Equilibrium Concentration and Rate of Arsenic Adsorption using Magnesium Compounds

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Abstract

To investigate the efficiency and kinetics of arsenic adsorption on adsorbents from contaminated water, a series of batch adsorption experiments were carried out with artificial arsenic contaminated water and several types of magnesium compounds. The magnesium compounds were used as arsenic adsorbents including MgO, Mg(OH)$_2$ and light and heavy types of MgCO$_3$. The results of analyses and evaluation of the experiments indicated that MgO has the lowest apparent arsenic equilibrium concentration and the highest arsenic adsorption efficiency. On the other hand, Mg(OH)$_2$ may have the highest arsenic adsorption rate.

Keywords: Arsenic removal, Magnesium compounds, Adsorption equilibrium concentration, Adsorption rate, Groundwater purification

1. INTRODUCTION

In some areas of developing countries, groundwater contaminated with arsenic has often been used as drinking water and may induce serious health problems. It is desired that effective and inexpensive 'arsenic removal agents' should be developed and provided. To obtain fundamental information for developing such kinds of arsenic removal agents, systematic experiments focused on chemical components that are presumed to be effective for arsenic removal should be performed and evaluated.

In general, iron, aluminum, zirconium and magnesium hydroxide are reported having selectivity in the adsorption of arsenic. In this study, we focused on examination of efficiency of 'magnesium components'. Batch adsorption tests were carried out with artificial arsenic contaminated water and several types of magnesium compound, including oxide, hydroxide and two types of carbonates. Arsenic equilibrium concentration and adsorption rate or removal rate were evaluated. In addition, leaching behavior of magnesium component was discussed.

2. EXPERIMENTAL

2.1 Adsorbents

4 types of magnesium compounds were tested as arsenic adsorbents or removal agents: MgO, Mg(OH)$_2$, MgCO$_3$ (light) and MgCO$_3$ (heavy). All the reagents were the products of Wako Pure Chemical Industries, Ltd. The difference between MgCO$_3$ (light) and MgCO$_3$ (heavy) is bulk density, and hereafter denoted as MgCO$_3$-L and MgCO$_3$-H, respectively.

The values of magnesium content a, mean particle diameter D_{p50} and specific surface area S_{BET} of each magnesium compound are shown in Table 1 (Sugita, 2014 and 2015).

Table 1 Characteristics of magnesium compounds

	a [%]	D_{p50} [μm]	S_{BET} [m^2/g]
MgO	59.08	1.54	4.3
Mg(OH)$_2$	40.55	4.13	22
MgCO$_3$-L	25.50	4.14	26
MgCO$_3$-H	24.83	15.00	24

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2.2 Artificial arsenic contaminated water

Powder reagent of disodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) was used as a source of arsenic. The reagent was dissolved in deionized water to produce a stock solution of 2000 mg/L. A part of the stock solution was diluted with deionized water to be a designed concentration. pH of the solution was adjusted to be neutral by adding HCl and/or NaOH solution. The solution was used as artificial arsenic contaminated water. The value of pH just after adjustment was defined as initial pH, pH_0.

2.3 Batch adsorption tests and analytical methods

A given amount of each type of magnesium compound was put into a non-glass tube and then added with 50 mL of the artificial arsenic contaminated water. The tube was shaken with a thermostatic shaker (150-180 rpm) for a given shaking time (i.e. reaction time) at room temperature. The supernatant solution was filtered with a filter having a pore size of 0.45 μm and recovered in a non-glass bottle. The time set for shaking was 1, 2, 3, 4, 5, 6 and 7 days, relatively long-term. The combination of initial arsenic concentration C_{AS0} [mg/L] and addition concentration of adsorbent W_{Ad}/V [g/L] were (a) $C_{AS0} = 1$ mg/L and $W_{Ad}/V = 0.2$ g/L, (b) $C_{AS0} = 10$ mg/L and $W_{Ad}/V = 1$ g/L. Here, W_{Ad} and V are addition amount of adsorbent [g] and liquid volume [L], respectively.

Arsenic and magnesium in solution were analyzed with ICP-MS (ICPM-8500, Shimadzu) and ICP-AES (SPS3500DD, SII), respectively.

