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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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**To cite this Article** Huang, J. G. and Liu, J. C.(1997) 'Enhanced Removal of As(V) from Water with Iron-Coated Spent Catalyst', Separation Science and Technology, 32: 9, 1557 – 1569

**To link to this Article:** DOI: 10.1080/01496399708004066

**URL:** <http://dx.doi.org/10.1080/01496399708004066>

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## Enhanced Removal of As(V) from Water with Iron-Coated Spent Catalyst

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### ABSTRACT

The effectiveness of pretreating a spent catalyst with an iron-salt solution to improve its As(V) removal capacity was studied. Various factors, such as types and concentrations of iron salt, pH, and initial As(V) concentration were investigated for their effects on the improvement of As(V) removal capacity. A significant increase in As(V) removal capacity can be achieved by iron-coated spent catalyst. Adsorption density of As(V) decreased with increasing pH. Langmuir adsorption isotherm was utilized to describe the adsorption reaction. Results from IR analysis and zeta potential measurement indicate that As(V) is specifically adsorbed onto iron-coated spent catalyst. This study shows that spent catalyst can be converted to a useful adsorbent for As(V) removal.

**Key Words.** Adsorption; Arsenic; pH; Spent catalyst; Zeta potential

### INTRODUCTION

Although it has been indicated that arsenic may be a micronutrient essential to life, its presence in exceeding concentration can be detrimental to human and animals. Blackfoot disease, a peripheral vascular disease

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found in certain coastal areas of Taiwan, for example, has been correlated to the consumption of groundwater containing arsenic (1). Arsenic is a by-product of nonferrous metal production, such as copper, lead, zinc, gold, or cobalt smelting (2). Arsenic compounds can also be found in wastewater from various industries, such as pharmaceutical, electroplating, and pesticide manufacturing (3). Because of its toxicity, the maximum allowable concentration of arsenic in Taiwan is 0.05 mg/L in drinking water and 0.5 mg/L in industrial effluent. Therefore, it is important to treat water and wastewater containing arsenic effectively. Existing methods of arsenic removal include adsorption (2–6), flotation (7–9), and precipitation (10). Among these methods, adsorption has been shown to be very efficient using different types of adsorbent. It has also been demonstrated that the presence of active metal on the adsorbent surfaces can greatly enhance the adsorption capacity of different types of adsorbents, such as activated carbon, coral, and sand (11–14).

Spent catalysts are solid wastes of significant amounts generated in various industries. Take petrochemical industry as an example: hydroprocessing, reforming, and desulfurization all produce spent catalysts (15). In Taiwan, more than 3000 metric tons of spent catalysts are annually generated by the refinery. Spent catalysts are usually regenerated 2 to 3 times before they are wasted. Though the spent hydroprocessing catalyst is categorized as a nonhazardous waste, the leaching of V and Ni during land treatment has been examined with caution (16). Since spent catalysts consist mainly of porous silica and alumina, some researches have focused on the feasibility of utilizing them as a secondary adsorbent to remove such contaminants as sulfide and fluoride from water (17, 18).

The major objective of the current study is to investigate the feasibility of utilizing iron-coated spent catalyst to remove arsenic from aqueous solution. In the current study, spent hydroprocessing catalyst will first be washed and coated with iron salt and then be used in the adsorption of As(V) from aqueous solution. Equilibrium adsorption experiments will be conducted. Effects of important parameters, such as types and concentrations of iron salt, pH, initial arsenic concentration, and solution chemistry on arsenic adsorption, will be explored.

## MATERIALS AND METHODS

### Preparation of Iron-Coated Spent Catalyst

Spent hydroprocessing catalysts were obtained from Research Institute of China Petroleum Corporation in Chia-Yi County, Taiwan. In order to remove any impurities which might cause interference, the spent catalyst was first washed. The procedure for spent catalyst wash was as follows.

