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https://hdl.handle.net/2324/7164801

出版情報：Journal of Chemical Engineering of Japan. 56 (1), pp.2212703-, 2023-05-19. Taylor and Francis
バージョン：

Journal of Chemical Engineering of Japan

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tjce20

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To cite this article: Hiromichi Kondo, Kazumasa Oshima, Tsuyoshi Yamamoto & Masahiro Kishida (2023) Kinetic Analysis on As(III) Oxidation in a Fixed-Bed Flow Reactor Filled with a Supported Platinum Catalyst, Journal of Chemical Engineering of Japan, 56:1, 2212703, DOI: 10.1080/00219592.2023.2212703

To link to this article: https://doi.org/10.1080/00219592.2023.2212703

JOURNAL OF CHEMICAL ENGINEERING OF JAPAN
2023, VOL. 56, NO. 1, 2212703
https://doi.org/10.1080/00219592.2023.2212703

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Kinetic Analysis on As(III) Oxidation in a Fixed-Bed Flow Reactor Filled with a Supported Platinum Catalyst

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ABSTRACT

In this study, the oxidation of As(III) was examined in a fixed-bed flow reactor filled with a SiO_2-supported Pt catalyst, and the reaction kinetics were analyzed. The results of the experiments with different concentrations of As(III) at small W/F suggest that the reaction follows the Langmuir-Hinshelwood (L-H) mechanism. However, at large W/F, the kinetic equations different from the L-H equation were obtained because the O_2 supply to the catalyst surface was rate-limiting. It was also demonstrated using this reactor that As(III) of an equivalent concentration as the mine effluent was almost completely oxidized to As(V) with only dissolved O_2.

ARTICLE HISTORY
Received 4 January 2023
Accepted 8 May 2023

KEYWORDS
As(III) oxidation; Pt catalyst; Reaction kinetic analysis; Plug-flow reactor

1. Introduction

Inorganic arsenic in wastewater is highly toxic to humans. Arsenic causes acute poisoning (Hughes 2002) or chronic poisoning, such as cancer (Chen et al. 2007; Wu et al. 2020), skin lesions (Banerji et al. 2019), and peripheral circulatory disorders (Tseng 1977). Considering its dangerous effects on human health, arsenic in industrial wastewater must be removed until it falls below the regulated concentration. The regulated concentration of arsenic in industrial wastewater in Japan is less than 1.3×10^{-3} mol m^{-3}. Inorganic arsenic is released in large quantities, especially from metal mines (Koide et al. 2012). The concentration of As in mine drainages varies, but in Japan, in some cases, the concentration of arsenic leached from excavated rock exceeded the regulatory limit, and the concentration was 1.1×10^{-2} mol m^{-3} (Igarashi et al. 2020), 1.3×10^{-2}–4.4×10^{-2} mol m^{-3} and 6.7×10^{-3}–3.7×10^{-2} mol m^{-3} (Koide et al. 2012).

Inorganic arsenic primarily exists as trivalent arsenite (As(III)) and pentavalent arsenate (As(V)) in water. As(III) is more toxic, soluble, and mobile than As (V) (Lenoble 2003). As(III) is also difficult to be removed by precipitation, adsorption, or flocculation methods. Conversely, As(V) can be easily removed by precipitation with the addition of iron (Tseng 1977). To remove As(III) from wastewater, it is often oxidized to As(V). However, owing to the stability of As(III), the oxidation process tends to proceed at a low reaction rate. The oxidation of As(III) requires a strong oxidant, such as hydrogen peroxide (Kim et al. 2015; Pettine et al. 1999), chlorine (Dodd et al. 2006), or ozone (Kim and Nriagu 2000). Alternatively, the reaction requires light emission, as in the case of photocatalysis (Lee and Choi 2002). These processes require continuous consumption of oxidants or ultraviolet irradiation, which increases the operational cost of As(III) oxidation treatment. Therefore, an oxidation method that does not use a strong oxidant or external energy is desirable.

