Arsenic removal from groundwater by a newly developed adsorbent

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Abstract A novel adsorbent, which had been developed for phosphate adsorption, was adopted for arsenic removal from groundwater. Adsorption isotherm, pH dependence of the isotherm and adsorption rate were studied by batch method. Furthermore, by using a granular adsorbent of 1.8 mm diameter which is commercially available, lab-scale experiments of continuous adsorption treatment of actual groundwater containing arsenic at 50 mg m^{-3} were conducted to examine the performance of the adsorbent. A large amount of arsenic, i.e., 10 g As kg^{-1}, was adsorbed at pH 7.0 and 10 mg As m^{-3} in equilibrium concentration. It was only a 5% higher amount compared to conventional activated alumina. However, twice the bed volume, i.e., total volume of effluent divided by empty column volume, was achieved till breakthrough by using this novel adsorbent. This may be because the pH decrease, which enlarges apparent adsorption capacity of the adsorbent, is caused by a self-pH decrease function of the adsorbent. The self-pH decrease function must be delivered by dissociation of Al (III) aquoion. The proton release was clearly observed in batch experiments.

Keywords Activated alumina; adsorption isotherm; arsenic; fixed bed operation; groundwater; intraparticle diffusion coefficient

Introduction

Arsenic, which is well known as a toxic element possessing carcinogenicity, exists stably as sulfide mineral in the earth crust. However, elevated arsenic concentrations are found in some groundwater used for drinking water, possibly due to excessive pumping of groundwater and/or soil contamination by high concentration of phosphate caused by infiltration of domestic wastewater etc, into soil. It is well known that serious arsenic pollution occurs in Bangladesh, west Bengal region in India, Inner Mongolia region in China, Thailand and Taiwan. In Japan, arsenic pollution occurs especially in Kyushu region, in the southern part of Japan. For example, Nakashima (1997) reported that values for arsenic exceeding the drinking water quality standard of Japan, i.e., 0.01 g m^{-3} were observed in the groundwater from 172 of 2,720 wells (1.8%).

Among the various methods used for the removal of arsenic from groundwater such as ion exchange, ultrafiltration reverse osmosis, adsorption-coprecipitation and adsorption, adsorption methods are considered to be very important because of their treatment stability, easy operation, narrow space for building the plant, no chemical reagent needed, no sludge produced. However, owing to poor adsorption capacity, the maximum continuous operation term (regeneration cycle) has been insufficient, so that few actual plants have been constructed in Japan.

Recently, a novel adsorbent prepared by treating activated alumina with aluminium sulfate has been developed for adsorption of phosphorus from wastewaters and become commercially available (Hano *et al*., 1997; Ashitani *et al*., 2002). It was expected that this adsorbent would be able to remove arsenic. This adsorbent satisfies the following general requirements: (1) high capacity and selectivity; (2) granular type; (3) high chemical and physical strength; (4) no hazardous pollutants contained; (5) simple regeneration; (6) low

cost and sustainable supply.

In the present study, the adsorption isotherm, pH dependence of the isotherm and adsorption rate were studied. Furthermore, by using a granular adsorbent of 1.8 mm diameter which is commercially available, lab-scale experiments of continuous adsorption treatment of actual groundwater containing arsenic at 50 mg m^{-3} were conducted to examine the performance of the adsorbent.

MATERIALS AND METHODS

Adsorbent and chemical reagents used

The adsorbent was kindly donated from Sumitomo chemical company, Ltd. Table 1 shows the physical and chemical properties of the adsorbent. This adsorbent was made from an activated alumina, and has a large specific surface area and pore volume. To conduct batch adsorption experiments, the adsorbent was crushed and sieved into the diameter ranged from 0.212 to 0.425 mm.

Disodium hydrogenarsenate, potassium hexahydroxoantimonate and sodium dihydrogenphosphate were used as model compounds of As (V), Sb (V) and P, respectively. These compounds were purchased from Wako pure chemical industries, Ltd. Antimony and phosphorus compounds were used to study the selectivity for the adsorbent.

The groundwater was collected from a well in Kagoshima University and disodium hydrogenarsenate was added to obtain the concentration of 50 mg m^{-3}. Finally, it was disinfected with sodium hypochlorite before feeding to columns. The principal water qualities of the groundwater are shown in Table 2. pH of the groundwater ranged from 6.93 to 7.02.