3. RESULTS

3.1 Changes in residual arsenic concentration

The residual concentration of arsenic in the filtrate, C_{AS} [mg/L] is plotted against reaction time t [d] and adsorbent types in Figure 1 corresponding to the above test conditions (a) and (b), respectively. C_{AS} seems to have stabilized substantially within 3 days for any of the magnesium compounds. $Mg(OH)_2$ appears to be the most quickly decreased and stabilized C_{AS}. However, MgO is found to be the most effectively decreased C_{AS}, as shown in Fig.1-(b).

3.2 Changes in leaching magnesium concentration

The leaching concentration of magnesium in the filtrate, C_{Mg} [mg/L] is plotted against t in Figure 2. During the adsorption with MgO, C_{Mg} reaches the highest value in a short reaction time (1-2 days), and then decreases with time. C_{Mg} for $Mg(OH)_2$ stabilizes substantially in 1 day. C_{Mg} for each of $MgCO_3$-L and -H increases drastically in 1st day and subsequently increases very gradually. Also, C_{Mg} for $MgCO_3$-H were clearly higher than that for $MgCO_3$-L.
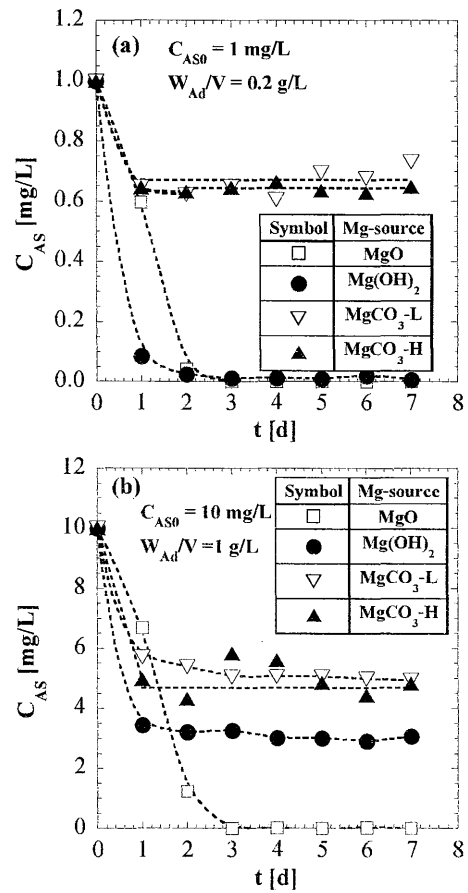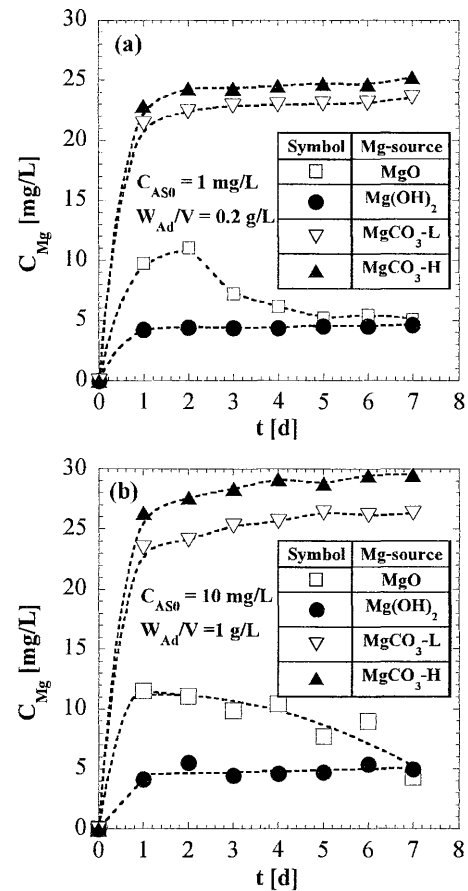