First, catalyst of 50 g was weighed and placed in a 1-L beaker filled with 500 mL of 0.1 N  $\text{HNO}_3$  and mixed for 1.5 hours. The suspension was then filtered with a 0.45- $\mu\text{m}$  membrane filter (Gelman). The catalyst was rinsed with 1 L of distilled water 3 times, then followed by washing with 500 mL of 0.1 N  $\text{NaOH}$ , and again rinsed with distilled water at the same solid-liquid ratio and mixing condition. The procedure was repeated 4 times. To coat the catalyst, pre-washed catalyst suspension of 250 mL was filtered, and 500 mL of ferric chloride or ferrous chloride solution was added to the spent catalyst, stirred for 48 hours, and filtered. The catalyst was rinsed with 500 mL of distilled water several times and stored in suspension.

### Characterization of Iron-Coated Spent Catalyst

The physicochemical properties of the spent catalyst before being coated with iron can be found in our previous work (16, 17). Both the specific surface area and the average size of spent catalyst did not change after being coated with iron salts. In order to confirm the presence of iron on the coated spent catalyst surfaces, the surface properties of spent catalyst were examined by x-ray diffraction. Iron-coated spent catalyst was vacuum dried at 120°C and analyzed by an x-ray diffractometer (Phillips, MO-710). The voltage was kept at 40 kV and then scanned from 10 to 70°. Samples for IR analysis were eluted several times with distilled water to remove electrolytes and ions that were not specifically adsorbed on the solid surfaces. Filtration and freeze-drying were applied in separating the solid and aqueous phases. Dried samples were each prepared as a pellet with 1 cm diameter and ca. 0.1 cm thick. The pellet was a mixture of 5 mg freeze-dried sample and 195 mg of  $\text{KBr(s)}$ . The sample placed in the IR spectroscopy (Jasco, IR-700) was scanned from wavenumbers of 400 to 4000  $\text{cm}^{-1}$ . Zeta potentials of colloidal systems were measured by a zeta meter (Photol Leza-600) at fixed ionic strength, temperature, and solid concentration.

### Adsorption Experiments

Sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) was used to prepare a stock solution of 1000 mg/L of As(V). The background concentration of arsenic on the spent catalyst was found to be negligible throughout the pH range of 2 to 11. In the batch adsorption experiment on pH effect, adsorption reactions were carried out in 50-mL brown glass bottles. Solid concentration was kept at 10 g/L. Ionic strength was adjusted to 0.05 M with  $\text{NaNO}_3$ . After the suspension, pH was adjusted with 0.5 N  $\text{HNO}_3$  and 0.5 N  $\text{NaOH}$ , then bottles were placed on a shaker and shaken at 150 rpm for 12 hours.

When the adsorption reaction was completed, equilibrium pH values were measured and recorded. The suspension was filtered through a 0.45- $\mu\text{m}$  membrane filter (MFS). The As(V) concentration in the filtrate was then measured by an ion chromatograph (Dionex DX-100). The amount of As(V) adsorbed was determined as the difference between the initial concentration and the equilibrium concentration. For the experiment on adsorption isotherm, procedures were the same except that the pH value was kept at  $4.0 \pm 0.1$ .

## RESULTS AND DISCUSSION

### Characteristics of Iron-Coated Spent Catalyst

Results of x-ray diffraction analysis on the surface properties of spent catalyst are shown in Figs. 1A to 1C. Only the typical absorption peak of aluminosilicates was detected for washed and uncoated spent catalyst (Fig. 1A). When the spent catalyst was coated with 0.01 M Fe(II), the absorption peaks of  $\alpha\text{-FeOOH}$  and  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  were detected, while those of aluminosilicates were not observed (Fig. 1B). When the spent catalyst was coated with 0.1 M Fe(III), the absorption peaks of aluminosilicates were not observed. The amorphous solids on the surfaces of spent catalyst are believed to be iron oxides (Fig. 1C). Results from XRD analysis confirmed that the spent catalyst is uniformly covered by iron oxides, either crystalline or non-crystalline. Since iron-coated spent catalyst was not

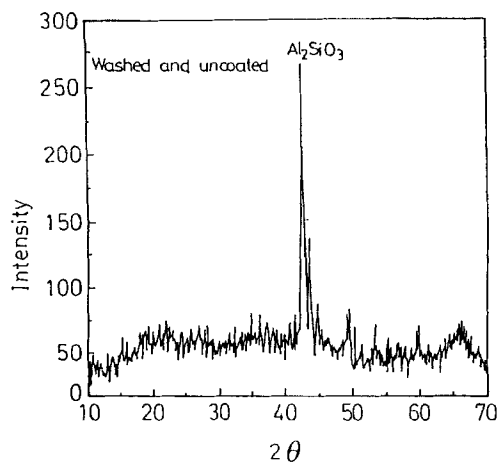


FIG. 1A X-ray diffraction spectrum of uncoated spent catalyst.

