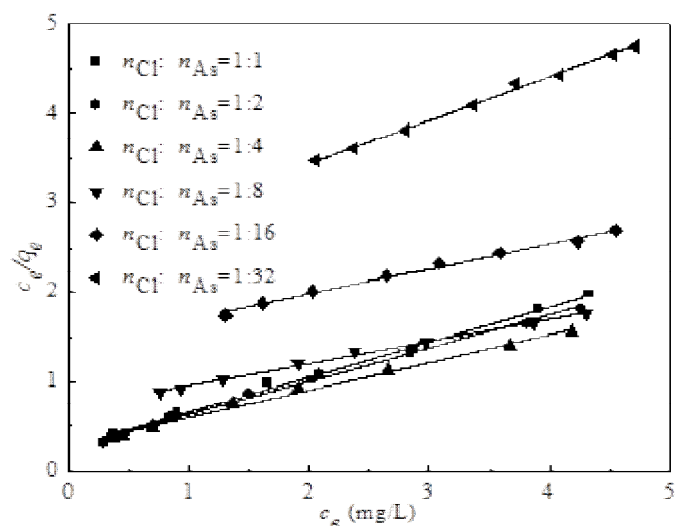
The effects of  $\text{Cl}^-$  on the removal of As(V) were illustrated in Figure 6, Figure 7 and Table 3. As is shown in above figures, with the increase of molar mass ratio of As and Cl ( $n_{\text{As}}:n_{\text{Cl}}$ ) from 1 to 8, the adsorption capacity of As(V) on N1 was gradually increased from 2.552 mg / g to 4.036 mg / g. then declined with the growth of  $n_{\text{As}}:n_{\text{Cl}}$ , and declined to 2.045 mg / g ( $n_{\text{As}}:n_{\text{Cl}}=32:1$ ).

Under these conditions an increase in the ionic strength of  $\text{Cl}^-$  increased the adsorption of As(V) due to the screening effect (Victoria et al. 2002). Further increase of the  $\text{Cl}^-$  concentration resulted in the adsorption capacity of As(V) declined, and competitive adsorption may be the main reason.



$c_0=5\text{mg/L}$ ;  $\text{AC}=0.3\sim 0.5\text{g/L}$ ;  $\text{pH}=7.0$ ;  $T=25\pm 0.2^\circ\text{C}$

Figure 6. Adsorption capacity of As(V) on N1 in different  $\text{Cl}^-$  concentrations.



$c_0=5\text{mg/L}$ ;  $AC=0.3\sim 0.5\text{g/L}$ ;  $\text{pH}=7.0$ ;  $T=25\pm 0.2^\circ\text{C}$

Figure 7. Adsorption capacity fitted with the Langmuir model on N1 in different  $\text{Cl}^-$  concentrations.

Table 3. Adsorption capacity of As(V) on N1 in different  $\text{Cl}^-$  concentrations.

$n_{\text{As}}:n_{\text{Cl}}$	$q_m$	$n_{\text{As}}:n_{\text{Cl}}$	$q_m$	$n_{\text{As}}:n_{\text{Cl}}$	$q_m$
	$\text{mg/g}$		$\text{mg/g}$		$\text{mg/g}$
1:1	2.552	4:1	3.221	16:1	3.541
2:1	2.678	8:1	4.036	32:1	2.045

## Conclusion

(1) The adsorption of As(V) on N1 and N2 were mainly monolayer adsorption. The adsorption of As(V) on N3 was mainly multilayer adsorption. N1 has a greater saturation adsorption capacity for arsenic, which means N1 has an effect of adsorption capacity for arsenic.

(2) With the increase of  $n_{\text{As}}:n_{\text{Fe}}$  from 0.25 to 2, the adsorption capacity of As(V) on N1 was slowly increased, and rapidly increased to 8.834 mg / g ( $n_{\text{As}}:n_{\text{Fe}}=4:1$ ), then slowly increased with the growth of  $n_{\text{Fe}}:n_{\text{As}}$ . Besides with  $n_{\text{As}}:n_{\text{Fe}}$  increased from 2 to 4, the ferrous combined on N1 rapidly enhance, and then largely increase the specific adsorption site, finally lead to a huge adsorption capacity of arsenate on N1.

(3) With the increase of  $n_{\text{As}}:n_{\text{Cl}}$  from 1 to 8, the adsorption capacity of As(V) on N1 was gradually increased. then declined with the growth of  $n_{\text{As}}:n_{\text{Fe}}$ , and declined to 2.045 mg / g ( $n_{\text{As}}:n_{\text{Fe}}=32:1$ ). The reason of above situation is the screening effect and competitive adsorption.

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