We have found that As(III) oxidation in water proceeds easily over supported noble metal catalysts, with only dissolved O_2 as the oxidant (Oshima et al. 2022; Zhao et al. 2017). In particular, the supported platinum catalyst showed a high reaction rate of 6.67×10^{-7} mol L^{-1} s^{-1} at 50 °C without a strong oxidant. In previous research, the As(III) oxidation rates with hydrogen peroxide, chlorine, and ozone were reported as 3.43×10^{-11} mol L^{-1} s^{-1} at 25 °C (Pettine et al. 1999), 4.17×10^{-8} mol L^{-1} s^{-1} at 20 °C (Ghurye and Clifford 2004), and 0.0126 mol L^{-1} s^{-1} at 20 °C (Dodd et al. 2006), respectively. The reaction rate over the Pt catalyst was higher than these previous results and the Pt catalyst is recyclable; therefore, the use of the Pt catalyst in the As(III) oxidation process is expected to significantly reduce the operation cost.

Although the catalytic process for As(III) oxidation has significant advantages as described above, there are two research issues that need to be addressed in the catalytic process. One issue is to analyze the reaction kinetics over the catalyst. Several kinetic studies on non-catalytic As(III) oxidation have been reported that the reaction was first-order for both As(III) and the oxidant (Dodd et al. 2006; Kim and Nriagu 2000; Pettine et al. 1999). In contrast,

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Supplemental data for this article can be accessed online at https://doi.org/10.1080/00219592.2023.2212703

kinetic analysis of catalytic As(III) oxidation remains largely unexplored. The catalytic reaction is generally affected by the adsorption and activation states of the reactants over the catalyst, and its kinetic equation differs from that of non-catalytic reactions. Oxygen is known to chemisorb on Pt surfaces even in water (Adžić and Wang 1998). Shan et al. reported that an adsorbent consisting of a lanthanum peroxide complex adsorbed As(III) and promoted its oxidation in water (Shan et al. 2022). The second research issue is to perform the reaction in a fixed-bed flow reactor packed with the catalysts. So far we have studied with a batch reactor with a dispersed powder catalyst (Oshima et al. 2022; Zhao et al. 2017). However, considering the scale-up and catalyst leakage, it is essential to conduct reaction experiments in a fixed-bed flow reactor packed with catalysts.

In this study, As(III) oxidation tests were performed in a fixed-bed flow reactor packed with a supported platinum catalyst. Taking advantage of the varied conditions, the kinetic equation for As(III) oxidation over the catalyst was examined.

2. Experimental

2.1. Preparation and characterization of Pt/SiO$_2$ catalyst

A silica-supported platinum catalyst (Pt/SiO$_2$) was prepared using the following impregnation method: Silica particles of 1 mm in diameter (CARiACT Q-50, Fuji Silicia Chemical Co., Ltd.) were impregnated with an aqueous solution of $Pt(NH_3)_2(NO_2)_2$ (Tanaka Kikinzoku Kogyo K.K.), evaporated, dried, and then reduced at 350 °C for 2 h under a 10%–H_2(N_2 balance) flow. The catalyst prepared using silica particle will be described as a granular catalyst. The prepared granular catalyst was ground in a mortar, which we will describe as a powder catalyst. The Pt content was 1.0 wt%.

Pt particle size was evaluated by CO chemisorption at 50 °C (BELCAT-B-SP, MicrotracBEL). X-ray diffraction (XRD) measurements were performed using Ultima IV (Rigaku Corporation) equipped with a Cu Kα radiation source at a scanning speed of 1° min^{-1}.