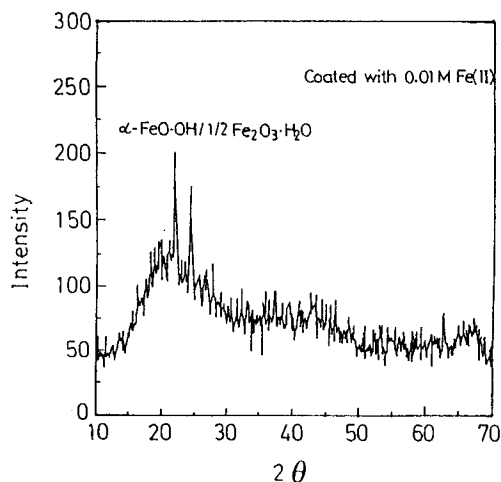


FIG. 1B X-ray diffraction spectrum of spent catalyst coated with Fe(II) of 0.01 M.

dried before it was used in the adsorption study, plus the fact that vacuum treatment might cause changes in iron form, it is possible that part of the iron might exist in dissolved form. Dissolved iron can be specifically adsorbed, in the form of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and hydroxylated species, on the

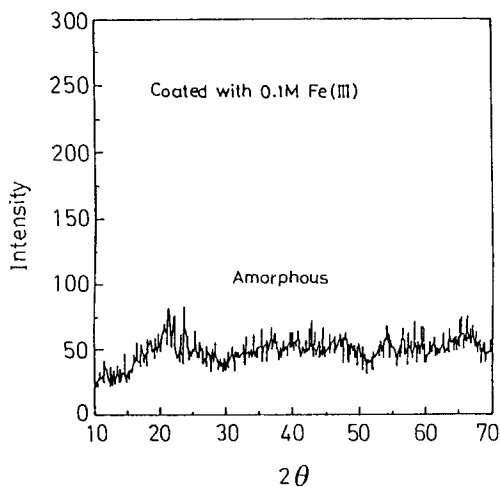


FIG. 1C X-ray diffraction spectrum of spent catalyst coated with Fe(III) of 0.1 M.

surfaces of spent catalyst. We did not try to differentiate iron oxide precipitate from adsorbed iron species. However, both are believed to affect the adsorption reaction.

### Adsorption of As(V) onto Iron-Coated Spent Catalyst

Effects of pH on the adsorption of arsenic onto various types of spent catalyst are illustrated in Fig. 2. When uncoated spent catalyst was used as the adsorbent, the maximum adsorption density of As(V) was found at pH of 4.5. The adsorption density of As(V) then decreased as pH shifted to the alkaline range. Similar effects of pH have been shown in As(V) adsorption onto activated alumina (3), iron oxide (13), and fly ash (6). When the spent catalyst was coated with iron salts, different adsorption

