Mechanism of As(V) removal in wastewater using Fe(III)-supported exchange resins

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Abstract

Today, mine development and natural pollution caused As contaminated water. In south-eastern Asia, some people use the groundwater containing As more than 10 µg/L for drinking, and it is worried that they are exposed to As addiction.

In this study, we focused on the construction of an economical and simplified process for treatment of As(V) contaminated drinking water. The (co-)precipitation method using ferrihydride is commonly applied for As(V) removal, but it generates many sludge and needs much time for liquid/solid separation. Objective of this study is simultaneous processing of As(V) removal and sold/liquid separation using Fe(III)-supported ion exchange resins.

At first, As(V) removal mechanism was investigated with batch beaker test, by ICP-AES analysis for filtrate and Electron probe micro analyzer (EPMA) and X-ray absorption fine structure (XAFS) analysis for solids. These results suggested that Fe(III) diffusion inside the resin was the rate-determining step, thereby requiring prolonged reactions for As(V) removal. These solid analysis results also suggested that As(V) was removed by the combination of surface precipitation of ferric arsenate and surface complexation to ferrihydrite.

Secondly column test packed Fe(III)-supported resin was also conducted for synthetic As(V) wastewater. Results showed As(V) was successfully removed under SV 9.82 hr^{-1} until 192 BV.

Keywords: wastewater treatment, As(V) removal, ion-exchange resin, column method

1. Introduction

Today, arsenate (As(V)) contaminated groundwater is confirmed because of mine development and natural pollution all over the world. According to the guideline of WHO, standard value of water for drinking about As(V) is less than 10 µg/ L. As(V) contaminated groundwater is serious problem especially in south-eastern Asia and some people use this groundwater for drinking[1]. Therefore, health hazard is worried because of As(V) addiction.

Coprecipitation method with ferrihydrite is conventional for As(V) removal. However, this method is generates voluminous precipitates which are difficult to separate liquid from solid. Therefore, easy and inexpensive treatment method for As(V) contaminated water is desired.

In this study, As(V) removal from wastewater with ion-exchange resin supported by Fe(III) was investigated. This treatment method could achieve As(V) removal and solid/liquid separation at a time. Therefore, this process should be suitable to treatment of relatively small scale of water treatment such as drinking water.

At first, Fe(III) was supported to ion-exchange resin. Dosage of ion-exchange resin was changed to draw sorption isotherm. To discuss about As(V) removal

mechanism using Fe(III)-supported resin, As(V) removal experiments were conducted with changing pH and reaction time in batch method. Concentration of As(V) after removal experiment was measured by ICP-AES, and sorption isotherm was drawn to reveal removal characteristic. In addition, Fe(III)-supported resin after As(V) removal was analyzed with electron probe micro analyzer (EPMA) and X-ray absorption fine structure (XAFS). With EPMA, Fe(III) and As(V) diffusion in resin was revealed before and after experiment. With XAFS, the existence form of Fe(III) was revealed. From the result, As(V) removal mechanism using Fe(III)-supported resin was considered.

In addition, As(V) removal experiment was conducted with column method to identify whether As(V) removal and solid/liquid separation were achieved at a time. Flow of wastewater and dosage of packed Fe(III)-supported resin were changed to compare removal capacity per space velocity.

2. Experiment method

2.1 Fe(III) supported to ion-exchange resin

In this study, strong acid cation exchange resin (SK104, R-Na) was used. Before experiment, ion-exchange resin was washed by pure water (Aquarius RFD 240Na, ADVANTEC).

In the experiment to support Fe(III) to ion-exchange resin, 1000 mg/dm^3 Fe(III) solution was prepared by dissolving Fe(NO$_3$)$_3$ ·9H$_2$O (Wako-Chemical) in 3000 mL beaker. The solution was adjusted to pH 2 by using HNO$_3$ and NaOH. In this time, NaOH was dropped as little as possible to prevent hydroxide precipitation. After pH controlling, ion-exchange resin was soaked. Solution and resin were stirred for predefined time and filtration was conducted. After filtration, concentration of Fe(III) in filtrate was measured with ICP-AES (SPS7800, Seiko instruments, Japan). Fe(III)-supported resin was dried for a day in thermal dryer and used for As(V) removal experiment.