2.2. As(III) oxidation tests

As(III) oxidation tests were performed using a fixed-bed flow glass reactor with an inner diameter of 8 mm (Figure 1). The amount of catalyst charged in the reactor was 0.03–1.4 g. In the experiments with powder catalysts, α-alumina particles were filled together with Pt/SiO$_2$. The reactant solution of As(III) was an aqueous $NaAsO_2$ (Sigma-Aldrich) solution adjusted to pH 3.0 using HCl (Sigma-Aldrich). No O_2 gas was supplied during the reaction and only the O_2 dissolved in the reaction solution was used for As(III) oxidation. The temperature was kept constant at 50 °C by placing the vessel containing the reactant solution and glass reactor in a water bath. The concentration of dissolved O_2 in the reactant solution was measured using a dissolved O_2 meter (YSI Pro Solo, Xylem Japan, Inc.). The reactant solution was continuously supplied to the reactor using a peristaltic pump and the outlet solution was collected in vessels at predetermined time intervals. The As(V) and total As concentrations were measured using the same spectroscopic techniques as those used in our previous studies. (Zhao et al. 2017). The As(III) concentration was calculated using the difference between the As(V) and total As concentrations. The O_2 concentration in the effluent solution was determined using the following mass balance equation:

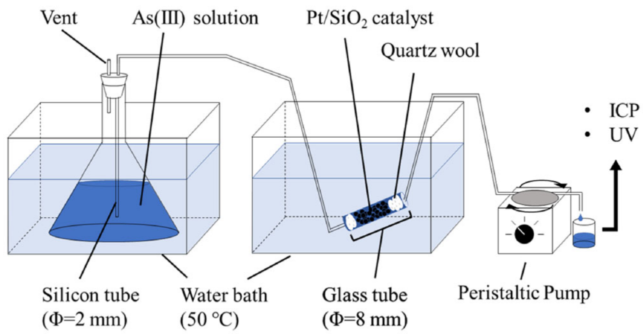

Figure 1. Experimental apparatus of As(III) oxidation tests.

$$[O_2]_{out} = [O_2]_{in} - \frac{1}{2}[As(V)]_{out} \tag{1}$$

Equation (1) was obtained from the following reaction equation.

$$2H_3AsO_3 + O_2 \rightarrow 2H_3AsO_4 \tag{2}$$

Here, $[O_2]_{in}$ and $[O_2]_{out}$ represent the dissolved O_2 concentrations at the reactor inlet and outlet, respectively, and $[O_2]_{in}$ was determined using a dissolved O_2 meter. $[As(V)]_{out}$ represents the As(V) concentration at the reactor outlet, and the As(V) concentration at the reactor inlet was always zero.

3. Results and Discussion

3.1. Stability of the Pt catalysts in the flow reactor

Prior to the As(III) oxidation test, the Pt particle size of the Pt/SiO$_2$ catalyst was evaluated using the CO pulse method. The average Pt particle size was 1.2 nm, which was almost the same as that in our previous research (Oshima et al. 2022; Zhao et al. 2017). The catalyst was also analyzed by powder XRD, but no peaks corresponding to Pt were detected; only a broad peak corresponding to an amorphous silica phase was observed at 22.24° (Figure S1). The results indicate that no large Pt particles existed in the catalyst.

The As(III) oxidation test using the flow reactor was carried out at an inlet As(III) concentration of 0.27 mol m^{-3}. which is almost the same concentration as that eluted from the copper mine. Figure 2 shows the results of three As(III) oxidation runs using the same powder catalyst. The space-time under these conditions was approximately 18 s. As(III) conversion reached a steady state within 180 min and showed stable conversion for 220 min. The As(III) conversion at steady state was 18%, which indicated that the As(III) was oxidized using Pt/SiO$_2$ only after 18 s of contact time in the fixed-bed flow reactor. The turnover frequency (TOF) per metallic surface area derived from CO

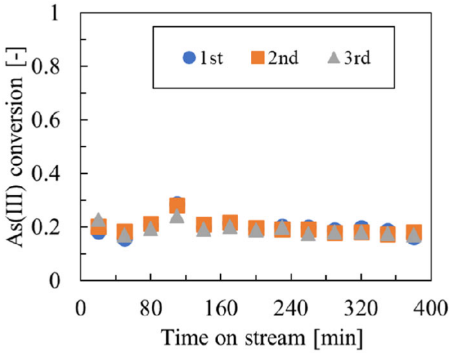

Figure 2. Stability of the powder Pt catalyst in the flow reactor. $[As(III)]_{in} = 0.27\ mol\ m^{-3}$, $W = 0.11$ g, $F = 1.0\ mL\ min^{-1}$, and $W/F = 3000\ kg\ s\ m^{-3}$.