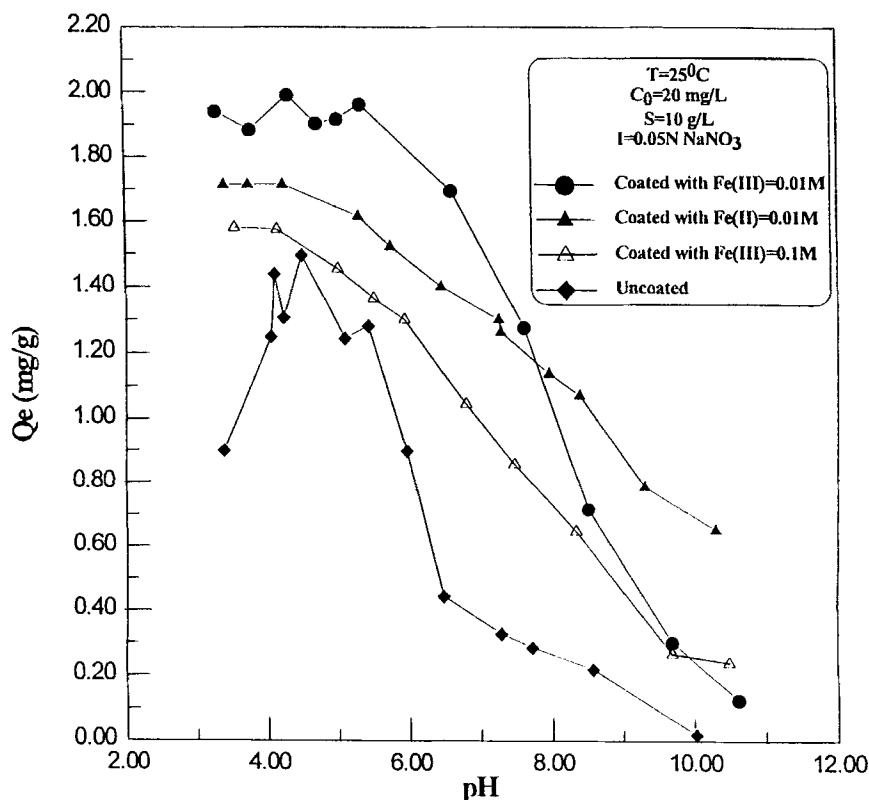


FIG. 2 Adsorption of As(V) onto spent catalyst as affected by pH: Initial concentration ( $C_0$ ) = 20 mg/L,  $I$  = 0.05 N  $\text{NaNO}_3$ ,  $S$  = 10 g/L, 25°C.

behavior was observed. Both Fe(II) and Fe(III) could enhance the adsorption reaction significantly over a wide pH range. Highest adsorption capacity (ca. 100% removal percentage under acidic condition) was found when the spent catalyst was coated with 0.01 M Fe(III). Adsorption of As(V) onto iron-coated spent catalyst was favorable under acidic conditions. Though the adsorption density of As(V) decreased when pH shifted to the alkaline range, it was not affected by pH when the pH was lower than ca. 5.0, as evidenced by the plateau of adsorption density (Fig. 2). Four adsorption isotherms of As(V) onto spent catalyst are shown in Fig. 3. At the pH of 4.0, the adsorption density of As(V) was the highest when the spent catalyst was coated with 0.01 M Fe(II). Spent catalyst coated with Fe(III) also shows enhanced As(V) adsorption, although to a lesser extent. Compared with Fig. 2, results might seem contradictory regarding

