



Arsenic removal properties by electrolyzed and calcined manganese dioxide

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ABSTRACT

As(V) removal properties of manganese dioxides which are commonly used for the removal of manganese in water treatment processes were evaluated in this paper. The following manganese dioxides were used: two types of powdered manganese dioxides powdered or electrolyzed MnO₂ (g-structure) and calcined MnO₂ (b-structure), and a granular MnO₂, which was prepared by coating MnO₂ onto a ceramic particle. The maximum arsenate adsorption capacity of the electrolyzed and calcined MnO₂ was 2.22 and 2.26 mg-As g⁻¹, respectively. The adsorption capacity of the granular MnO₂ was 0.543 mg-As g⁻¹ and this value corresponded to the MnO₂ content (23.2%) of the granular adsorbent. When an arsenate solution of 0.1 mg-As L⁻¹ was fed into the column (10 mm i.d.; 100 mm long) packed with the granular MnO₂ at SV = 20 h⁻¹, the column received 28.9 L of the feed solution (3,580 times the bed volume) before the breakthrough point (0.01 mg-As L⁻¹). The adsorption isotherms for the electrolyzed and granular MnO₂ were approximated by the modified Langmuir equations. On the other hand, the adsorption isotherm for the calcined MnO₂ was approximated by the Freundlich equation. Based on the adsorption isotherms, the As(V) adsorption amounts at 0.01 mg-As L⁻¹ of the equilibrium concentration were evaluated as follows: 1.27 mg-As g⁻¹ for the electrolyzed MnO₂, 1.20 mg-As g⁻¹ for the calcined one, and 0.29 mg-As g⁻¹ for the granular one. Since granular MnO₂ has been commonly used for the removal of manganese from water treatment systems, the process can be also applied to arsenate removal.

Keywords: Arsenic, Adsorption, Manganese dioxide, Modified langmuir isotherm

1. Introduction

Ground water polluted by arsenic compounds occurs in many parts of the world, and many people have been exposed to the risk of their toxicity [1-4]. The international standards for an acceptable amount of arsenic in drinking water are regulated at 0.01 mg L⁻¹ [5], and approximately 14.6 million people throughout the world are reported to suffer from drinking water that contains arsenic at 0.03 mg L⁻¹ or highly [6]. Most cases are found in the developing countries. Meng et al. [7] described that 22% of the surveyed wells had an arsenic concentration of 100-250 g L⁻¹. Guo et al. [8] also reported that ground water containing 192.3 g L⁻¹ of as caused severe clinical symptoms in China. Therefore, cost effective techniques for the removal of arsenic come from drinking water needed to be determined and developed.

The removal of arsenic compounds can be conducted by coagulation, adsorption, ion exchange, and membrane separation.

Aluminum sulfate and ferric sulfate are commonly used as a coagulant [7, 9-11], and this method can be applied to the treatment of household drinking water [8, 12], although a relatively large amount of sludge can be produced. Membrane separation, such as reverse osmosis, is one of promising technologies for the treatment of drinking water [13, 14]. However, membrane separation process requires very expensive equipment, and the treatment of the retentate water produced in this process is necessary because arsenic is enriched in the retentate. The sorption processes have been applied to the removal of arsenic because of the following advantages: effective removal property, less sludge production, simple system arrangement, and easy operation.

Aluminum oxide and ferric oxides have been widely used in the removal of arsenic as an adsorbent [15-18]. Lanthanide compounds, such as cerium, yttrium, and lanthanum, have been developed as an effective adsorbent for arsenic [19-21], but they are very expensive. The following adsorbents and ion exchangers have



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also been used: Activated carbon [22], titanium oxide [23], zirconia pillared montmorillonite [24], sand coated with iron oxide [25], ferrihydrite [17], hematite/feldspar [26], biopolymers [27], metal-loaded clay [28], combined ion exchanger [29], and natural loam soil [30].

Manganese dioxide was also suggested for the adsorption of arsenic. It was observed that Mn^{2+} -rich hydrous manganese oxide accumulates arsenic in lake sediments [31] and that ferruginous manganese ore adsorbed arsenic [32]. In addition, Manganese dioxide was reported to be useful for the oxidation of As(III) to As(V) [33, 34]. Manganese dioxide has been commonly used for manganese removal in water treatment processes, where the water is chlorinated before it is fed into the manganese dioxide column. The above information suggests that conventional manganese removal process can be used for the removal of arsenic.