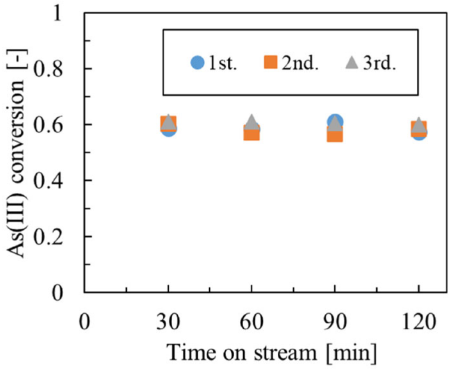

Figure 3. Stability of the granular Pt catalyst in the flow reactor. $[As(III)]_{in} = 0.27\ mol\ m^{-3}$, $W = 0.49$ g, $F = 3.0\ mL\ min^{-1}$, and $W/F = 10{,}000\ kg\ s\ m^{-3}$.

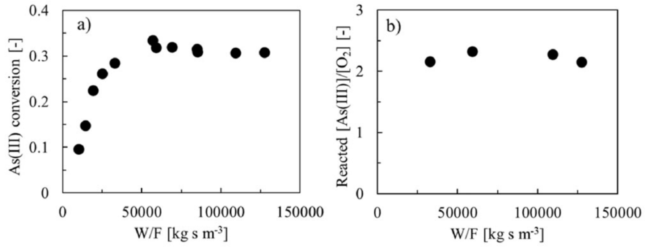

Figure 4. Dependency of (a) As(III) conversion and (b) ratio of reacted As(III) and O_2 concentration on W/F. Granular catalyst, $[As(III)]_{in} = 1.3\ mol\ m^{-3}$.

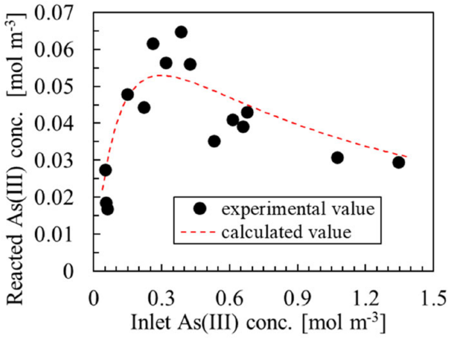

Figure 5. Dependence of reacted As(III) concentration on inlet As(III) concentration. Powder catalyst, $W = 0.03$ g, $F = 2.0\ mL\ min^{-1}$, and $W/F = 900\ kg\ s\ m^{-3}$.

chemisorption in its steady-state conversion was $2.7 \times 10^{-4}\ s^{-1}$. In addition, the catalyst exhibited almost the same conversion three times, indicating good durability (Figure 2). Thus, the fluctuations in the conversion up to 150 min were not due to a change in catalytic properties, but owing to fluctuations in the solution flow in the reactor.

Figure 3 shows the results of the As(III) oxidation using the granular catalyst in the same conditions. The As(III) conversion at a steady state was 58%, and the granular catalyst also catalyzed well the As(III) oxidation reaction. Thus, it was demonstrated that the Pt/SiO_2 catalyst could promote As(III) oxidation at a similar concentration to that found in the effluent from the copper mine. Moreover, the reaction proceeded with only dissolved O_2 in the reaction solution and with a contact time of only a few dozen seconds. Only the steady-state values will be shown under the reaction results in the subsequent sections.

3.2. Composition of reaction solution

To confirm the validity of Eq. (1), the reaction tests were conducted by varying the ratio of catalyst weight to volume flow rate (W/F). To observe changes in the O_2 concentration, the As(III) concentration was set to $1.3\ mol\ m^{-3}$ in excess of the O_2 concentration. The $[O_2]_{in}$ measured by the dissolved O_2 meter was always $0.19\ mol\ m^{-3}$, which is almost consistent with the value reported in the literature, that is, $0.20\ mol\ m^{-3}$ at 50 °C (Dong-Hyo et al. 2020). Figure 4(a) shows the dependency of As(III) conversion on W/F. The As(III) conversion increased with W/F, reaching a constant at 32% with W/F above $50{,}000\ kg\ s\ m^{-3}$. Thus, even though As(III) remained, the reaction did not proceed even if W/F was increased. This was considered to be due to the complete consumption of another reactant, O_2. Therefore, the reacted amount of O_2 was determined by setting the O_2 concentration at the reactor outlet to zero, and the ratio of the reacted amount of O_2 to that of As(III) was calculated. The results are shown in Figure 4(b). From this figure, the values of As(III)/O_2 was close to 2, that is consistent with the stoichiometric ratio of Eq. (2), confirming that there was no external O_2 contamination inside the reactor.