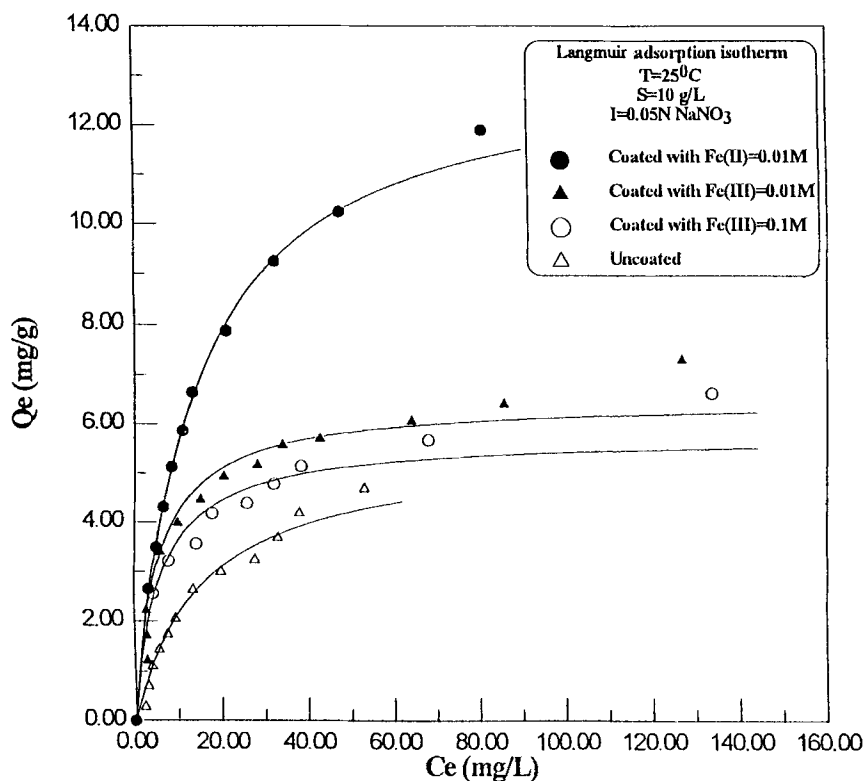


FIG. 3 Adsorption isotherms of As(V) onto spent catalyst at pH 4.0:  $I = 0.05\text{ N NaNO}_3$ ,  $S = 10\text{ g/L}$ ,  $25^{\circ}\text{C}$ .



the highest adsorption capacity found among spent catalyst prepared under different coating conditions. However, it is observed under close scrutiny (Fig. 2) that residual As(V) concentration was ca. 2.5 mg/L for catalyst coated with 0.01 M Fe(II), and the residual As(V) concentration of less than 1.0 mg/L for catalyst coated with 0.01 M Fe(III). Though spent catalyst coated with 0.01 M Fe(II) exhibits highest adsorption capacity as equilibrium concentration of As(V) increases (Fig. 3), it is in fact indistinguishable when the equilibrium concentration of As(V) is low with regard to the order of adsorption capacity among coated spent catalyst. It is therefore proposed that spent catalyst coated with 0.01 M Fe(III) has the best adsorption capacity toward As(V) when the equilibrium concentration of As(V) is low, while spent catalyst coated with 0.01 M Fe(II) shows best adsorption capacity under high equilibrium concentration As(V). Langmuir adsorption isotherm was utilized to model the adsorption reaction. Results are shown in Table 1. The adsorption densities of As(V) onto iron-coated spent catalysts are better or comparable to other adsorbents (2–4, 6.) Though the adsorption capacity of coated spent catalyst is less than that of iron oxyhydroxide (13), there are many potential ways to improve the coating procedures, e.g., better pH control, drying, high temperature treatment of the coated catalyst, and utilizing other coating materials.

### IR Analysis

Positive identification of adsorbed As(V) was provided using infrared (IR) absorption spectroscopy. The infrared spectra of pure sodium arsenate, hydrous Fe(II)-coated spent catalyst, and spent catalyst containing As(V) are given in Fig. 4. The IR spectrum of hydrous Fe(II)-coated spent catalyst is shown in Fig. 4(i). The IR spectrum of spent catalyst with adsorbed As(V) is shown in Fig. 4(ii). The IR spectrum of sodium arsenate is shown in Fig. 4(iii). The absorption bands observed at 594, 720, 855,

TABLE I  
Langmuir Constants<sup>a</sup> for the Adsorption of As(V) onto Iron-Coated Spent Catalyst

	Uncoated	0.01 M Fe(II)	0.01 M Fe(III)	0.1 M Fe(III)
$Q_m$ (mg/g)	6.0	13.1	7.7	7.4
$K$ (L/mg)	0.054	0.075	0.068	0.058