Batch adsorption experiment

Different amounts of the adsorbent were added to 100 ml of deionized water, and the solution was shaken at 298K. At appropriate time intervals, the pH was adjusted using hydrochloric acid or sodium hydroxide. After the pH was stabilized within the range of the prescribed pH±0.1, the flasks were shaken for a further 168 hours to reach the adsorption equilibrium.

The intraparticle diffusion coefficients based on the concentration in solid, D_i', were evaluated at 298K by Boyd's method (Boyd et al., 1947) according to Eqs. (1) and (2).

$$F = Q_t / Q_\infty \tag{1}$$

$$-\ln (1 - F^2) = 4 \pi^2 D_i' t / d^2 \tag{2}$$

where F ($-$) is the adsorption coverage, Q_t (eq kg^{-1}) the amount adsorbed at time t, Q_∞

Table 1 Physical and chemical properties of adsorbent

Chemical composition (%)					Physical property		
Al$_2$O$_3$	Na$_2$O	SiO$_2$	Fe$_2$O$_3$	Al$_2$(SO$_4$)$_3$	Packing density (kg m^{-3})	Pore volume (m^3 kg^{-1})	BET Specific surface area (m^2 kg^{-1})
68.8	0.1	0.02	0.02	31	1030	1.5×10^{-4}	1.95×10^5

Table 2 Principal water quality of groundwater

Element	Al	As	B	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	P	Pb	Si	Sr	Zn
Concentration (g m^{-3})	n.d.	n.d.	0.8	22.9	n.d.	n.d.	n.d.	n.d.	8.1	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	38.8	0.1	0.06

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(eq kg^{-1}) the equilibrium amount adsorbed, d (m) the diameter of the adsorbent and t (s) the adsorption time. The values of D_i' were obtained from the slope of the plots of $-\ln(1-F^2)$ versus t.

Fixed bed operation

Fixed bed operations were performed by using the following columns; (1) a mini-column of 4.0×10^{-3} m inner diameter and 7.0×10^{-2} m length in which the adsorbent or the activated alumina of 0.319 mm diameter, 6.3×10^{-7} m^3 was packed, or (2) a large column of 4.0×10^{-2} m inner diameter and 5×10^{-1} m length in which the adsorbent of 1.8 mm diameter, 4.0×10^{-4} m^3 was packed.

The concentrations of arsenic and antimony were determined by graphite furnace atomic absorption spectrophotometry using a Thermo Elemental SOLAAR MQZ instrument, and the concentration of phosphate was determined with molybdenum blue method according to Japan Industrial Standard K0102.

Results and discussion

Adsorption capacity

This novel adsorbent was made from activated alumina by supporting aluminium sulfate for the purpose of phosphate adsorption. It is well known that activated alumina can adsorb arsenic ion, so that the adsorbent is expected to be able to adsorb arsenic ion. Thus, the adsorption isotherm of arsenic was measured in order to confirm that the adsorbent could favorably adsorb arsenic ion. In the present study, only arsenic ion, i.e., As (V), was used and arsenious ion, i.e., As (III), was not used since the aim of the study is to remove arsenic from groundwater used as raw water for drinking water. Arsenious ion should be oxidized into arsenic ion during chlorine treatment in water purification process. The adsorption isotherms of As (V), P and Sb (V) were measured and shown in Figure 1 on the basis of mass concentration.
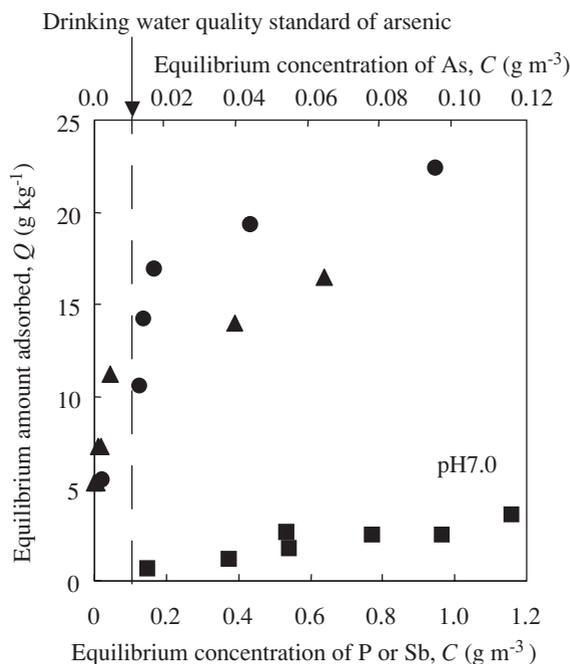
Figure 1 Adsorption isotherms of different anions based upon mass concentration. ●, As; ▲, P; ■, Sb