Fig.1 Change in C_{AS} with time

Fig.2 Change in C_{Mg} with time

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3.3 Changes in pH

pH of the solution increased immediately and rapidly after addition of any magnesium compounds. The final pH of the filtrate, pH_f is plotted against t in Figure 3. pH_f for MgO increases in the early times and subsequently decreases gradually. On the other hand, changes in pH_f for $Mg(OH)_2$, $MgCO_3$-L and -H are not observable. pH_f for $Mg(OH)_2$ is the lowest and the difference between $MgCO_3$-L and -H is not clear.
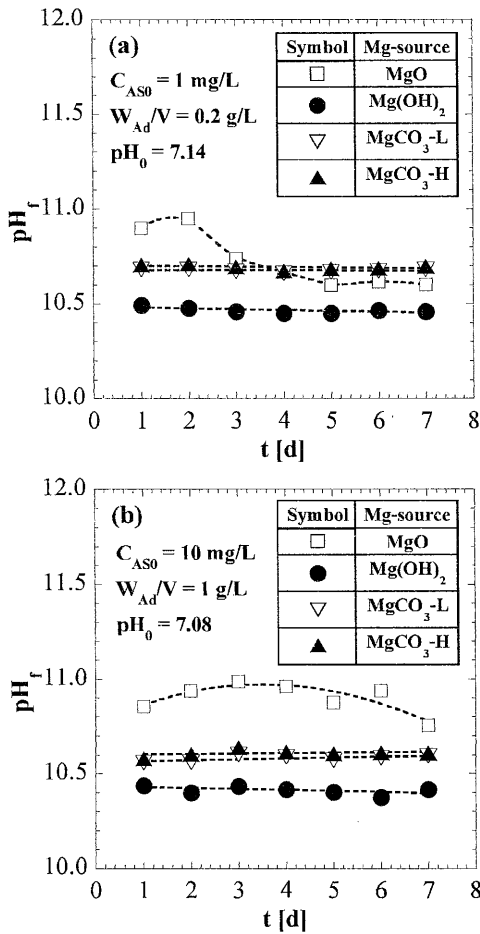

Fig.3 Change in pH_f with time

4. DISCUSSION

4.1 Residual concentration of arsenic against final pH and leaching concentration of magnesium

C_{AS} is plotted against pH_f and C_{Mg} in Fig.4 and 5, respectively. It is shown that the data for each type of magnesium compound except for MgO are close to each other. The data for $Mg(OH)_2$ distribute in the lower left of the figures. The data for $MgCO_3$-L and –H distribute in the upper right of the figures. However, there is no special correlation between C_{AS} and pH_f or C_{Mg}. For MgO, pH_f or C_{Mg} changes even though C_{AS} remains zero. Therefore, the declines in C_{Mg} and pH_f for MgO as seen in Fig.2 and 3 should be considered to be independent of the adsorption reaction of arsenic on MgO particles.
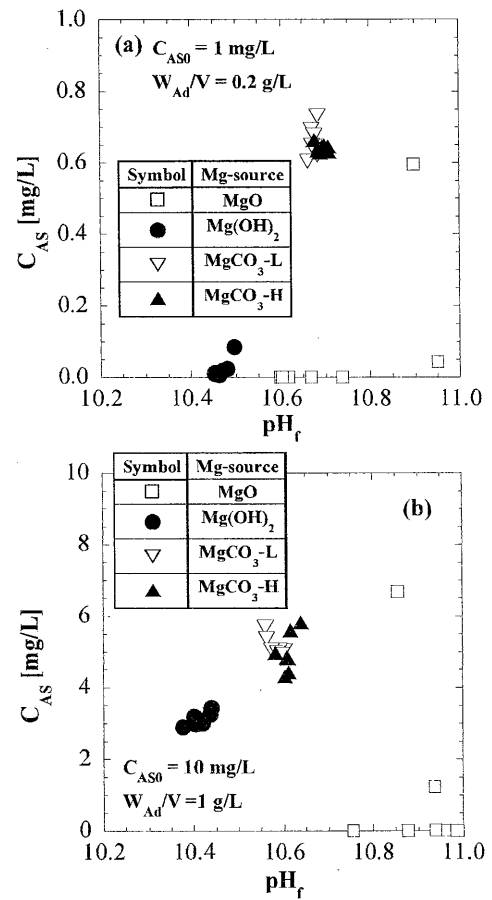

