

Removal of Arsenic from Water Environment by Electrodialysis

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Abstract

The potential application of electrodialysis (ED) membranes in water treatment and desalination requires an improved understanding of the factor that govern the rejection of contaminants. In this study, separation of arsenic from aqueous solution by electrodialysis was investigated. The results demonstrated that the pH shows no significant effect on mass transfer coefficient (k) in the voltage range investigated. The mass transfer coefficient (k) increased by increasing voltage, and the mass transfer coefficient for As(V) is always higher than that for As(III).

Keywords: Arsenic, Electrodialysis, Mass transfer coefficient

1. Introduction

Arsenic is one of inorganic trace contaminants and is found in natural and engineered aquatic environments. The occurrence of arsenic leads an important environmental and public health concern. Arsenic is often found in surface and groundwater where it is mostly present as inorganic forms of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)) [1]. Electrodialysis (ED) is a membrane separation process based on the selective migration of aqueous ions through cation-exchange and anion-exchange membranes because of an electrical driving force. Ion separation is closely associated with the characteristics of the ion-exchange membrane, especially its permselectivity. ED was firstly used for the desalination of saline solution, while other applications such as the treatment of industrial effluents, have gained importance [2]. This study has investigated the influence of pH, initial concentration and electrical potential of ED for the removal of arsenic.

2. Experiments

The ED was conducted with Acilyzer AX3B (ASTOM) at 25°C. Arsenic solution was prepared to the concentration from 5 mg/L to 60 mg/L with 0.01 mol/L NaCl as a feed solution. The solution of 0.01 mol/L NaCl was prepared as a

concentrate solution. Each ED experiment was conducted for 1 h and the samples were collected each 10 min.

The mass transfer coefficient (k) will be calculated by the equation:

$$-k t = \ln ([A]_t / [A]_0)$$

Where $[A]_t$ and $[A]_0$ are the As concentration in feed solution at time t and initial, respectively

3. Results and Discussion

The effect of pH on the rejection of As on the mass transfer coefficient (k) is shown in Figure 1. The mass transfer coefficient (k) is increased with pH in the case of As(V), whereas it is decreased with pH in the case of As(III). The As(V) exists in several stable forms in the aqueous media, such as H_3AsO_4 , $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} , and the dominant As(V) species at pH = 10 is anionic $HAsO_4^{2-}$ and AsO_4^{3-} . Likewise, the dominant As(V) species at pH = 8 is also anionic $HAsO_4^{2-}$ and $H_2AsO_4^-$. Higher mass transfer of As(V) was therefore obtained at high pH range, because the oxy anion having larger negative charge was increased, leading higher driving force for the mass transfer.

Nevertheless, in the case of As(III), the As(III) species

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The effect of pH on the rejection of As on *k* exist as neutral H_3AsO_3 at $pH < 9$ and small amount of anionic $H_2AsO_3^-$ is appeared at $pH > 9$. The mass transfer coefficient (*k*) of As(III) was therefore found to be lower than the *k* of As(V).

Figure 2 shows the effect of discharged voltage on the removal of As. It can be seen that the removal of As (V) was faster and higher than that of As (III). In the case of As(V), the mass transfer coefficient (*k*) was increased with voltage applied, because the dominant species of As(V) is anion. On the other hand, the *k* of As(III) was stable against the voltage, because the dominant species of As(III) is neutral.

4. Conclusion

The removal of As(V) and As(III) from aqueous solution by using membrane-based technologies of ED was investigated. The results show that the pH of the aqueous phase is not affected on the mass transfer coefficient (*k*) within the voltage range of this study. The mass transfer coefficient (*k*) increased with increasing the discharged voltage of ED, and the mass transfer coefficient (*k*) in the case of As(V) is always higher than that of As(III).