2.2 As(V) removal experiment in batch method

Synthetic wastewater containing As(V) was used in As(V) removal experiment. Firstly, 10 mg/dm^3 of As(V) solution was prepared by dissolving Na$_2$HAsO$_4$ ·7H$_2$O (Kanto-Chemical) into pure water. Ion strength was adjusted to 0.05 mol/L by using HNO$_3$ and NaOH. This synthetic solution was moved to 300 mL beaker and controlled the pH by using 1 M HNO$_3$ and 1 M NaOH. After this, Fe(III)-supported resin was soaked and this solution was stirred for predefined time. Filtration (Φ0.45)

was conducted, concentration of As(V) in filtrate was measured with ICP-AES. Separated Fe(III)-supported resin was dried in thermal dryer for a day. This resin was analyzed with EPMA (JXA-8100, JELO, Japan) and XAFS (BL9A and NW-10A in KEK-PF, NW-15 in SAGA-LS).

2.3 As(V) removal experiment in column method

In column experiment, synthetic wastewater was prepared by the same way written in batch method. The size of acrylic column was as follows; 9 mm of inner diameter and 150 mm of length. Bounded material, Fe(III)-supported resin and bounded material were packed in order into this column before experiment.

Amount of packed Fe(III)-supported resin was 0.5 g, 1.0 g and 2.0 g. The height of packed resin in column was 20 mm, 40 mm and 80 mm in order. Synthetic wastewater was sent by tube pomp (EYELA, MP-2000 and SMP-21) from bottom to upper side to fill column with wastewater, and flow rate was set to 25~100 mL/h. Drained water was obtained per constant time, and As(V) concentration was measured with ICP-AES.

3. Result and discussion

3.1 Fe(III) supported to ion-exchange resin

First, dosage of ion-exchange resin was changed to draw sorption isotherm. The relationship between dosage of Fe(III)-supported resin and residual Fe(III) concentration was shown in Fig1 and sorption isotherm was shown in Fig 2. In this experiment, reaction time was set to 1 hour.
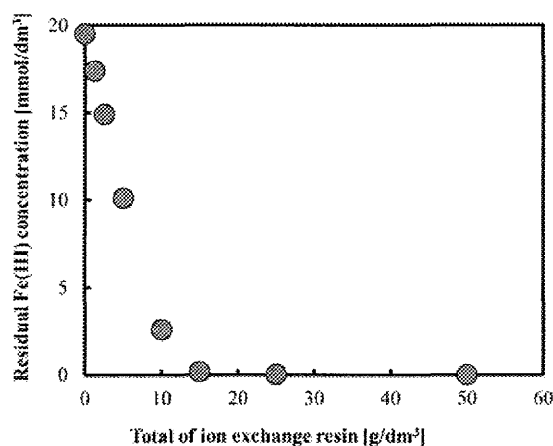

Fig 1 Relationship between residual Fe(III) concentration and dosage of ion exchange resin
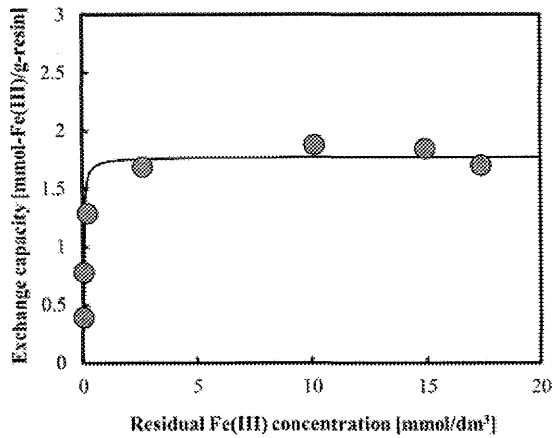
Fig 2 Sorption isotherm about Fe(III) supported to ion exchange resin

From Fig 1Fig , amount of supported Fe(III) was saturated when dosage of ion-exchange resin was less than 10 g-resin/dm^3. From Fig 2, sorption isotherm showed a Langmuir type, and maximum exchange capacity was 1.73 mmol-Fe/g-resin. This result suggested that almost all counter ion was changed to Fe(III) in 1 hour reaction because neutral salt decomposing capacity of this resin was about 5.00 meq/ g-resin.

From these results, experiment condition of preparing for Fe(III)-supported resin was determined as follows; 1 h of reaction time and 10 g-resin/dm^3 of dosage of ion-exchange resin.