$$^a Q = Q_m K C_e / (1 + K C_e)$$

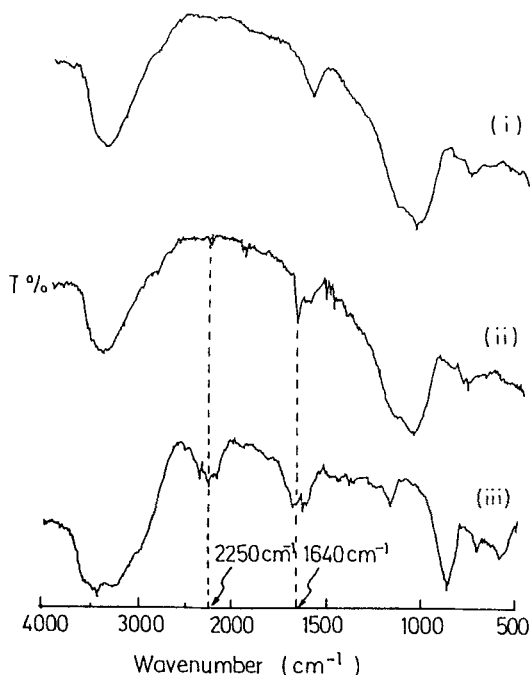


FIG. 4 IR spectra of (i) spent catalyst without As(V), (ii) spent catalyst with As(V), and (iii)  $\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$ .

1177, 1636, and  $2250\text{ cm}^{-1}$  are in good agreement with the reported spectrum of  $\text{Na}_2\text{HASO}_4$  (13). The absorption bands at 1640 and  $2250\text{ cm}^{-1}$ , which were not observed in Fig. 4(i), were detected in spent catalyst with As(V) [Fig. 4(ii)]. These bands shifted slightly from the corresponding ones observed in the spectrum of sodium arsenate. The shift in absorption bands is due to the lowering of symmetry of arsenate ion as a result of interaction between As(V) and hydrous catalyst. Judging from the IR spectrum analysis, it is proposed that As(V) is specifically adsorbed onto hydrous Fe(II)-coated spent catalyst surfaces.

### Zeta Potential of Colloidal Systems

Zeta potentials of colloidal systems as affected by pH are shown in Figs. 5A to 5C. The isoelectric point (IEP) of washed spent catalyst was found at 4.5. When the washed catalyst was coated with 0.01 M  $\text{FeCl}_2(\text{aq})$ , a slight shift of the IEP toward the alkaline range was observed and the

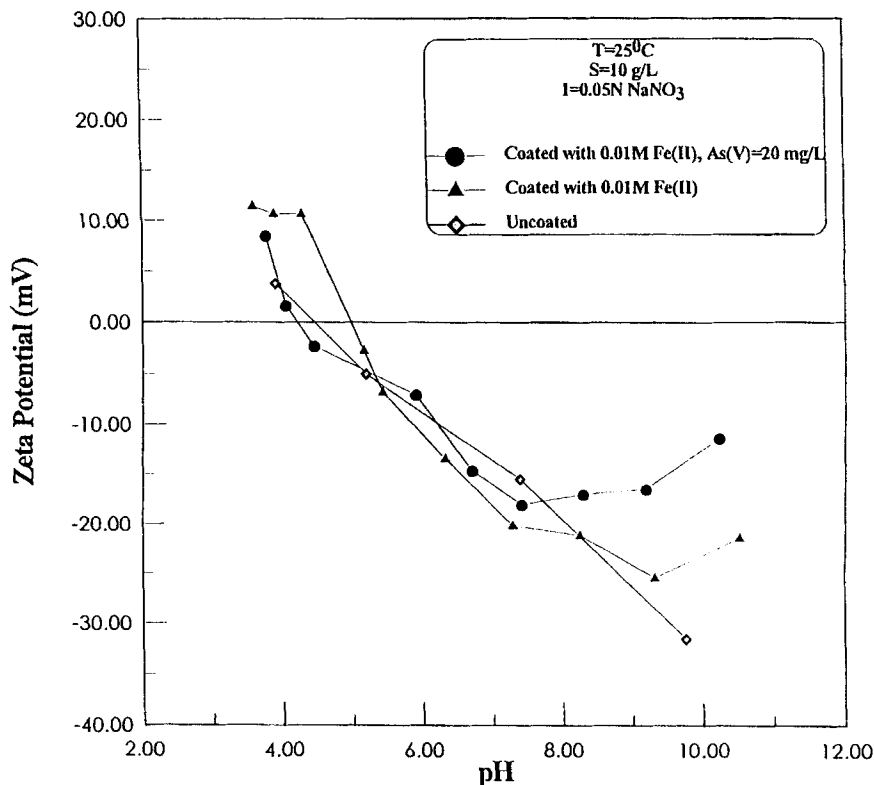


FIG. 5A Zeta potential of spent catalyst coated with 0.01 M of Fe(II) as a function of pH: ionic strength ( $I$ ) = 0.05 N  $\text{NaNO}_3$ , solid concentration ( $S$ ) = 10 g/L,  $25^{\circ}\text{C}$ .