3.3. Reaction mechanism

Kinetic analysis is important for elucidating the reaction mechanism. Figure 5 shows the dependency of the reacted As(III) concentration on the inlet As(III) concentration. In this experiment, the W/F value was much smaller than that of previous experiments shown in 2.1 and 2.2 because the kinetic analysis required low As(III) conversion (6.7–32%). The reacted As(III) concentration increased with increasing inlet As(III) concentration, showing a maximum value at inlet As(III) concentration of $0.3\ mol\ m^{-3}$, and then decreased. This result indicates that the reaction rate also increased until the As(III) inlet concentration reached $0.3\ mol\ m^{-3}$ and decreased at higher concentrations. This trend suggests that the As(III) species in water are competitively adsorbed on the catalyst with dissolved O_2.

In general, because O_2 is chemisorbed on Pt surfaces (Adžić and Wang 1998), two possible mechanisms exist for oxidation reactions over the Pt/SiO_2 catalyst. One is the Langmuir–Hinshelwood (L-H) mechanism, in which both the reactants (As(III) and O_2) are adsorbed on the Pt catalyst surface. According to the L-H mechanism, the kinetic equation can be expressed as Eq. (3).

$$-r_{As} = \frac{K_1[O_2]\ [As(III)]}{(1 + K_2[As(III)] + K_3[O_2])^2} \tag{3}$$

K_1 is the kinetic constant and K_2 and K_3 are the adsorption equilibrium constants of As(III) and O_2, respectively. The other mechanism is the Eley–Rideal (E-R) mechanism, in which only O_2 is adsorbed on the catalyst surface, and the kinetic equation is expressed as Eq. (4).

$$-r_{As} = \frac{K_4[O_2]\ [As(III)]}{1+K_5[O_2]} \tag{4}$$

K_4 is the kinetic constant and K_5 is the adsorption equilibrium constant of O_2.

Equations (3) and (4) show different dependences on the As(III) concentration. As observed in Eq. (3), the numerator and denominator demonstrate first-order and second-order rates with respect to As(III) concentration. Therefore, the reaction rate in Eq. (3) increases with increasing As(III) concentration, reaches a maximum value, and decreases subsequently. This trend is consistent with the results shown in Figure 5. However, as shown in Eq. (4), the numerator and denominator demonstrate first-order and zero-order rates with respect to As(III) concentration. Therefore, the reaction rate in Eq. (4) increases with increasing As(III) concentration before reaching an asymptote. The results strongly suggest that the As(III) oxidation reaction over the Pt catalyst in aqueous solution proceeds via the L-H mechanism. By analyzing the experimental results of Figure 5 using the Eq. (3) of the L-H mechanism, the following equation was obtained.

$$-r_{As} = \frac{4.4\ \times\ 10^{-3}[As(III)][O_2]}{\left(3.4[As(III)]\ +\ 0.17[O_2]\ +\ 1\right)^2}\ \text{mol kg}^{-1}\ \text{s}^{-1} \tag{5}$$

We have previously performed As(III) oxidation tests over Pt/TiO_2 catalysts in a batch reactor with a continuous O_2 supply and reported that the reaction rate was linear with the As(III) concentration (Zhao et al. 2017). This report differs from the results shown in Figure 5, suggesting the L-H mechanism. This difference may be due to the O_2 concentration in the water. In the batch reaction experiment, excessive gaseous O_2 was continuously supplied during the reaction; however, in the tube reactor, O_2 was only dissolved in the feed solution, and no O_2 was supplied from outside to the system during the reaction. In a batch reactor continuously fed with O_2, the adsorption of O_2 may be dominant on the catalyst surface, and the amount of As(III) adsorbed may be relatively small. In this case, the term As (III) in the denominator of Eq. (3) can be neglected, and the reaction rate is therefore first-order, relative to the As(III) concentration.