3.2 As(V) removal experiment in batch method

Relationship between pH and sorption density was shown in Fig 3.Dosage of Fe(III)-supported resin was set to 1.0 g-resin/dm^3, reaction time was set to 1 hour. Initial pH was changed from 1 to 13.
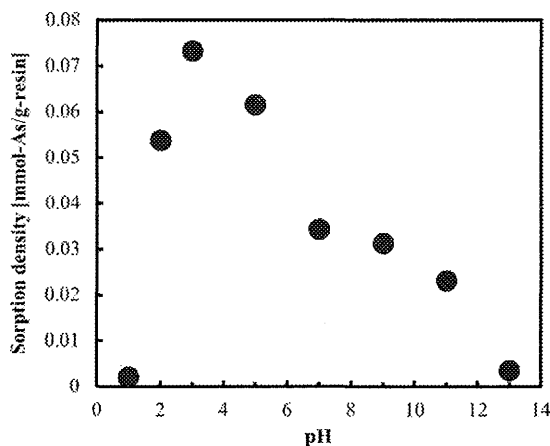

Fig 3 Relationship between sorption density and pH about As(V) removal experiment in batch method

From Fig , maximum sorption density was obtained in pH 3. From this result, As(V) removal characteristic and mechanism was investigated in the condition of pH 3.

To discuss removal characteristic, sorption isotherm at pH 3 was drawn. Dosage of Fe(III)-supported resin was changed 0.1~20 g-resin/dm^3 and reaction time was set to 1 hour. Result was shown in Fig 4.
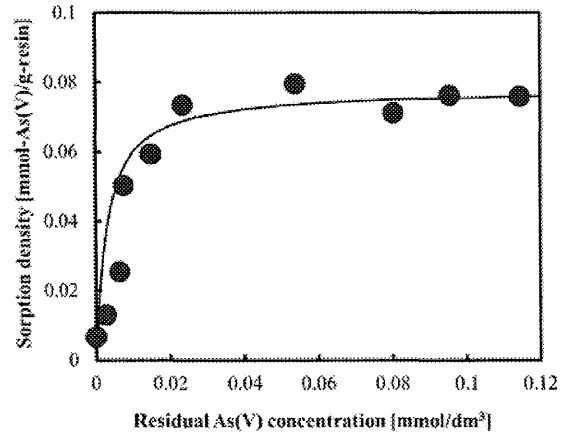

Fig 2 Sorption isotherm about As(V) removal experiment in batch method at pH 3

From Fig4, sorption isotherm shows a Langmuir type, and maximum sorption density was 0.078 mmol-As/g-resin. This value was equal to 0.045 mmol-As/mmol-Fe.

To remove contaminated As(V), coprecipitation method with ferrihydrite was commonly used. This removal process was achieved with both surface complex and surface precipitation. In this coprecipitation process, maximum sorption density reached to 1.00 mmol-As/mmol-Fe. On the other hand, maximum sorption density only in adsorption process was 0.205 mmol-As/mmol-Fe and main mechanism of As(V) removal was mainly surface complexation[2].

As(V) sorption density by Fe(III)-supported resin was much smaller than that to ferrihydrite. This was probably because reaction time was short to remove As(V) with Fe(III)-supported resin. Therefore, experiment in longer reaction time was conducted.

In this experiment, initial pH was adjusted to 3, and dosage of Fe(III)-supported resin was 0.1 g/dm^3. The result was shown Fig 5.
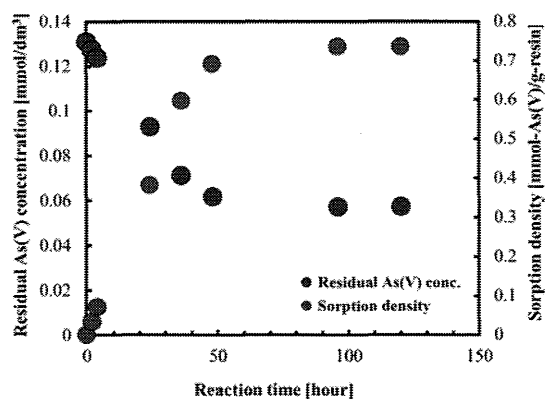
Fig 5 Residual As(V) concentration and sorption density in 120 hours reaction

From Fig 5, it took for 96 hours to reach equilibrium for As(V) removal using Fe(III)-supported resin. In this experiment, maximum sorption density was 0.74 mmol-As/g-resin, and this value was equal to 0.43 mmol-As/mmol-Fe. This result was larger than the value obtained in adsorption method with ferrihydrite. Therefore, removal mechanism of As(V) by Fe(III)-supported resin should involve both of surface complexation and surface precipitation.