It was confirmed that the adsorbent could adsorb not only phosphate ion but also arsenic ion and antimonite ion. The amount of arsenic adsorbed at pH 7.0 at the Japanese drinking water quality standard, i.e., 0.01 g m^{-3}, was recorded as 9.20 g kg^{-1}, which was 3.82-29.6 times higher than with the other adsorbents such as zirconium oxide-supported activated carbon (Kobayashi *et al*, 1983), granular ferric hydroxide (Driehaus *et al*, 1998) or organo-modified natural zeolitic material (Misaelides *et al*, 1998).

To discuss the selectivity of the ions for the adsorbent, the adsorption isotherms needed to be arranged on the basis of equivalent concentration. Hence, the results shown in Figure 1 were arranged and plotted in Figure 2. But for antimonite, the arrangement was not done and not plotted in the figure because a reliable disassociation constant was not obtained from any literature. As shown in Figure 2, both the adsorption isotherms were able to be adjusted to Langmuir equation. The slope of the regression line for arsenic ion was smaller than that for phosphate ion, indicating that the selectivity of phosphate ion was greater. Consequently, it should be better to apply the adsorbent for removing arsenic from ground-water containing less phosphate. In general, selectivity of arsenic ion for activated alumina is greater than that of phosphate ion. The reason for the disagreement between activated alumina and the adsorbent was under investigation.

So far, the novel adsorbent has been confirmed to give remarkable adsorption capacity, so that the effect of supporting aluminium sulfate was examined. As shown in Figure 3, significant increase of the amount adsorbed by the supporting was observed especially in the high concentration of arsenic. Consequently, the supporting aluminium sulfate onto activated alumina was concluded to be effective against increasing the capacity for arsenic ion adsorption.
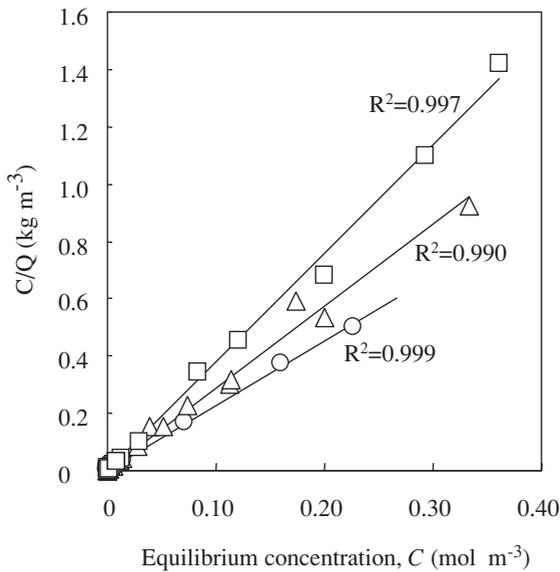
Effect of pH