5. REFERENCES

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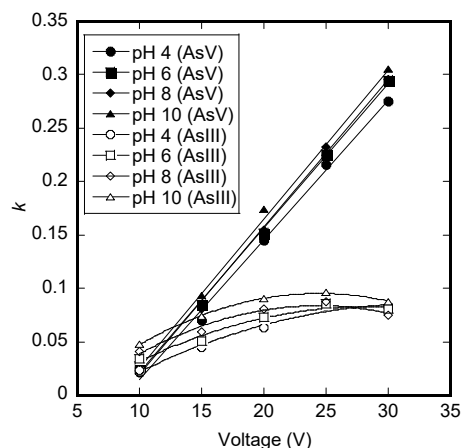


Figure 1 Effect of discharged voltage on the mass transfer coefficient (*k*) of As

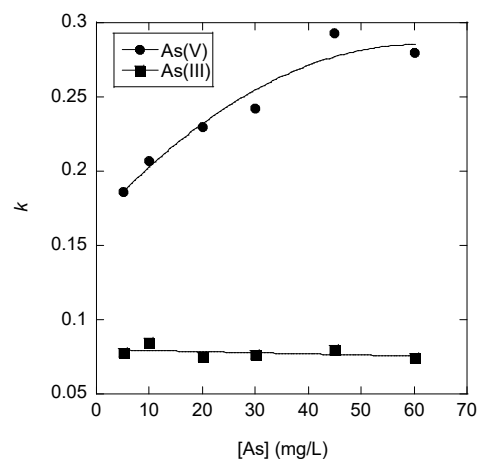


Figure 2 Effect of As concentration on the mass transfer coefficient (*k*) of As

Preparation of Yttrium-Iron Binary Composites and Their Arsenic Adsorption Properties

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Abstract

Removal of arsenic is the important issue to be resolved immediately because arsenic is harmful to the environment and the human body. Recently, the development of binary oxide containing iron oxide has gained considerable attention. In this study, novel magnetic binary oxides containing iron and yttrium (FeY_x (x = molar ratio Y to Fe, 0.5, 1, 2)) were prepared and their adsorption behaviors of As(III) and As(V) were evaluated. The specific surface area and the point of zero charge (PZC) of FeY_x increased with increasing x . FeY₂ had larger specific surface area (183 m²g⁻¹) and higher PZC (10.3) than FeY_{0.5} and FeY₁. All adsorption experiments were carried out by batch method and the effects of pH and arsenic concentration on arsenic removal were investigated. The adsorption percentage of As(III) and As(V) using FeY₂ was higher than 90 % in the wide region of pH 6.0-10.5 and decreased slightly at higher pH than the PZC. The adsorption isotherms of As(III) and As(V) with FeY₂ at 303 K fitted the Langmuir model well. The maximum adsorption capacities of As(III) and As(V) on FeY₂ were 1.12 and 3.26 mmolg⁻¹, respectively. FeY₂ is expected as a high performance adsorbent for As(III) and As(V).

Keywords: Adsorption, Arsenic, Yttrium, Iron, Binary Composites

1. INTRODUCTION

In recent years, arsenic contamination of rivers, seawater and groundwater is caused by dissolution of mineral and soil and human activities such as mining (Nriagu 2007). To minimize health risks as chronic arsenic poisoning, the environmental standard values of 0.01 mg/dm³ is provided by WHO (Nriagu 2007). Arsenic in natural water exists as inorganic form of arsenite (As(III) and arsenate (As(V)). Therefore removal of inorganic arsenic is the issue to be resolved immediately. In the previous study, it was found that the magnetite and the ferrite synthesized with high point of zero charge and large specific surface area can effectively remove for arsenic (Ohe 2007, 2010a, 2010b). Recently, the development of binary oxide containing iron oxide has gained considerable attention (Gupta 2009, Zhang 2013) and

As(III) was effectively removed by them. Yu *et al.* (2015, 2016) reported that yttrium-manganese binary oxide and hydrated yttrium oxide had high capacity for As(V) in a wide range of pH. Wassay *et al.* (1996) found that a basic yttrium carbonate efficaciously removed As(V) at pH 7. However the adsorbents with yttrium were lower adsorption capacity for As(III) than As(V) at pH 7. In this study, a novel magnetic binary composite with iron and yttrium was prepared and its adsorption properties of As(III) and As(V) were evaluated.

2. EXPERIMENTAL

2.1 Synthesis and characterization of Fe-Y magnetic binary oxide (FeY_x)

FeY_x was prepared by a coprecipitation method. A

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composition ratio of Y / Fe = 0.5, 1, 2 (= x) using an iron(II) chloride and an yttrium(III) chloride was dissolved in 1 mol·dm⁻³ hydrochloric acid. The mixed solution was added to 1 mol·dm⁻³ aqueous sodium hydroxide solution under nitrogen gas at 363 K. The solid separated from suspension using centrifuge was dried under vacuum at room temperature. The products were evaluated by an X-ray diffraction analysis, measurement of point of zero charge, element analysis, and measurement of specific surface area by a nitrogen gas adsorption method at 77K.