In this paper, manganese dioxide (MnO_2) as an adsorbent is focused on the removal of As (V). Two types of powdered MnO_2 and one granular MnO_2 were used. The effects of pH and the adsorption isotherms were examined. The removal capacity of the granular MnO_2 was also examined by column adsorption experiments.

2. Materials and Methods

2.1. Materials

Two types of powdered manganese dioxides (MnO_2) were employed for the batch type adsorption experiments: Electrolyzed MnO_2 (α -structure, hexagonal) and calcined MnO_2 (β -structure, tetragonal) were prepared from the electrolyzed MnO_2 calcinating at $350^\circ C$ for 2 h. The average particulate size of the powder MnO_2 was 4.88 μm , where it was 7.77 μm for 90% and 2.52 μm for 10%. The specific surface area was measured by a N_2 gas adsorption isotherm at 77 K on the basis of the BET adsorption theory. The specific surface areas of the electrolyzed and calcined MnO_2 were 83 and 8 $m^2 g^{-1}$, respectively. Granulated MnO_2 was also used for both the batch type and column adsorption experiments. Granular MnO_2 (average particle size: 0.4 mm) was prepared by coating with calcined MnO_2 and electrolyzed MnO_2 (3:7) on a ceramic particle. The total content of MnO_2 was 23.2%. The particulate size of the granular MnO_2 used in this study was a little smaller than that which is commonly used for the treatment of water (0.45-0.7 mm) [35].

A stock solution of 10 $mg-As L^{-1}$ of sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) was prepared and diluted to an appropriate concentration for the experiments. The pH adjustment of the solution was carried out with dil-HCl and dil-NaOH.

2.2. Batch Type Adsorption Procedure

The adsorption isotherms of the powdered MnO_2 were obtained by batch type adsorption experiments under the following conditions: An appropriate amount of powdered adsorbent (0.02 to 0.55 g) came into contact with 100 mL of an arsenic solution containing 5.0 $mg-As L^{-1}$. The mixture was shaken longer than 2 d at $25^\circ C$. The adsorbent in the mixed solution was removed by filtration with a H-PTFE membrane filter (0.1 μm) and the arsenate concentration of the filtrate was analyzed by the membrane ex-

traction-absorptometric method for a visual determination with the detection tube method using molybdenum blue, which was developed in our laboratory [36] and it can detect 10 $g L^{-1}$ of As(V) [27]. In the experiments, the pH level was not adjusted.

A similar procedure was employed for the granular adsorbent. 1 g of the adsorbent came into contact with a 100 mL solution (1.0 or 10 $mg-As L^{-1}$) for more than 1 week. Since a state of equilibrium was achieved within 5 d, the experiments were conducted for the same length of time. The effects of co-existing anion on the removal of arsenate were examined by the addition of Na_2HPO_4 without pH adjustment, where 1.0 g of MnO_2 , 100 mL of 10.0 $mg-PO_4-PL^{-1}$ and 100mL of 10.0 $mg-AsL^{-1}$ were employed. The effects of pH on the arsenate removal were also examined with the granular adsorbent.

2.3. Column Adsorption Procedure

Granular MnO_2 was packed into a column (10 mm i.d.; bed height: 100 mm; bed volume: 7.85 cm^3). The arsenate solution of 0.1 $mg-As L^{-1}$ was fed into the column under up-flow conditions, with a space velocity (SV) of 10 or 20 h^{-1} . In the case of the common manganese removal process for water treatment, raw water is fed into SV = 30-15 h^{-1} for a column of 300-600 mm in height.

3. Results and Discussion

3.1. pH Effects

The effects of pH on the removal rate of arsenate with MnO_2 were examined first with granular MnO_2 as an adsorbent. The removal rate was significantly influenced by pH, as shown in Fig. 1. The removal increased with a decrease in the pH and stable removal rates (more than 80%) were obtained with a pH range of less than 5.7.