In general, the effect of pH on anion adsorption is significant. Thus, the effect of pH on the adsorption isotherm of the adsorbent was studied and the results were shown in Figure 4. Obviously, the slope of adsorption isotherm decreased with decreasing the pH, indicating that operation of adsorption treatment should be done to keep pH low.
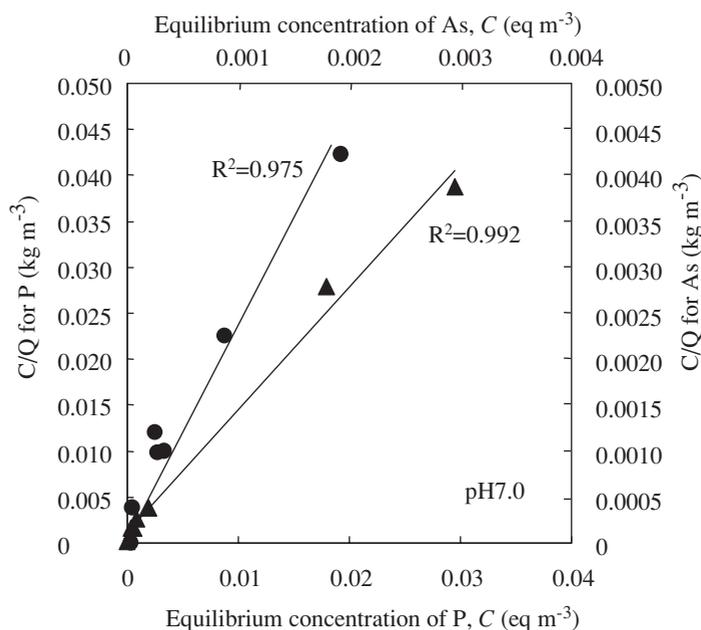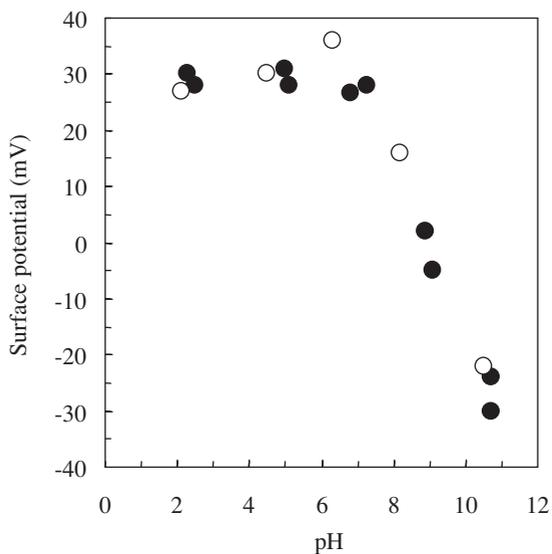

Figure 2 Langmuir plots. ●, As; ▲, P
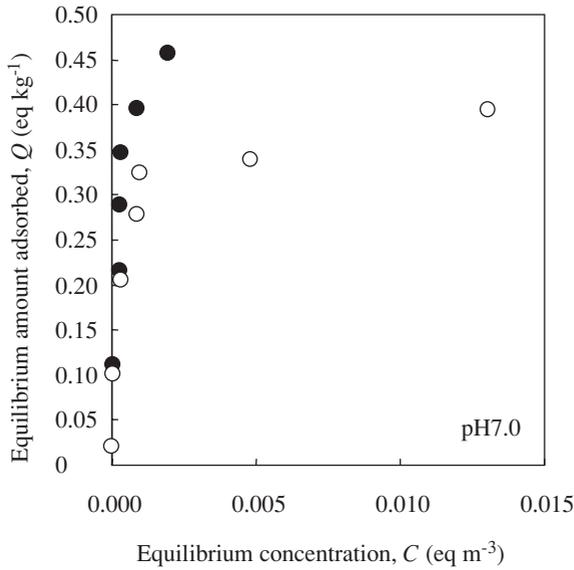
Figure 3 Effect of support of aluminium sulfate onto activated alumina. Closed symbols, the adsorbent (supported); open symbols, activated alumina (unsupported)

Figure 4 Effect of pH on adsorption isotherm based upon mol concentration. ○, pH 6.0; △, pH 7.0; □, pH 8.0

Both the change of surface potential of the adsorbent and disassociation degree of arsenic ion may be reasons of the pH effect. Figure 5 shows pH dependence of surface potential of the adsorbent. As shown in Figure 5, it was significantly decreased at pH 8.0, but there was no significant difference between pH6.0 and 7.0. Therefore, the surface potential is considered to be a minor reason and the change of disassociation degree of arsenic ion should be a main reason of the pH effect. Thus, the adsorption isotherms shown in Figure 4 were arranged on the basis of equivalent concentration and shown in Figure 6. No significant difference was observed within all the pH conditions. The mean electric charges of arsenic ion are 1.10, 1.52 and 1.91 respectively for pH 6.0, 7.0 and 8.0. The ratio of the mean electric charge between pH 6.0 and 8.0 is 1.74. The main reason of the pH effect was confirmed to be the change of disassociation degree of arsenic ion.