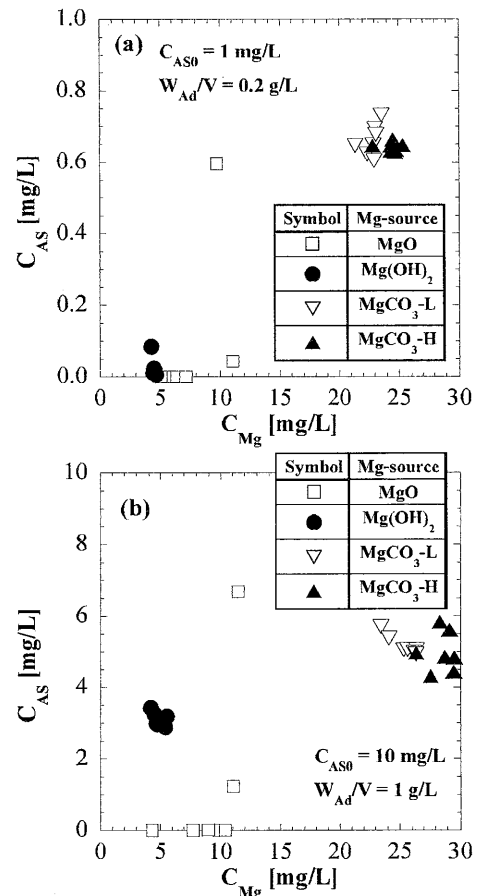Fig.4 Correlation diagrams of C_{AS} and pH_f

Fig.5 Correlation diagrams of C_{AS} and C_{Mg}

4.2 Leaching concentration of magnesium against final pH

C_{Mg} is plotted against pH_f in Figure 6. A clear correlation between C_{Mg} and pH_f can be observed for MgO, but not for $Mg(OH)_2$ and two types of $MgCO_3$.
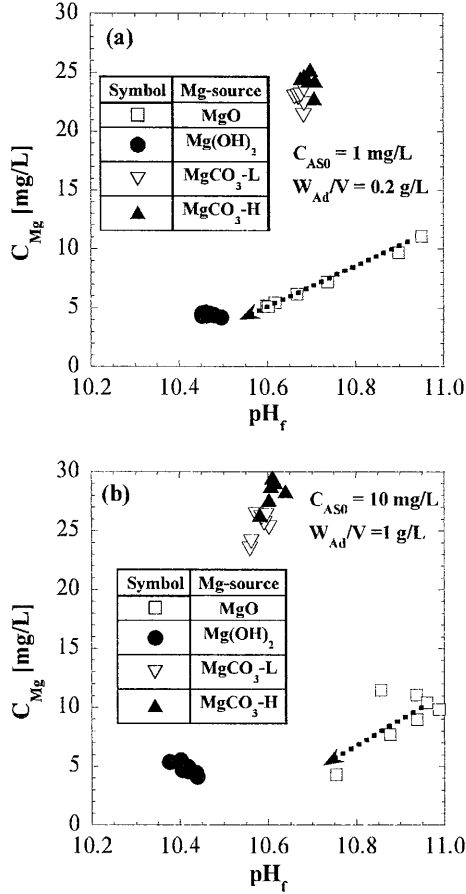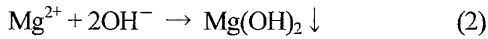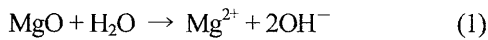

Fig.6 Correlation diagrams of C_{Mg} and pH_f

4.3 Reactions of dissolution and precipitation for MgO

With regard to MgO, the main mechanism of declines in C_{Mg} and pH_f is considered that a part of magnesium ion dissolved from MgO particles precipitated as $Mg(OH)_2$.

$$MgO + H_2O \rightarrow Mg^{2+} + 2OH^- \tag{1}$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow \tag{2}$$

When one magnesium ion is decreased, two hydroxide ions will be decreased. Here, C_{Mg} [mg/L] is converted to [Mg^{2+}] [mmol/L] using the atomic weight of magnesium M_{Mg} (=24.305).

$$[Mg^{2+}] = C_{Mg} / M_{Mg} \tag{3}$$

The hydroxide concentration, [OH^-] can be calculated using pH_f and the dissociation constant of water, K_W (10^{14} at 25°C).