3.4. Kinetic equation

According to the emission regulations for As in wastewater, the conversion of As(III) to As(V) is required to be close to 100%. To achieve high conversion, the reaction experiments were performed using powder and granular Pt/SiO_2 catalysts with a W/F higher than 900 kg s m^{-3}. Figure 6(a,b) show the reacted As(III) and outlet concentrations of As(III) and O_2, respectively, when the inlet As(III) concentration was

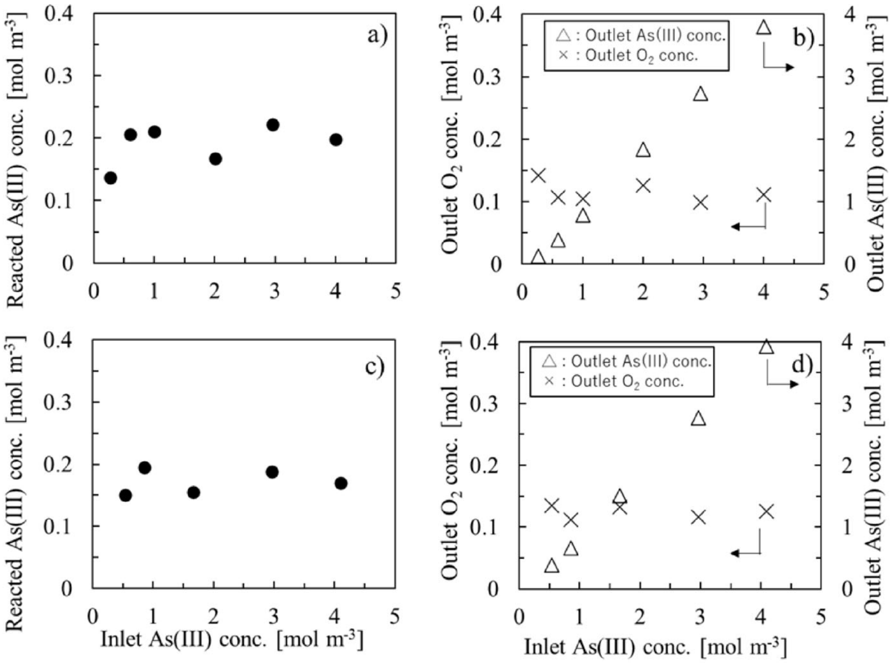

Figure 6. Reacted concentration of As(III) and outlet concentration of As(III) and O_2 at different inlet As(III) concentrations. $W = 0.20$ g and $F = 1.7$ mL min^{-1}, and $W/F = 7000$ kg s m^{-3}. (a) reacted As(III), with granular catalyst, (b) outlet As(III) and O_2, with granular catalyst, (c) reacted As(III), with powder catalyst, (d) outlet As(III) and O_2, with powder catalyst.

varied using the powder catalyst. In Figure 6(a), the amount of reacted As(III) remained constant at inlet As(III) concentrations above 1.0 mol m^{-3}, indicating that the reaction rate was constant in this concentration range. It is noteworthy that in the concentration range where the reaction rate was constant, both As(III) and O_2 remained at the reactor outlet, and the outlet As(III) concentration varied in response to the inlet As(III) concentration. This result indicates that the reaction rate is independent of the As concentration. The outlet O_2 concentration was constant, as shown in Figure 6(b); which means that the reaction rate depends only on the O_2 concentration under these condition.