The surface of hydrous MnO_2 binds H^+ and OH^- ions together and acts as an amphoteric hydroxide [37]. The pH of the point of zero charge (pHpzc) is ca. 2.8. The sorption of a cation such as Mn^{2+} on MnO_2 occurs by the formation of surface complex or by an ion exchange. Since the exchange reaction releases H^+ ion from the MnO_2 surface, the sorption of a cation increases with

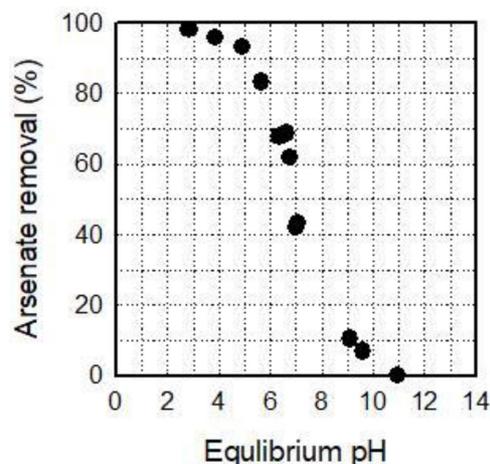


Fig. 1. Effects of pH on arsenate removal by granular MnO_2 .

an increase in the pH. On the other hand, since arsenate species are H_2AsO_4^- and HAsO_4^{2-} under experimental conditions, the sorption of the anions may be affected in an opposite way, with respect to the pH. Therefore, the effect of pH on arsenate removal as shown in Fig. 1 may be interpreted by the properties of the MnO_2 surface. Similar adsorption properties were observed for aluminum oxide [15] and ferric hydroxide [18].

Since the pH range of the arsenate solutions prepared in this work was between 5.49 and 6.35, the pH was not adjusted in the following experiments. When MnO_2 is applied to the actual treatment, however, the pH may be adjusted.

3.2. Adsorption Isotherm

A state of equilibrium was attained for about 24 h as shown in Fig. 2. Saturated adsorption amounts were observed with more than 1 mg-As L^{-1} of the equilibrium concentration, as shown in Fig. 3. Their values were not significantly influenced by the type of MnO_2 : 2.26 mg-As g^{-1} for the calcined MnO_2 and 2.22 mg-As g^{-1} for the electrolyzed MnO_2 .

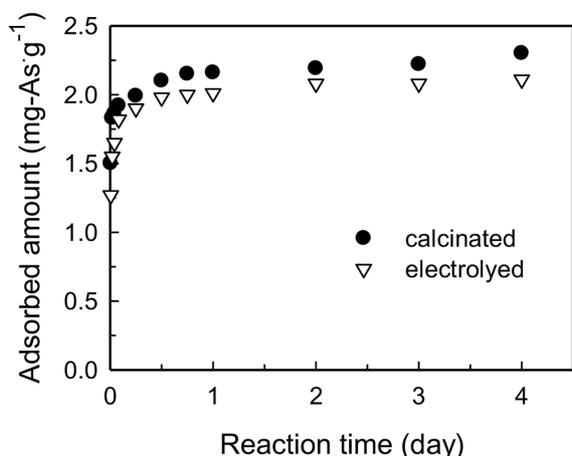


Fig. 2. Profiles of adsorbed amounts with contact time. Conditions: 0.02-0.55 g of MnO_2 adsorbent, 100mL of 5.0 mg-As L^{-1} arsenic solution.

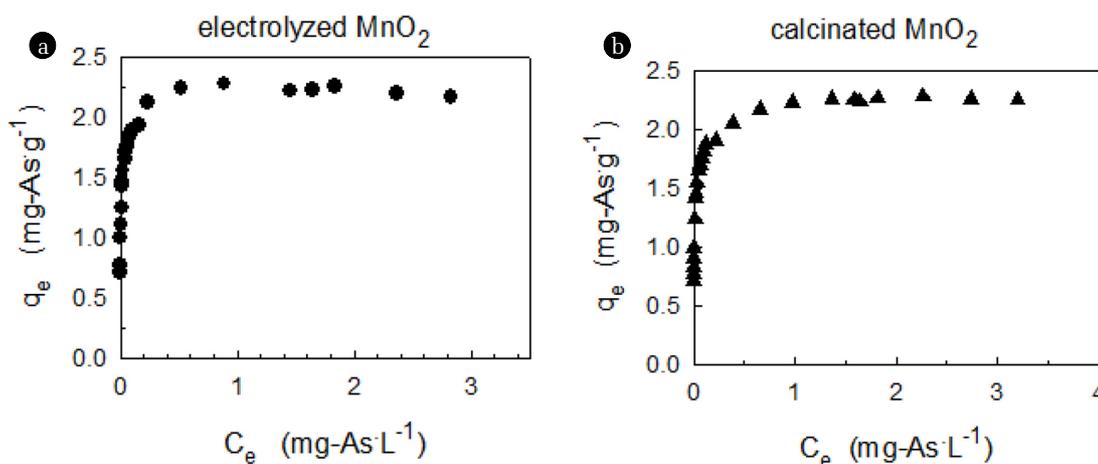


Fig. 3. Relationship between adsorption amount (q_e) and concentration (C_e). Conditions: temperature at 25°C, 48 h of reaction time.