These results showed that reaction time affected to sorption density in As(V) removal process. Therefore, it was identified that As(V) removal mechanism with Fe(III)-supported resin was different from the mechanism of supporting Fe(III) to ion exchange resin. In addition, it was suggested that diffusion inside the Fe(III)-supported resin was rate-determining step in As(V) removal process.

3.3 EPMA analysis

To discuss As(V) removal mechanism, it was investigated that diffusion of Fe(III) and As(V) inside Fe(III)-supported resin with EPMA. Fe(III)-supported resin before and after As(V) removal in pH 3 were analyzed and results between them were compared. Fe and As distribution at line AB, which was cross-section surface of resin, were observed as shown in Fig 6.
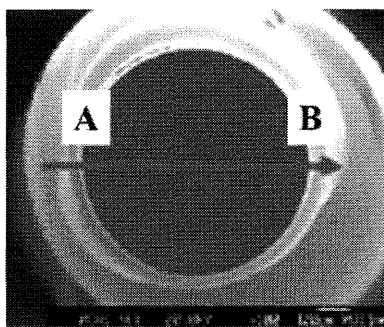

Fig 6 SEM picture of cross-section surface of Fe(III)-supported resin
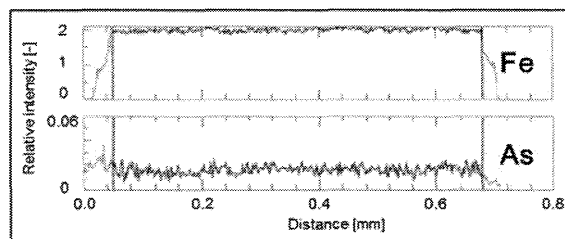

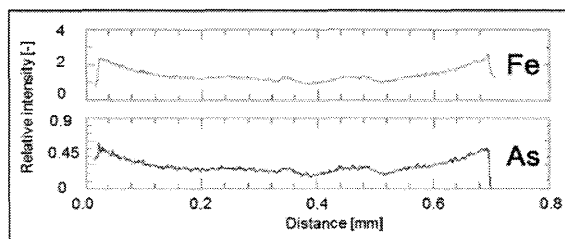Fig 7 Fe(III) and As(V) diffusion of Fe(III) supported resin

Fig 8 Fe(III) and As(V) diffusion of Fe(III) supported resin after As(V) removal

From Fig 7, Fe(III) existed on line AB uniformly before As(V) removal. On the other hand, from Fig 8, Fe(III) and As(V) were more concentrated around surface after As(V) removal. This was probably because supported Fe(III) was exchanged with H^+ or Na^+ in synthesis wastewater, because concentration of Na^+ or H^+ was higher than Fe(III) in wastewater. In this process, Fe(III) inside resin moved outside with ion-exchanging and As(V) was captured by this Fe(III) moving to surface of resin. Thus, Fe(III) and As(V) were more concentrated around surface of resin. These results also suggested that As(V) removal was affected by diffusion of Fe(III) inside Fe(III)-supported resin.

3.4 XAFS analysis

By using XAFS analysis, existence form of Fe and As inside resin was investigated. Edge absorption spectrum of Fe-K edge was measured to evaluate As(V) removal mechanism.

Fig. 9 showed Fe-K edge XANES spectrum of Fe(III)-supported resin before and after As(V) removal experiment in pH 3. As reference sample, ferrihydrite and poorly crystalized ferric arsenate were also analyzed.
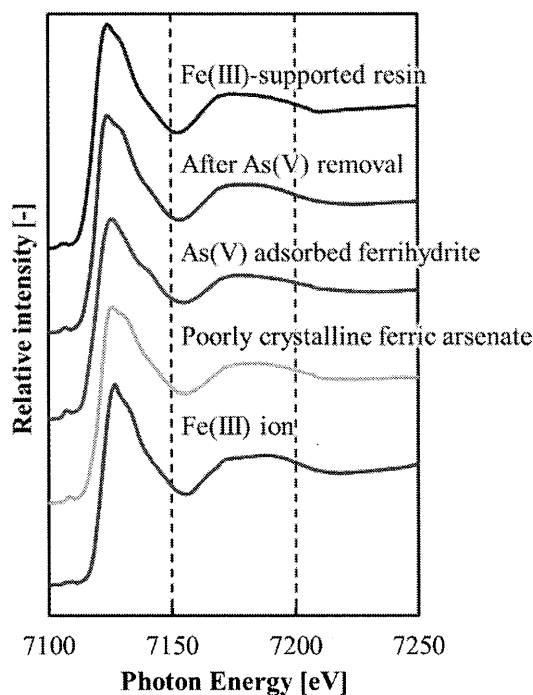
Fig 9 Fe-K edge spectrum of Fe(III)-supported resin before and after As(V) removal experiment