To facilitate calculation, the unit of [OH^-] is set to [mmol/L].

$$[OH^-] = 10^{pH-14} \times 10^3 \tag{4}$$

For MgO, [OH-] is plotted against [Mg^{2+}] in Fig.7, except for the data at early reaction times.
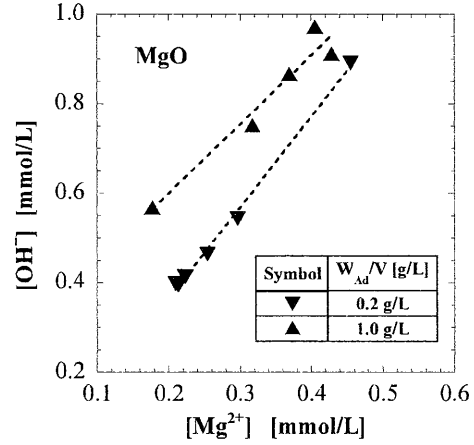

Fig.7 Correlation diagram of [OH^-] and [Mg^{2+}]

According to Eq.2, the slopes of the approximately-straight lines should be 2, theoretically or ideally. Actually, the slopes of W_{Ad}/V = 0.2 g/L and 1 g/L were approximately 2.0 and 1.5, respectively. The value of W_{Ad}/V = 0.2 g/L matches with the theoretical value. On the other hand, the value of W_{Ad}/V = 1 g/L was smaller than the theoretical value. This is considered due to dissolution of carbon dioxide from the atmosphere. Carbon dioxide dissolves easily in alkaline solution and hydroxide ions are consumed simultaneously with the following reactions.

$$2OH^- + CO_2 \rightarrow HCO_3^- + OH^- \tag{5}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{6}$$
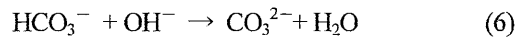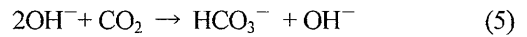
pKa_1 = 6.11 and pKa_2 = 9.87 for H_2CO_3 (CSJ, 2004)

In addition, it is also possible that the hydroxide ions can be consumed in forming of magnesium-arsenate salts.

4.4 Apparent equilibrium arsenic concentration

C_{AS} seems to become almost constant within 3 days, as shown in Fig. 1. The average values of C_{AS} from 3rd to 7th days are therefore defined as "apparent equilibrium concentration of arsenic, C_{ASe}" and were calculated with exclusion of a few irregular data, specifically, the data at 7th day for MgCO_3-L at C_{AS0} = 1 mg/L and those at 3rd and 4th days for MgCO_3-H at C_{AS0} = 10 mg/L. C_{ASe} are shown in Table 2 with the standard deviation of C_{ASe}, σ [mg/L].

Table 2 Apparent equilibrium concentration of arsenic

C_{AS0}[mg/L]	Adsorbent	C_{ASe}[mg/L]	σ [mg/L]
1	MgO	0.000	0.000
1	Mg(OH)$_2$	0.013	0.004
1	MgCO$_3$-L	0.657	0.034
1	MgCO$_3$-H	0.644	0.012
10	MgO	0.007	0.009
10	Mg(OH)$_2$	3.055	0.118
10	MgCO$_3$-L	5.020	0.052
10	MgCO$_3$-H	4.704	0.192

For MgO at C_{AS0} = 1 mg/L, arsenic in the filtrate was below detection limit. The magnitude relation of C_{ASe} is as follows.

$$MgO < Mg(OH)_2 < MgCO_3\text{-}H < MgCO_3\text{-}L$$

4.5 Apparent equilibrium magnesium concentration

As shown in Fig. 2, C_{Mg} for Mg(OH)$_2$ seems to become almost constant since fist day. C_{Mg} for MgO seems to come close to that for Mg(OH)$_2$ with time. The reason is that MgO is converted into Mg(OH)$_2$ by hydration (Eq.1 and 2). Although the reaction rate of hydration seems to be not so quick, C_{Mg} for Mg(OH)$_2$ appears to become similar to that of MgO at 7th day. On the other hand, C_{Mg} for each of MgCO$_3$-L and -H increases drastically at 1st day and subsequently increases very gradually. Although the state might not finally reach the true equilibrium, the values of C_{Mg} at 7th day are defined as "apparent equilibrium concentration of magnesium, C_{Mge}" and shown in Table 3.