Since saturated adsorption amounts were observed for the two types of adsorbents, a Langmuir type of isotherm was expected to be in the range of less than 1 mg-As L^{-1} of the equilibrium concentration. In the case of the electrolyzed MnO_2 , however, the reciprocal of the adsorption amount ($1/q_e$) was not correlated linearly with the reciprocal of the equilibrium concentration ($1/C_e$) as shown in Fig. 4(a). Freundlich plot did not also show linear correlation (Fig. 4(c)). However, it was correlated linearly with $1/\sqrt{C_e}$ (Fig. 4(b)), and the adsorption isotherm can be expressed by the following modified Langmuir equation:

$$q_e = \frac{24.8\sqrt{C_e}}{1+9.53\sqrt{C_e}} \quad (r = 0.997) \quad (1)$$

A similar relationship was observed for phosphate adsorption on a hydrotalcite compound [38]. This type of equation was well known in the case of chemisorption of hydrogen on metal surface [39, 40], where a hydrogen molecule occupies two adsorption sites. On the other hand, in the case of the calcined MnO_2 , both Langmuir and Freundlich equations gave similar correlation coefficients, which were smaller than that for the electrolyzed MnO_2 . The following two types of adsorption isotherms were used in the experimental results.

$$q_e = \frac{40.5\sqrt{C_e}}{1+1.93\sqrt{C_e}} \quad (r = 0.963) \quad (2)$$

$$q_e = 2.51C_e^{0.163} \quad (r = 0.970) \quad (3)$$

The results of X-ray diffraction (XRD), shown in Fig. 5, indicated the following: Electrolyzed MnO_2 was composed of a hexagonal structure (γ -type) and the calcined MnO_2 contained at least two types of tetragonal structures (pyrolusite and the other). Therefore, the calcined MnO_2 may have a variety of adsorption energy levels of the active sites, and this may cause that the adsorption isotherm was not expressed by a Langmuir equation. The XRD patterns of the manganese dioxides after arsenate adsorption were not varied because of very low adsorption amounts.

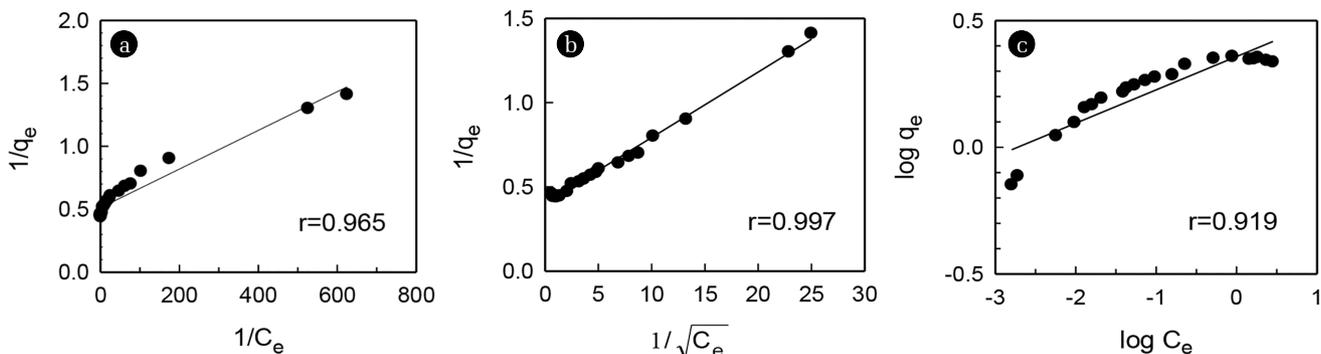


Fig. 4. Adsorption isotherm of the electrolyzed MnO₂ ($C_e < 1$ mg-As·L⁻¹). Conditions: temperature at 25°C, 48 h of reaction time.