Compared with reference spectrum, pre edge was obtained around 7112 eV in spectrum of ferrihydrite and poorly crystalline ferric arsenate. On the other hand, pre edge was not obtained in spectrum of Fe(III). In addition, main peak of ferrihydrite and poorly crystalline ferric arsenate was broad, whereas it of Fe(III) was sharp. Moreover, small shoulder was obtained in different area between these reference materials. That is, Fe(III) was around 7137 eV, ferrihydrite was around 7146 eV and poorly crystalline ferric arsenate was around 7135 eV.

In spectrum of Fe(III)-supported resin, weak pre edge around 7112 eV, weak shoulder around 7137 eV and quite weak peak around 7146 eV were obtained. In addition, main peak was relatively sharp. These result identified that existence form of Fe in Fe(III)-supported resin was mainly Fe(III) associated with ferrihydrite.

On the other hand, in spectrum of Fe(III)-supported resin after As(V) removal, main peak became broad, and shoulder was obtained around 7135 eV. These results identified that existence form of Fe inside Fe(III)-supported resin after As(V) removal was Fe(III), ferrihydrite and poorly crystalline ferric arsenate.

Weight ratio of existence form of Fe was calculated by REX2000, which was calculating software for XAFS. Result was shown in Table 1.

Table 1 weight ratio of Fe in Fe(III)-supported resin before and after As(V) removal

Experiment	As(V) adsorbed ferrihydrite	Poorly crystalline ferric arsenate	Fe(III) ion
Fe(III) support	35.0	-	65.0
As(V) removal	40.4	25.8	33.8

From Tabble 1, Fe existence form inside Fe(III)-supported resin was Fe(III) and ferrihydrite. After As(V) removal, amount of Fe(III) decreased, and ferrihydrite and poorly crystalline ferric arsenate were precipitated. These resulted suggested that As(V) removal mechanism using Fe(III)-supported resin was achieved in both coprecipitation process and adsorption process and As(V) removal mechanism involved both of surface complexation and surface precipitation.

3.5 As(V) removal experiment in column method

To consider whether As(V) removal and solid/liquid separation were achieved at the same time, As(V) removal experiment with column was conducted. Flow rate of synthesis wastewater and amount of packed Fe(III)-supported resin were changed to discuss about relationship between breakthrough time and amount of saturated As(V) removal per space velocity. Space velocity (SV) was calculated by Eq. (1) (Q; flow rate [m³/hr], S; cross-section area of column [m²], h; height of packed resin [m])

$$SV = \frac{Q}{S \times h} \qquad (1)$$

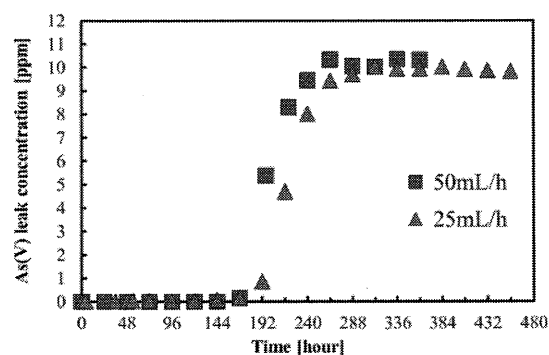Each breakthrough curve when the space velocity was 9.82, 19.65 and 39.3 hr⁻¹ was shown Fig 10-12.
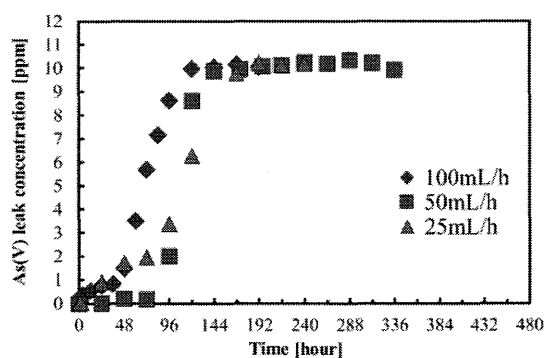