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Figure 5 pH dependence of surface potential. Closed symbols, the adsorbent (supported); open symbols, activated alumina (unsupported)

So far, the effect of pH is conclude to be negligible when the adsorption isotherm was plotted based upon equivalent concentration, so that the equation for the adsorption isotherm of arsenic was calculated by the least square method by using all the data shown in Figure.6 and submitted as Eq.(3).

$$Q = \frac{0.512 \times 821C}{1 + 821C} \tag{3}$$

where C (eq m^{-3}) is the equilibrium arsenic concentration, Q (eq kg^{-1}) the equilibrium amount adsorbed.
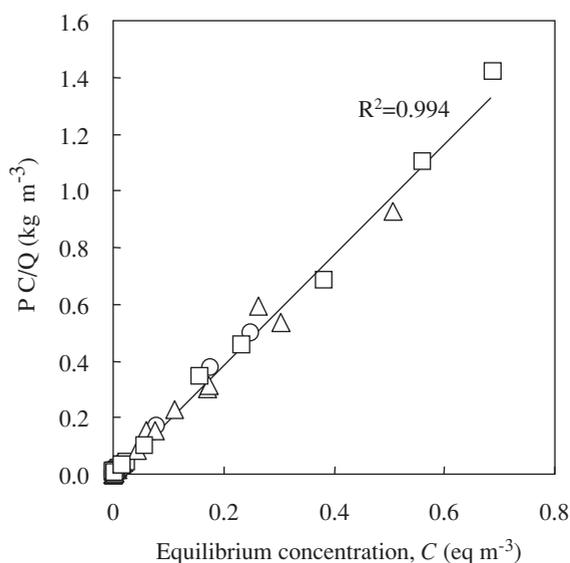
Figure 6 Effect of pH on adsorption isotherm based upon equilibrium concentration. ○, pH 6.0; △, pH 7.0; □, pH8.0

Adsorption rate

The intraparticle diffusion coefficient based on the concentration in solid, D_i', was evaluated by batch method, and the obtained value was compared with that of the activated alumina. The time course of arsenic concentration in aqueous phase was measured and the adsorption coverage was calculated with equation (3). The calculated values are plotted in Figure 7. The maximum adsorption coverage was 9.32%. The arsenic concentration in the aqueous phase was changed from 59.5 mg m^{-3} to 44.3 mg m^{-3}. It was confirmed that Boyd's method could be applicable for the present use since the relationships between $t^{1/2}$ and $-\ln(1-F^2)$ did not downturn and were almost linear.

The value of D_i' at 298K was calculated as 3.2×10^{-15} m^2 s^{-1} from the slope of the regression line in Figure 7. The obtained value was almost the same as that for the activated alumina, i.e., 3.9×10^{-15} m^2 s^{-1} (data not shown). Since the pores of the adsorbent must be packed with aluminium sulfate, D_i' was predicted as smaller value. Compared with the activated alumina, the Brunauer-Emmett-Teller (BET) surface area and pore volume of the adsorbent decreased 29.0 and 61.5%, respectively. Nevertheless, no significant difference in D_i' was observed. Consequently, supporting aluminium sulfate on the activated alumina causes the increase of the adsorption capacity for arsenic and the insignificant decrease of adsorption rate of arsenic, which is valuable for producing a high performance adsorbent.