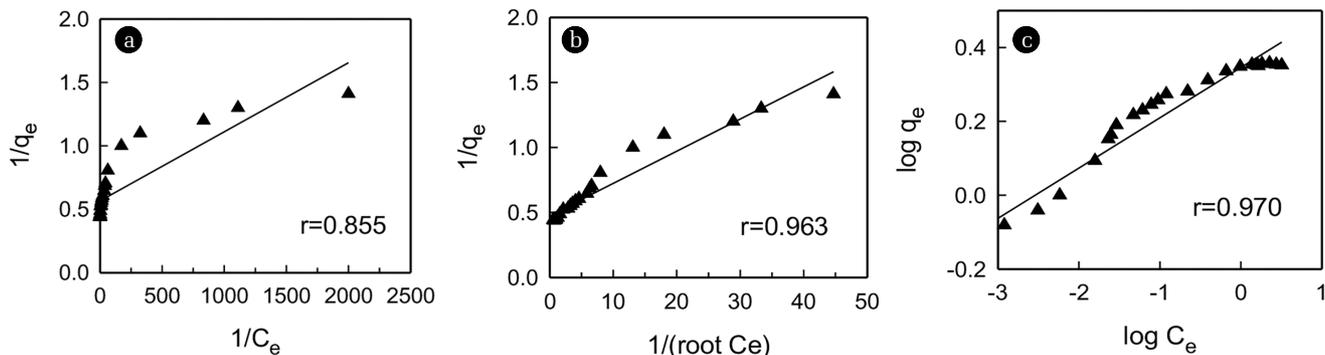


Fig. 5. Adsorption isotherm of the calcined MnO₂ ($C_e < 1$ mg-As·L⁻¹). Conditions: temperature at 25°C, 48 h of reaction time.

Although different adsorption isotherms were obtained for the two types of adsorbents, almost similar the maximum adsorption capacity amounts (2.26 or 2.22 mg-As g⁻¹) and the equilibrium adsorption amounts (1.20 or 1.27 mg-As g⁻¹) at 0.01 mg-As L⁻¹ of the equilibrium concentration were almost the same for both types of MnO₂.

The maximum adsorption capacity amounts of the electrolyzed and calcined MnO₂ were similar, although the specific surface areas were significantly different. Considering the specific surface areas, the calcined MnO₂ had a higher adsorption capacity per unit area. Even in the case of the calcined MnO₂, the monolayer adsorption was suggested as follows: The occupied surface area by arsenate at the maximum adsorption amount was evaluated to be 3.8 m² g⁻¹, where the radius of the AsO₄³⁻ ion is assumed to be 0.25 nm. Since the crystalline structure may affect the adsorption capacity, it is important to clarify the adsorption mechanism in order to develop an effective MnO₂ adsorbent.

In the case of the granular adsorbent, the saturated adsorption amount was 0.548 mg-As g⁻¹ at more than 2.2 mg-As L⁻¹ of the equilibrium concentration, as shown in Fig. 6. The ratio of the value against that of the powdered MnO₂ (2.22 or 2.26 mg-As g⁻¹) corresponded to the MnO₂ content (23.2%). The adsorption isotherm, in the range of less than 0.1 mg-As L⁻¹, was also approximated by the following modified Langmuir equation, which was similar to that of the electrolyzed MnO₂:

$$q_e = \frac{3.69\sqrt{C_e}}{1 + 6.80\sqrt{C_e}} \quad (r = 0.967) \quad (4)$$

The adsorption amount at 0.01 mg-As L⁻¹ of arsenic concentration, the drinking water standards for arsenic, was evaluated as 0.543 mg-As g⁻¹. This value also corresponded to the content of MnO₂ in the granular adsorbent.