2.2 Adsorption experiment

The adsorption test was carried out by a batch method. In order to investigate the effect of pH on the adsorption of arsenic, the aqueous As(III) and As(V) solutions were prepared at concentrations of 0.10 mmol·dm⁻³. The solution was adjusted to pH 3.5 - 12.0 by 10 mmol·dm⁻³ HCl and NaOH. In the adsorption isotherm for arsenic, aqueous As(III) and As(V) solutions were prepared at concentrations of 0.10 - 2.0 mmol·dm⁻³ and 0.10 - 4.0 mmol·dm⁻³, respectively. The pH of the solution was adjusted to 7.0 by 10 mmol·dm⁻³ BES buffer solution. All batch tests were carried out as follows. 15 cm³ of the solution was added to the sample tube with 10 mg of FeYx. The suspension was shaken in a thermostat at 303 K, 120 rpm for 24 h. After shaking, the sample was filtered through a hydrophilic PTFE 0.45 μm membrane filter, and the As concentration in filtrate was analyzed by ICP atomic emission spectrometer. Adsorption percentage and amount of adsorption were calculated by Eqs. (1) and (2).

$$A = (C_i - C_e) / C_i \times 100 \quad (1)$$

$$q = (C_i - C_e) \times 15 / 10 \quad (2)$$

Where *A* and *q* are adsorption percentage (%) and amount of adsorption (mmol·g⁻¹), respectively. *C_i* and *C_e* represent the initial and the equilibrium concentration (mmol·dm⁻³) of arsenic, respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of FeYx (x=0.5, 1, 2)

XRD patterns of prepared FeYx were shown in Fig.1. The diffraction peaks of the FeYx were attributed to characteristic peaks of Fe₃O₄. The increase of x was gradually widening the half value width of the diffraction peak and decreased the intensity of the peak. The broad peak of YOOH appeared with increasing a molar ratio of Y/Fe. The points of zero charge (PZC) of FeY2, FeY1 and Fe-Y0.5 were determined by zeta potential measurement, and they are 10.3, 9.8 and 8.8, respectively. The surface of the FeYx is positively charged at pH < PZC and becomes negatively charged at pH > PZC. The specific surface areas were 183, 166 and 140 m²·g⁻¹, respectively. The relation of

the specific surface area and the PZC versus x was shown in Fig. 2. From this result, it was found that the PZC and the specific surface area increased with increasing x. Because the FeYx has magnetic property, the arsenic-loading FeYx is easily separated from suspension by magnet.

3.2 Effect of pH on As(III) and As(V) adsorption

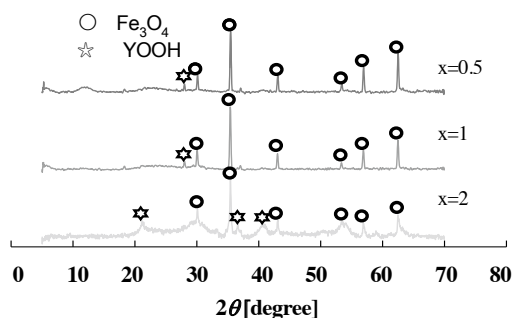


Fig.1 XRD patterns of FeYx (x = 0.5, 1, 2).

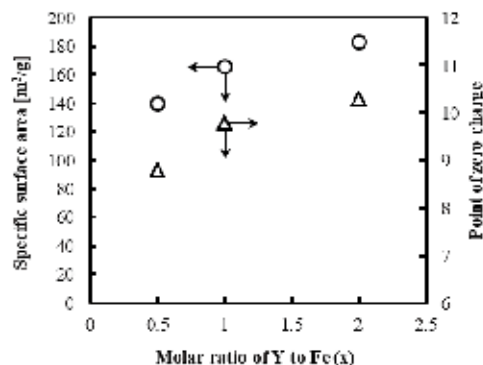


Fig. 2 Plots of the specific surface area and the point of zero charge versus molar ratio of Y to Fe.