However, the As(III) concentration dependence of the reaction rate in Figure 6 cannot be explained by the L-H mechanism. In this case, it is possible that the transfer rate of O_2 may be the rate-limiting step of As(III) oxidation reaction. Figure 6(c,d) shows the results of reaction experiments using granular catalysts under the same conditions as (a) and (b). The results indicated the same trend as those obtained for the powder catalyst. Specifically, the catalyst particle size did not affect the reaction rate under high As concentration conditions. This result at least indicates that mass transfer within the catalyst particles does not affect the reaction rate. If a mass transfer is the rate-limiting step of the reaction, the O_2 supply to the catalyst surface may limit the reaction.

Since the above results suggest that the diffusion rate of O_2 is rate-limiting of the reaction at As(III) concentrations above 1 mol m^{-3}, the kinetic analysis was performed using the first-order rate equation for O_2 concentration (Eq. (6)).

$$-r_{As} = K_6[O_2] \tag{6}$$

The amount of reacted As(III) was then examined under As(III) inlet concentrations of 4.0 mol m^{-3} by changing the W/F, and kinetic analysis was performed with respect to O_2 concentration at the reactor outlet. The results are shown in Figure 7. The dashed line shows the results of fitting using Eq. (6), assuming an integral reactor. The fitting curve was in good agreement with the experimental plots, and the rate constant K_6 was obtained as follows:

$$K_6 = 6.9 \times 10^{-5}\ m^3\ kg{-}cat^{-1}\ s^{-1} \tag{7}$$

This result strongly suggests that O_2 supply to the catalyst surface is rate-limiting at high As(III) concentrations. In other words, the As (III) oxidation on the catalyst occurs so rapidly, a limited O_2 supply is available under these reaction conditions.

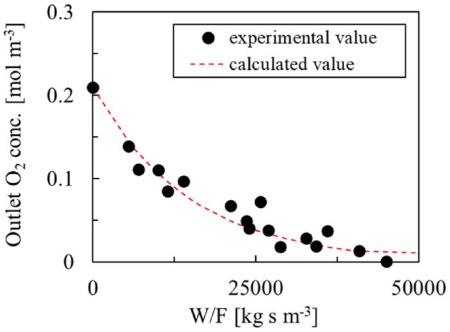

Figure 7. Kinetic analysis under excess As(III) concentration relative to O_2, As(III) inlet concentration = 4.0 mol m^{-3}, granular catalyst.

Although the kinetic equation is shown in Figure 7 at a high As(III) concentration of 4.0 mol m^{-3}, various As(III) concentrations in mine wastewater have been reported to be much lower (Igarashi et al. 2020; Koide et al. 2012; Tomioka et al. 2005). Reaction experiments were conducted at an inlet As(III) concentration of 0.27 mol m^{-3}, which is almost the same concentration as that eluted from the copper mine. The results are shown in Figure 8. The reacted amount of As(III) increased with the W/F. The dashed line in Figure 8 is the result of curve fitting with the experimental data using Eq. (5). The calculated values did not fit the experimental values, indicating that the As(III) oxidation rate under these conditions was much slower than the reaction rate given in Eq. (5). The reason of this result is thought that the rate of O_2 supply to the catalyst is not sufficient for the reaction rate at the catalyst surface and oxidation rate was declined.

When the results of this experiment were fitted again with the equation for the L-H mechanism (Figure S2), the denominator values were almost constant (Figure S3) except for the condition where W/F was very small. This was thought to be because the supply rate of the reactant to the catalyst surface was not sufficient, resulting in a lower concentration of the reactant on the catalyst surface and a correspondingly smaller adsorption volume. Therefore, the following power law kinetic equation was used in this condition:

$$-r_{As} = K_7[As(III)][O_2] \tag{8}$$

K_7 is a constant. This equation corresponds to the numerator in the kinetic equation of the L-H mechanism.

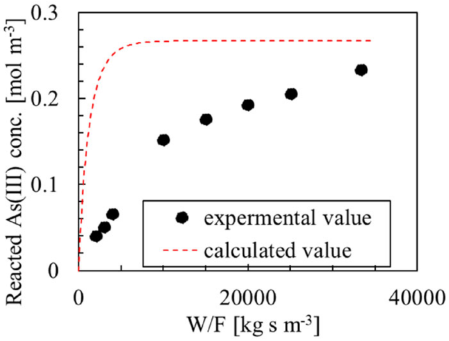

Figure 8. Dependence of reacted As(III) concentration on W/F. Granular catalyst, inlet concentration = 0.27 mol m^{-3}.