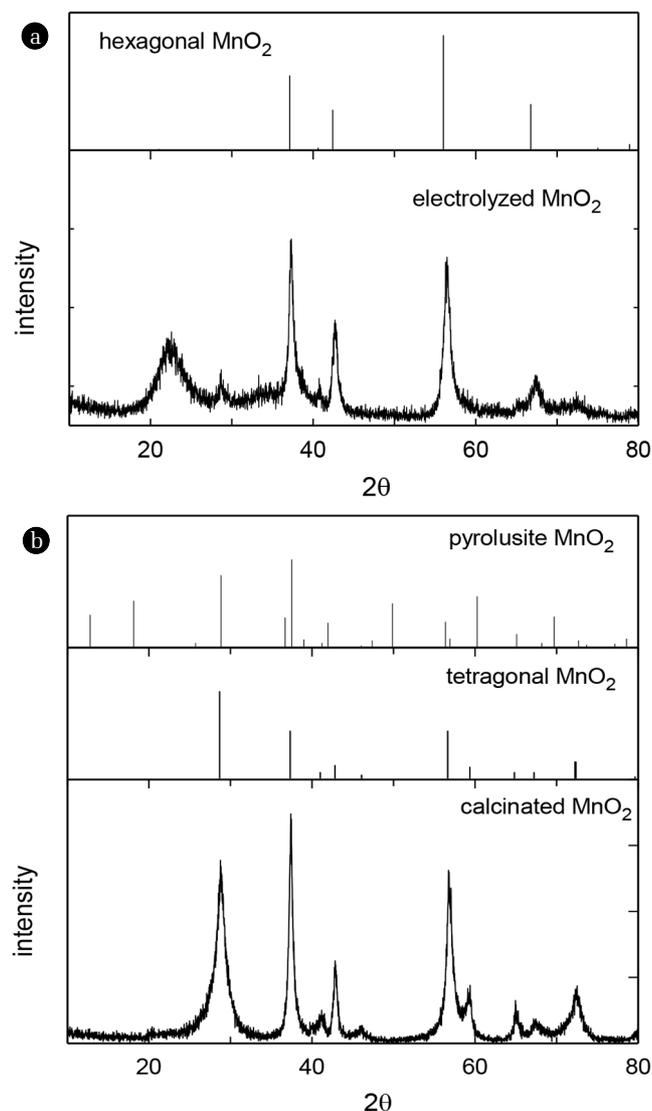
Lin and Wu [15] examined the arsenate adsorption properties of the activated alumina (specific surface area: 115-118 m² g⁻¹) and the adsorption isotherm was analyzed by both the Langmuir and Freundlich equations. The Langmuir equation provided a better correlation than Freundlich equation and the maximum adsorption capacity was 15.90 mg-As g⁻¹. However, the calculated adsorption amount at 0.01 mg-As L⁻¹ of the equilibrium concentration was 1.41 mg-As L⁻¹, which is similar to those of the powdered manganese dioxides. Guo et al. [8] reported that the adsorption isotherm of granular ferric hydroxide (specific surface area: 226-252 m² g⁻¹) for arsenate was expressed by Freundlich type, where the calculated adsorption amount at 0.01 mg-As L⁻¹ was 7.98 mg-As g⁻¹. The adsorption capacity amounts of these adsorbents are also listed in Table S1. The granular MnO₂ showed a significantly lower adsorption capacity than the other adsorbents listed in Table 1. Considering that the MnO₂ content of the granular MnO₂ was low (23.3%), it is necessary to increase the MnO₂ content for improvement of the adsorption capacity.

For the adsorption processes, co-existing anions such as phosphate may influence adsorption capacity. It was reported that 0.1-2 mg L⁻¹ of phosphate and fluoride could reduce significantly the arsenic adsorption capacity [41]. Although the effects of fluoride ions have not been clarified in this work clearly, the adsorption capacity of the granular MnO₂ for phosphate was also examined, and 0.188 mg-P g⁻¹ of the maximum adsorption amount was

Table 1. Summary for the Adsorption Amount by the Powder and the Granular Adsorbent

adsorbent	Max. capacity (mg-As g ⁻¹)	Adsorbed amount (mg-As.g ⁻¹) at 0.01 mg-As L ⁻¹	remark	Ref.
electrolyzed	2.22	1.27		
MnO ₂ calcinated	2.26	1.20		
granular	0.548	0.290		
Activated alumina	15.90	1.41	Langmuir type	[14]
Ferric hydroxide	-	7.98	Freundlich type	[7]