IEP was at 5.1 (Fig. 5A). Additionally, the corresponding zeta potential of spent catalyst coated with Fe(II) was greater than that of the uncoated spent catalyst at the identical pH. The changes of surface charge and the subsequent shift of IEP are caused by the precipitate of  $\alpha\text{-FeOOH}$  and  $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ , and the specific adsorption of Fe(II). However, in the presence of 20 mg/L As(V), the zeta potential shifted to the acidic range, and the IEP became 4.3. This has been indicated (3, 8, 13). The shift is caused by the specific adsorption of  $\text{H}_2\text{AsO}_4^{-3}$  ions onto iron-coated spent catalyst. A similar pattern of the change of zeta potential and the shift of IEP was also found when spent catalyst was coated with 0.01 and 0.1 M  $\text{FeCl}_3(\text{aq})$ , respectively.

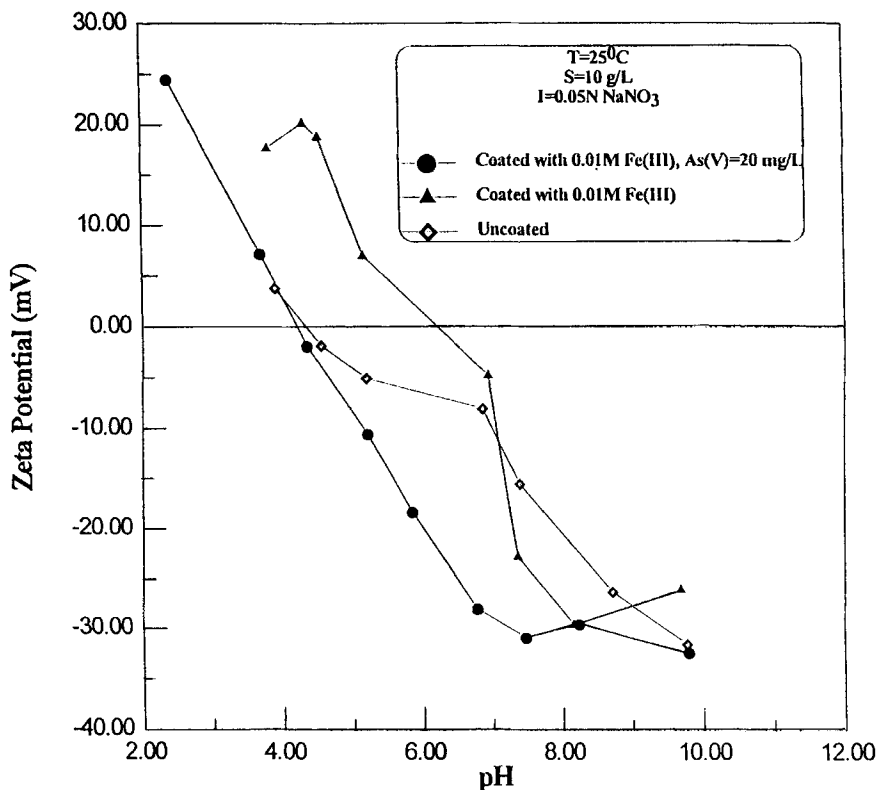


FIG. 5B Zeta potential of spent catalyst coated with 0.01 M of Fe(III) as a function of pH: ionic strength ( $I$ ) = 0.05 N  $\text{NaNO}_3$ , solid concentration ( $S$ ) = 10 g/L,  $25^{\circ}\text{C}$ .