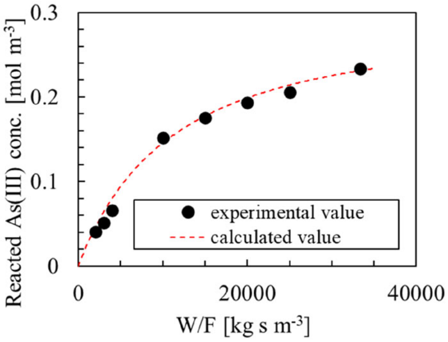

Figure 9. Fitting results with power law kinetic equation. Granular catalyst, As(III) inlet concentration = 0.27 mol m^{-3}.

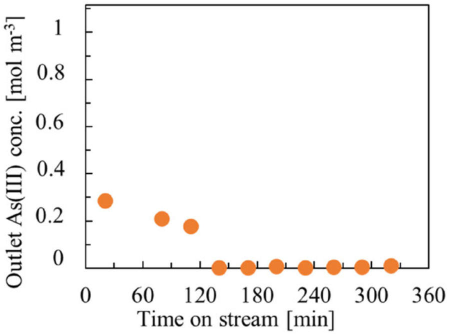

Figure 10. Oxidation of realistic concentration of As(III) to below-regulated concentration. Granular catalyst, As(III) inlet concentration = 0.267 mol m^{-3}, $W = 1.41$ g, $F = 0.60$ mL min^{-1}, and $W/F = 140{,}000$ kg s m^{-3}.

The results are shown in Figure 9. The calculated results fitted well with the experimental results, and the value of K_7 was obtained as follows:

$$K_7 = 4.7 \times 10^{-4}\ \mathrm{m^6\ kg^{-1}\ mol^{-1}\ s^{-1}} \tag{9}$$

Using Eqs. (8) and (9), the W/F required to convert As(III) at concentrations generally contained in mine effluent (0.27 mol m^{-3}) below the Japanese discharge standard (1.3×10^{-3} mol m^{-3}) was calculated to be 140,000 kg s m^{-3}. At this W/F, we conducted the oxidation reaction of 0.27 mol m^{-3} As(III) using the reactor. The results are shown in Figure 10. At a steady state after 90 min, As(III) was almost completely oxidized to As(V) and the As(III) concentration at the reactor outlet was below the Japanese discharge standard. In addition, at this W/F, the contact time for the catalyst is approximately 11 minutes, a condition that is industrially feasible.

It was demonstrated that at a concentration similar to that in the mine effluent, As(III) can be almost completely oxidized using only dissolved O_2, without an external O_2 supply and at a feasible contact time for the catalyst. The validity of Eqs. (8) and (9), obtained from the kinetic analysis, was also demonstrated.

4. Conclusion

In this study, we investigated the oxidation behavior of As(III) in water, using a fixed-bed flow reactor filled with a supported Pt/SiO_2 catalyst and obtained the following results:

1. As(III) is well oxidized by dissolved O_2 in a fixed-bed flow reactor filled with a supported 1.0 wt%-Pt/SiO_2 catalyst.
2. Kinetic analysis of the reaction with powdered catalyst and a small suggested that the reaction followed the Langmuir–Hinshelwood mechanism.
3. The reaction rate was analyzed by varying As(III) concentration for each condition. The kinetic equations were also obtained, which indicated that the O_2 supply to the catalyst was rate-limiting under a wide range of conditions. Specifically, the As (III) oxidation on the catalyst occurs so rapidly, limited O_2 supply is available under various reaction conditions.
4. As(III) at the same concentration found in mine wastewater can be almost completely oxidized with only dissolved O_2 in the reaction solution and with a feasible W/F of 1.4×10^5 kg s m^{-3}.

These findings are significant for the development of As wastewater treatment processes.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by JSPS KAKENHI (grant number 18H03856) and JST SPRING (grant number JPMJSP2136).

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