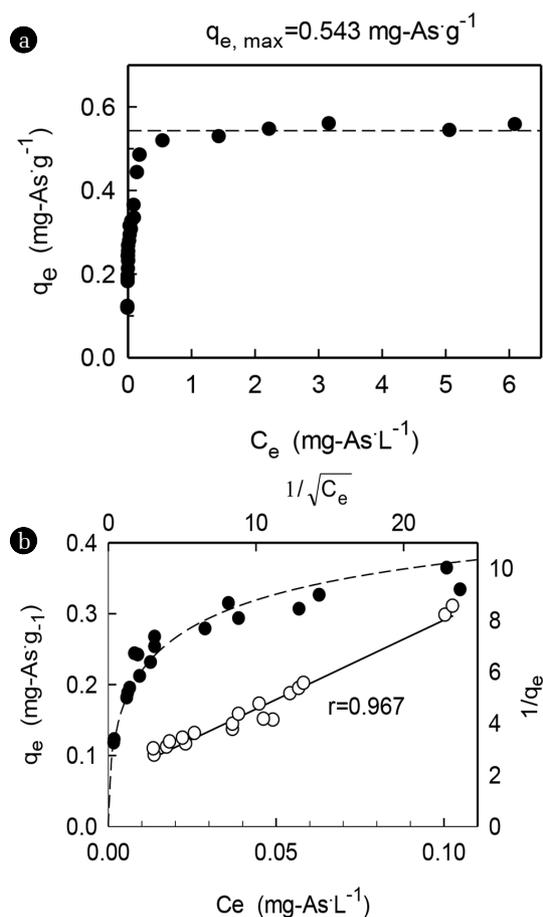
*calculated by the adsorption isotherm

**Fig. 6.** X-ray diffractograms of electrolyzed MnO₂ and calcined MnO₂.

obtained. Since the mole adsorption capacity for arsenate and phosphate were almost the same, the co-existing phosphate may suppress the arsenate removal performance of MnO₂ as shown in the effect of phosphate solutes on arsenate removal with hydrocalcite compound [42]. The selectivity between arsenate and phosphate should be examined by further research.

3.3. Column Adsorption

A solution containing 0.10 mg-As L⁻¹ was fed into a column packed with granular adsorbent and the breakthrough curves are obtained as shown in Fig. 7. When the breakthrough point was 0.01 mg-As L⁻¹, the ratios of the treated water volumes to the bed volume were evaluated to be 3880 for SV = 10 h⁻¹ and 3,580 for SV = 20 h⁻¹, respectively. The effect of SV was not significant under the flow conditions. Considering the operating conditions that the experiments were carried out with a short column (100 mm length), it was concluded that the arsenate was removed effectively even by MnO₂.

**Fig. 7.** Adsorption isotherm of the granulated MnO₂. Conditions: temperature at 25°C, 10 d of reaction time.

MnO₂ is commonly used to remove manganese in the treatment of drinking water. In this process, chlorination is applied before feeding into the MnO₂ column. In considering the process flow, arsenic is also removed simultaneously by this process. Since the manganese removal processes have been applied widely, the results obtained in this work may be of use in the design of an arsenic removal facility, although the effects of co-existing ions such as phosphate must be evaluated by further research.

4. Conclusions

The arsenate removal properties of manganese dioxides as adsorbents were investigated and the results obtained in this work are summarized as follows:

1) The removal increased with a decrease in the pH and stable removal rates (more than 80%) were obtained with a pH range of less than 5.7.

2) Saturated adsorption amounts were not significantly influenced by the type of MnO₂: 2.26 mg-As g⁻¹ for the calcined MnO₂ and 2.22 mg-As g⁻¹ for the electrolyzed MnO₂ at more than 1 mg-As L⁻¹ of the equilibrium concentration.

3) The adsorption isotherm for the electrolyzed MnO₂ was approximated by a modified Langmuir equation, but the calcined MnO₂ showed lower correlation factors for both Langmuir and Freundlich equations.

4) Considering that the MnO₂ content of the granular MnO₂ was low (23.3%), it is necessary to increase the MnO₂ content for improvement of the adsorption capacity.

5) When the solution containing 0.1 mg-As L⁻¹ was fed into the column packed with the granular MnO₂, the breakthrough point was 0.01 mg-As L⁻¹ and the ratios of the treated water volumes to the bed volume were evaluated to be 3,880 for SV = 10 h⁻¹ and 3,580 for SV = 20 h⁻¹, respectively.

Author Contributions

Y.J.J. (Professor) wrote the manuscript based on the experiment results. Y.K. (Professor) conducted the experiments and analyzed the experimental data.

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