Fixed bed operation

In order to confirm the effect of supporting aluminium sulfate, deionized water containing 1.4 g m^{-3} of arsenic was fed into the mini-columns continuously. The breakthrough curves for the adsorbent and the activated alumina are shown in Figure 8. Compared to the activated alumina, more than double bed volume, i.e., total volume of effluent divided by empty column volume, was achieved by using the adsorbent. Obviously, the effect of supporting aluminium sulfate was observed. Up to ca. 5,000 bed volumes was achieved till breakthrough by using this novel adsorbent although high concentration of arsenic was fed at high space velocity of 50 h^{-1}. In the beginning of feeding, pH of the effluent from the column packed with the adsorbent decreased to ca. 5, but for the effluent from the column packed with the activated alumina, no significant pH decrease was observed.
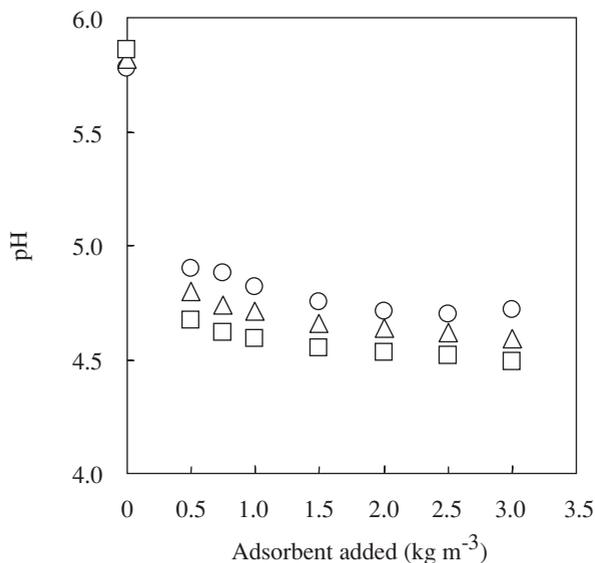
The reasons why more than double bed volume was achieved by using the adsorbent are
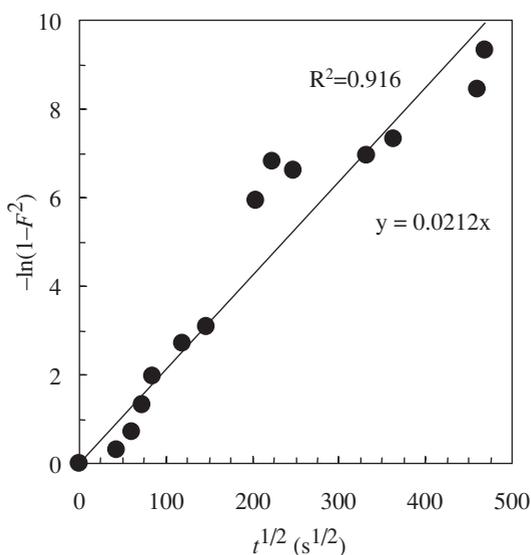

Figure 7 Boyd's plot
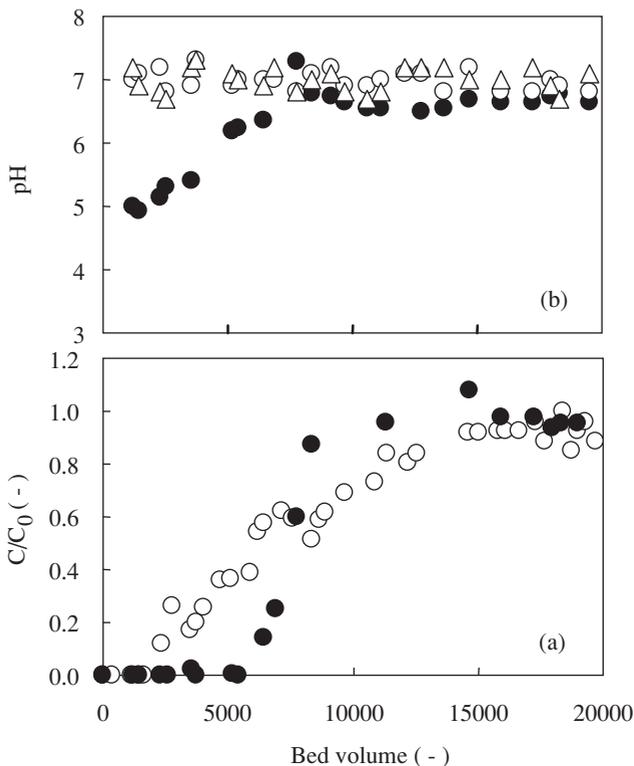
Figure 8 Breakthrough curves of arsenic (a) and pH behavior of effluent from column (b). ●, the adsorbent (supported); ○, activated alumina (unsupported); △, pH of influent groundwater