Fig. 3 shows the effect of pH on As (III) and As (V) adsorption by FeY2. FeY2 had the adsorption percentage higher than 90% of As(III) and As(V) in a wide pH range (6.3 - 10.5). These results were suggested that As(III) and

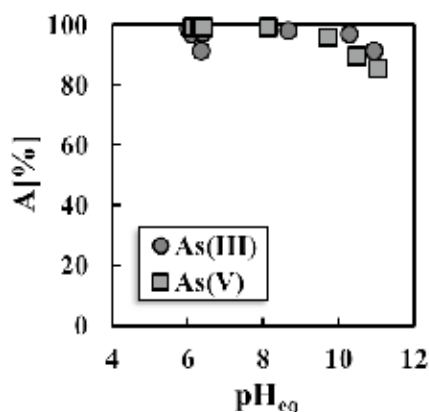


Fig. 3 Effect of pH on adsorption percentage of arsenic with FeY2.

As(V) were adsorbed on the adsorbent surface positively charged at $\text{pH} < \text{PZC}$. In the region of $\text{pH} > \text{PZC}$, the surface of FeY2 is negatively charged, which was caused electrostatic repulsion with the anion species of As(III) and As(V). Increase of PZC enhanced the arsenic adsorption performance of FeYx at high pH.

3.3 Adsorption isotherms of As(III) and As(V)

The maximum adsorption capacity and the adsorption equilibrium constant of As(III) and As(V) on FeYx were investigated by adsorption isotherms. The adsorption isotherms of As (III) and As (V) at 303 K are shown in Fig. 4. The data was correlated with Langmuir adsorption model (Eq.(3)).

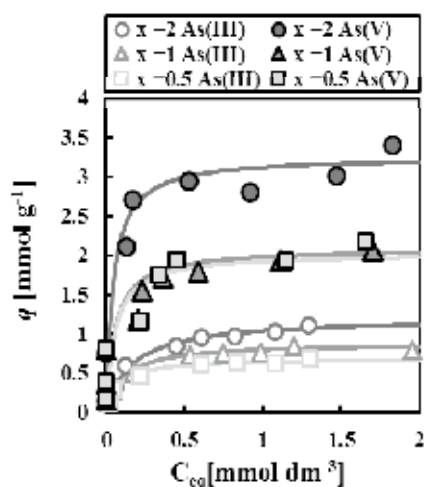


Fig. 4 Adsorption isotherms of As(III) and As(V) on Fe-Yx at 303K.

$$q = K_L q_{\max} C_e / (1 + K_L C_e) \quad (3)$$

$$q / C_e = 1 / K_L q_{\max} + C_e / q_{\max} \quad (4)$$

The maximum adsorption capacity (q_{\max} , mmol g^{-1}) and the adsorption equilibrium constant (K_L , $\text{dm}^3 \text{mmol}^{-1}$), respectively were determined from the intercept and the slope obtained by Eq.(4) which derived from rearranging Eq.(3).

The q_{\max} values of As (III) on FeY2, FeY1 and FeY0.5 were 1.21, 0.893 and 0.693 mmol g^{-1} , respectively. K_L values were 6.15, 8.83 and 12.7 $\text{dm}^3 \text{mmol}^{-1}$, respectively. In the adsorption of As (III), q_{\max} and K_L increased with increasing the molar ratio of Fe to Y and increasing the amount of Fe in the FeYx composition, respectively. The q_{\max} of As(III) on three FeYx adsorbents were higher than that of yttrium-manganese binary composite (0.373 mmol g^{-1})(Yu 2015).

The q_{\max} values of As (V) on FeY2, FeY and Fe-Y0.5 were 3.26, 2.09 and 2.03 mmol g^{-1} , respectively, and K_L

values were 22.4, 18.0 and 18.2 $\text{dm}^3 \text{mmol}^{-1}$, respectively. The adsorption performance for As(V) was enhanced with increasing the amount of yttrium in the FeYx composition. The q_{\max} and the K_L of As(V) on FeY2 were 2.5 times and 3.6 times for those of As(III), respectively. At pH 7.0 most of the surface on FeY2 has the adsorption site charged positively because of high PZC value. This result suggests that As(V) is adsorbed by electrostatic attractive force between FeY2 surface charged positively and anion species of As (V). The q_{\max} of As(V) on FeY2 are much higher than those on Cu-Fe, 1.10 mmol g^{-1} (Zhang 2013) and Fe-Ti 0.19 mmol g^{-1} (Gupta 2009) binary oxides. Therefore FeY2 is expected for adsorbent of As(III) and As(V).

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