Table 3 Apparent equilibrium concentration of magnesium

W_{Ad}/V [g/L]	Adsorbent	C_{Mge} [mg/L]
0.2	MgO	5.09
0.2	Mg(OH)$_2$	4.64
0.2	MgCO$_3$-L	23.56
0.2	MgCO$_3$-H	25.28
1	MgO	4.30
1	Mg(OH)$_2$	4.99
1	MgCO$_3$-L	26.33
1	MgCO$_3$-H	29.39

The magnitude relation of C_{Mge} is as follows.

$$MgO \doteqdot Mg(OH)_2 << MgCO_3\text{-}L < MgCO_3\text{-}H$$

C_{Mge} for MgO is expected to become finally equal to that for Mg(OH)$_2$, since MgO is converted into Mg(OH)$_2$ with time.

4.6 Dissolution and residual ratios of adsorbent

Initial amount of magnesium presented as solid, W_{Mg} [g] is expressed by the following formula.

$$W_{Mg} = W_{Ad} \times (\alpha/100) \qquad (7)$$

The dissolution ratio of magnesium for adsorbent, β [%] can be calculated with the following equation.

$$\beta = C_{Mg} / (1000W_{Mg}/V) \times 100 \qquad (8)$$

The amount of magnesium dissolved into the solution should be equal to the amount of magnesium lost from the adsorbent. Therefore, the residual ratio of magnesium present as solid, γ is represented by the following formula.

$$\gamma = 100 - \beta \qquad (9)$$

The values of β and γ calculated using the data at 7th day are shown in Table 4.

Table 4 Dissolution and residual ratios of magnesium

W_{Ad}/V [g/L]	Adsorbent	β [%]	γ [%]
0.2	MgO	4.31	95.69
0.2	Mg(OH)$_2$	5.72	94.28
0.2	MgCO$_3$-L	46.19	53.81
0.2	MgCO$_3$-H	50.90	49.10
1	MgO	0.73	99.27
1	Mg(OH)$_2$	1.23	98.77
1	MgCO$_3$-L	10.32	89.68
1	MgCO$_3$-H	11.89	88.11

The magnitude relation of γ is as below.

$$MgCO_3\text{-}H < MgCO_3\text{-}L < Mg(OH)_2 < MgO$$

It should be noted that γ for MgO contains Mg in Mg(OH)$_2$ reconstituted from MgO and the true value of γ for the original MgO must be lower than γ for MgO in Table 4.

4.7 Arsenic distribution ratio between solid and liquid phases

Assuming that the residual ratio of adsorbent is equals to that of magnesium, arsenic adsorption amount per unit weight of adsorbent which remains as solid, δ [mg/kg] can be calculated by the following equation (10).

$$\delta = (C_{AS0}C_{AS}) / \{(\gamma/100)(W_{Ad}/V)\} \times 10^3 \qquad (10)$$

Correspondingly, arsenic partition ratio between solid and liquid, ε [L/kg] can be defined by the following formula.

$$\varepsilon = \delta / C_{ASe} \qquad (11)$$

The values of δ and ε are summarized in Table 5.

C_{AS0} [mg/L]	W_{Ad}/V [g/L]	Adsorbent	δ [mg/kg]	$\varepsilon \times 10^{-3}$ [L/kg]
1	0.2	MgO	5224	— *
1	0.2	Mg(OH)$_2$	5268	405
1	0.2	MgCO$_3$-L	2494	3.80
1	0.2	MgCO$_3$-H	3583	5.56
10	1	MgO	10073	1439
10	1	Mg(OH)$_2$	7014	2.30
10	1	MgCO$_3$-L	5647	1.12
10	1	MgCO$_3$-H	5874	1.25

Table 5 The values of δ and ε

* Indeterminate, because the corresponding C_{ASe} is zero.