Fig 10 breakthrough curve at SV = 9.82 hr⁻¹

Fig 11 breakthrough curve at SV = 19.65 hr^{-1}

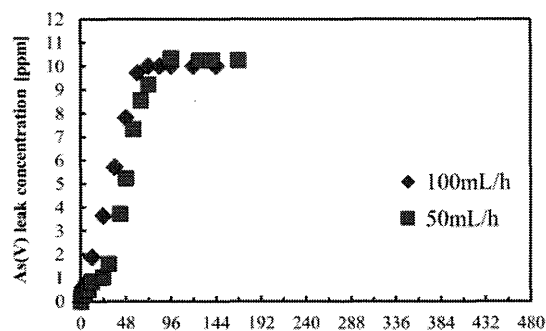

Fig 12 breakthrough curve at SV = 39.30 hr^{-1}

From Fig 10-12, it was identified that breakthrough was more inhibited and amount of As(V) removal increased as space velocity became small. Maximum sorption density was 0.76 mmol-As/g-resin in 9.82 hr^{-1}. This value was almost equal to the value we obtained in batch method. In this time, Fe(III)-supported resin treated 192 BV of wastewater. In other words, Fe(III)-supported resin treated wastewater of 192 times as large as volume of resin packed into column. These results identified that As(V) removal and solid/liquid separation were achieved at the same time.

When space velocity was same value, breakthrough curves were alike. However, amount of As(V) removal decreased as flow rate became large in the same space velocity. This is probably because As(V) removal mechanism was rate-determining step. When flow rate was large, Fe(III)-supported resin could be attached with wastewater only for short time and Fe(III) ion inside resin could not be exchanged with Na$^+$ and H$^+$ in solution enough. Thus, it was considered that diffusion of Fe(III) was inhibited and amount of As(V) removal decreased in large flow rate.

4. Conclusion

In this study, As(V) removal experiment using Fe(III)-supported resin in batch method was conducted to discuss about As(V) removal characteristic and mechanism. After this, As(V) removal experiment with column packed with Fe(III)-supported resin was also conducted to consider whether As(V) removal and solid-liquid separation were achieved at the same time.

Fe(III) ion was exchanged with counter ion inside resin in 1 hour. From sorption isotherm, maximum exchange capacity was 1.73 mmol-Fe/g-resin. By XAFS analysis, existence form of Fe inside Fe(III)-supported resin was 65 % of Fe(III) and 35 % of ferrihydrite. With EPMA analysis, Fe(III) was distributed uniformly inside ion exchange resin.

Sorption density obtained in batch method was 0.078 mmol-As/g-resin in 1 hour reaction, 0.74 mmol-As/g-resin in 96 hours reaction. With EPMA analysis, it was revealed that Fe(III) and As(V) were concentrated around surface of resin. By XANES analysis, it was identified that As(V) removal using Fe(III)-supported resin was achieved in both coprecipitation process and adsorption process and As(V) removal mechanism involved both of surface complexation and surface precipitation. From these results, Fe(III) inside resin diffused to outside gradually and As(V) was captured by Fe(III) around surface. Precipitates of ferrihydrite and surface precipitation should cover the surface of resin and prevented that Na$^+$ and H$^+$ ions in solution exchanged with Fe(III) inside resin. Therefore, As(V) removal process with Fe(III)-supported resin needed long time for reaction.

From the result of As(V) removal experiment with column method, breakthrough time was 192 hours when space velocity was 9.82 hr^{-1}. In this case, sorption density was 0.76 mmol-As/g-resin, and 192 BV of wastewater was treated. It was identified that As(V) removal and solid/liquid separation were achieved at the same time. Breakthrough was more inhibited as space velocity and flow rate were small. This is probably because diffusion of ion inside resin was rate-determining step. Therefore, When flow rate was large, Fe(III)-supported resin was not attached with solution for long time, and amount of saturated As(V) removal decreased.

5. Reference

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