Combining results from adsorption experiment, IR analysis, and zeta potential measurement, it is proposed that As(V) is mainly specifically adsorbed onto the iron-coated spent catalyst. However, the electrostatic interaction cannot be ruled out from the adsorption reaction, especially when positively charged iron species are formed on the surface of spent catalyst. It has been indicated that both electrostatic force and specific interactions are involved in As(V) adsorption onto activated alumina (3, 6). What we observed in the current study confirms that As(V) is strongly adsorbed onto hydrous solids. Our previous work (17) has shown that spent catalyst could be utilized to remove fluoride from aqueous solution. In the current work we demonstrated that spent catalyst possesses adsorp-

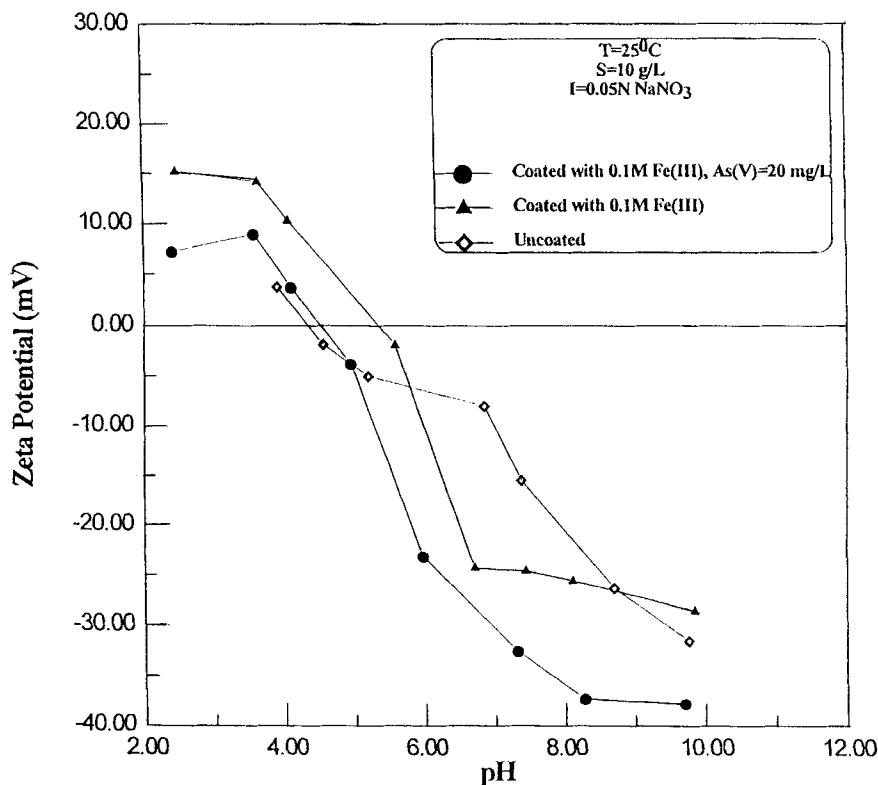


FIG. 5C Zeta potential of spent catalyst coated with 0.1 M of Fe(III) as a function of pH: ionic strength ( $I$ ) = 0.05 N  $\text{NaNO}_3$ , solid concentration ( $S$ ) = 10 g/L,  $25^{\circ}\text{C}$ .

tive capacity toward As(V). Furthermore, the adsorption could be significantly enhanced through iron salts coating. In view of these results, spent catalyst can potentially be converted to a useful adsorbent to remove contaminants from aqueous solutions.

## SUMMARIES

Our feasibility study of utilizing spent hydroprocessing catalyst to remove As(V) from aqueous solution leads to the following conclusions:

1. Iron-coated spent catalyst could potentially be utilized as a useful adsorbent in removing As(V) from aqueous solutions. The adsorption capacity is comparable to those of other adsorbents.

2. Adsorption density of As(V) onto spent catalyst is favorable under acidic conditions. It decreased with increasing pH. Langmuir adsorption isotherm can fit the adsorption reaction well.
3. It is proposed that As(V) is specifically adsorbed onto the iron-coated spent catalyst. In addition, electrostatic interaction is possibly also involved in the adsorption reaction.
4. Spent catalyst can potentially be converted to a useful adsorbent.

### ACKNOWLEDGMENT

The authors would like to thank Dr. Ju S. Y. of CPC for providing the spent catalyst.

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Received by editor July 25, 1996

Revision received November 1996