The magnitude relation of ε is as below.

$$MgCO_3\text{-}L \leqq MgCO_3\text{-}H \ll Mg(OH)_2 \ll MgO$$

The results illustrate that MgO can remove arsenic the most efficiently among the four magnesium compounds.

4.8 Arsenic adsorption rate

Arsenic adsorption rate, R_{AS} [mg/L/d] is defined as the arsenic adsorption amount per a day. The arsenic adsorption rate of the n-th day, $R_{AS(n)}$ is represented by the following equation.

$$R_{AS(n)} = (C_{AS(n)} - C_{AS(n-1)}) \diagup (t_{(n)} - t_{(n-1)}) \tag{12}$$

where, n = 1-7. R_{AS} are plotted against time in Fig. 8. R_{AS} for Mg(OH)$_2$ is the highest among those of 1st day. For the magnesium compounds except for MgO, R_{AS} of the 1st day is the highest among the 7 days. For MgO, R_{AS} of 2nd day is the highest among the 7 days. The average of R_{AS} of 1st up to 3rd day that the arsenic adsorption reaction is almost finished, $R_{AS(1-3)}$ is shown in Table 6. $R_{AS(1-3)}$ for MgO is the highest among those for the magnesium compounds. The difference in $R_{AS(1-3)}$ is considered to be due to the difference in C_{ASe}. Essentially, Mg(OH)$_2$ seems to have the highest arsenic adsorption rate.

5. CONCLUSSIONS

MgO was found to have the lowest apparent equilibrium arsenic concentration and the highest arsenic adsorption efficiency among the magnesium compounds. Mg(OH)$_2$ was considered to have essentially the highest arsenic adsorption rate. If the reaction time for arsenic removal treatment is set to a shorter duration (less than a day), Mg(OH)$_2$ will be the best arsenic adsorbent. The apparent equilibrium magnesium concentration for MgO might become finally equal to that for Mg(OH)$_2$ since MgO would be converted into Mg(OH)$_2$ over time.
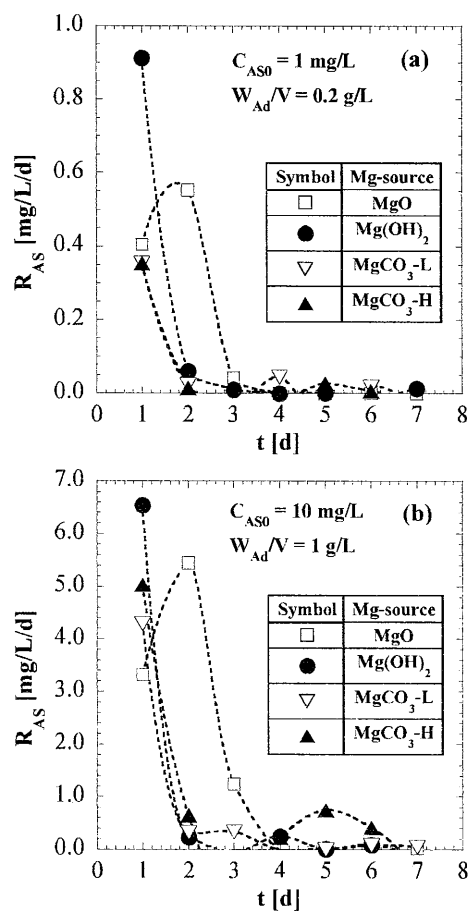

Fig.8 Change in arsenic adsorption rate with time

C_{AS0} [mg/L]	W_{Ad}/V [g/L]	Adsorbent	$R_{AS(1-3)}$ [mg/L/d]
1	0.2	MgO	0.333
1	0.2	Mg(OH)$_2$	0.329
1	0.2	MgCO$_3$-L	0.117
1	0.2	MgCO$_3$-H	0.118
10	1	MgO	3.33
10	1	Mg(OH)$_2$	2.24
10	1	MgCO$_3$-L	1.65
10	1	MgCO$_3$-H	1.39

Table 6 The value of $R_{AS(1-3)}$

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