Figure 9 pH decrease by self-pH control function of the adsorbent. Initial arsenic concentration (mg m^{-3}): ○, 0; △, 10; □, 100

considered to be the enlargement of adsorption capacity and pH decrease in the column. Only 5% enlargement of the adsorption capacity was achieved by the support at 0.01 mg m^{-3} as shown in Figure 3, whereas the significant pH decrease was caused by the support as shown in Figure 8. Since pH profile must be established in the column, quantitative
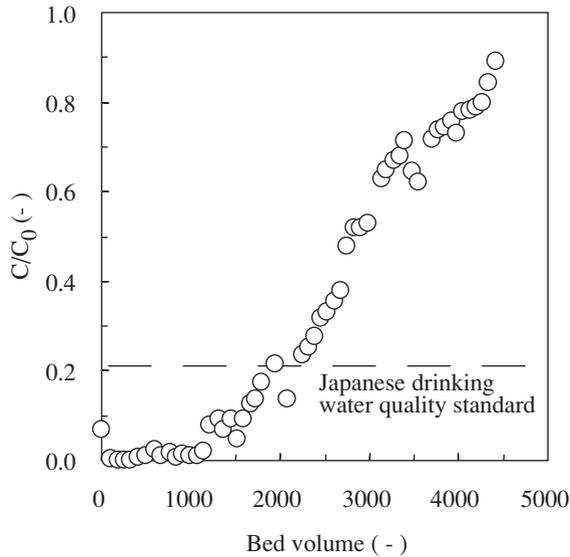
Figure 10 Lab-scale experiments of continuous adsorption treatment of actual groundwater

discussion is difficult to be made. But considering that the ratio of the mean electric charge between pH5.0 and 7.0 is 1.82, the main reason for the high performance of the adsorbent may be the pH decrease caused by the adsorbent itself, namely, a self-pH decrease function.

In order to confirm that the adsorbent involves the self-pH decrease function, various amounts of the adsorbent were added into deionized water containing arsenic at 0, 10 or 100 mg m^{-3}, and the pH change was measured. As shown in Figure 9, pH decreased obviously with increasing amount of the adsorbent added, indicating that the adsorbent involves the self-pH decrease function. The pH decrease conspicuously occurred when the concentration of coexisting arsenic was higher. The self-pH decrease function must be served by dissociation of Al (III) aquoion according to Eq. (4). Disassociation constant for the first disassociation is 1.3×10^{-5}, which means Al (III) aquoion has capability to decrease pH down to 5.

$$[Al(H_2O)_6]^{3+} \rightleftarrows [Al(H_2O)_5(OH)]^{2+} + H^+ \tag{4}$$

Lab-scale continuous adsorption treatment of actual groundwater
By using a granular adsorbent of 1.8 mm diameter which is commercially available, lab-scale experiments of continuous adsorption treatment of actual groundwater containing trace arsenic at 50 mg m^{-3} were conducted to examine the performance of the adsorbent. As shown in Figure 10, without pH adjustment, up to ca. 2,000 bed volumes was achieved till the concentration of arsenic in the effluent exceeded the Japanese drinking water quality standard, i.e., 0.01 mg m^{-3}.

In the actual groundwater, some of the inhibitors coexisted with arsenic. Especially for phosphorus, its concentration was one-fifth of that of arsenic. Nevertheless, a large bed volume could be achieved.

Unfortunately, only the adsorbent of 1.8 mm diameter is commercially available. However, much smaller particles should be available in fixed bed operations in water purification processes. Particle diameter must affect dramatically the bed volume till breakthrough because according to Eq. (2) the adsorption rate becomes greater in inverse proportion to the diameter squared.

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Conclusions and perspectives

Adsorption capacity of a novel adsorbent was 9.20 g kg^{-1} at pH 7.0 at Japanese drinking water quality standard, i.e., 0.01 g m^{-3}, which was remarkably higher than other adsorbents. By using the adsorbent, more than double the continuous adsorption treatment term compared to that for the conventional activated alumina was achieved. This may be because the adsorbent shows a self-pH decrease function. In the future, by using much smaller particles of the adsorbent, a feasible treatment is hopefully proposed for removing arsenic from groundwater.

Acknowledgement

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