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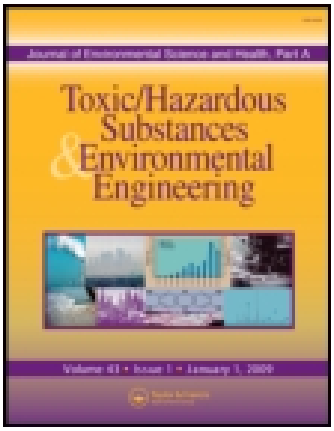

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Arsenic Removal Using a Biopolymer Chitosan Sorbent

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Arsenic Removal Using a Biopolymer Chitosan Sorbent

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An agricultural waste, chitosan, was converted to bead form to evaluate the feasibility of its use to remove As(III) and As(V) from water in both batch and continuous operations. In batch tests, the effect of pH, temperature, coexisting ions, and arsenic concentrations were studied. Studies of kinetic adsorption, recovery of arsenic by desorption solution, and reuse of chitosan beads were also carried out. Additionally, wastewater containing arsenic discharged from the manufacturing of GaAs supports was treated in a continuous operation. Results indicated that chitosan beads favored the adsorption of As(V), but not As(III). The optimal pH value for As(III) and As(V) removal was near 5. The insignificant difference for As(V) and As(III) adsorption by chitosan beads was found in the 25–40°C range. Ion coexistence below 50 mg/L did not affect arsenic removal. The optimal desorption solution for the arsenic recovery was H_2SO_4 with a 71% efficiency for As(V), which was amenable to efficient regeneration for multiple reuse (about 15 times). In continuous tests, the chitosan bead column exhibited excellent arsenic removal from actual wastewater without any pretreatment. The results provide strong evidence of the promise the application of chitosan bead has for arsenic removal.

Key Words: Arsenic; Chitosan; Adsorption; Sorbent.

INTRODUCTION

Arsenic contamination of drinking water and groundwater is a widely overlooked problem that has gained international attention. Exposure to arsenic-contaminated drinking water has caused serious health problems in various areas or countries including Taiwan, Argentina, Chile, and the United States.[1] Particularly, well-known high-As groundwater areas have been found in some areas of Asia, such as Taiwan, India, and Vietnam.[2]

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Arsenic is classified as one of the most toxic and carcinogenic chemical elements. It potentially causes cancer of the bladder, lungs, skin, kidney, liver, and prostate.[3] Besides its tumorigenic potential, arsenic has been shown to be genotoxic. Thus, arsenic removal from industrial effluents, groundwater, and even drinking water systems has become very important. At present, the WHO guideline value, the EC maximum admissible concentration, and the USEPA limit for As in drinking water is 10 μg/l.[4] Moreover, the standard allowances of As concentration in industrial effluents and drinking water in Taiwan are set at 500 μg/l and 10 μg/l, respectively.

In Taiwan, anthropogenic sources of arsenic compounds are often the by-products of pesticide, chemical, pharmaceutical, and semiconductor manufacturing.[5] Several mg/L of arsenic compounds are always found in the effluent of these above industries. As science and technology have developed, arsenic pollution has shifted from groundwater to industrial wastewater, especially for effluent from the manufacturing of GaAs supports in some Asian areas. These effluents contained relatively high As(V) and trace As(III) concentrations compared to groundwater polluted by arsenic compounds. In addition, these electronic wastewaters are characterized by fewer variations of chemical species in wastewater relative to those in groundwater.

Many arsenic removal technologies have been developed. These technologies are generally divided into three types according to the removal mechanism. They include precipitation, membrane, and adsorption. To be sure, combination processes or technologies can be used if required. Aluminum salt and iron salt are popular coagulants in removing arsenic compounds by the coagulation precipitation method.[6] However, the production of highly toxic sludge has limited their application.[7] Arsenic in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite As(III) or pentavalent arsenate As(V). Membrane technology is more effective in removing As(V) than As(III).[7,8] Therefore, to achieve efficient arsenic removal, an extra oxidizing agent (i.e., chlorine) added to water is usually required in order to convert As(III) to As(V). Unfortunately, these membranes are easily injured by these agents, and membrane life is substantially shortened. The adsorption technique is regarded as a promising method or process because many successful cases can be cited in support.[9] In the past, activated alumina, active carbon, alginate gels, polymeric hybrid, and natural solids have been applied to the removal of arsenic from water.[7,10–12] Most of them, however, present a problem in terms of either cost, removal capacity, or regeneration efficiency. Thus, an efficient, cheap, and environmentally friendly adsorbent is called for.

Chitosan is a kind of polysaccharide prepared by the de-*N*-acetylation of chitin, the material out of which the shells of crustaceans like crabs and shrimp are made.[13] Chitosan is biodegradable, biocompatible and nontoxic, making it an environmentally friendly substance.[14] Since the free amino groups on chitosan can serve as sites of coordination binding for metals, some reports

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in the literature have demonstrated chitosan's high adsorption capacity for various metal ions such as Cd(II), Cu(II), Cr(III), Pb(II), Zn(II), Ni(II), Hg(II), U(VI) and V(IV).[15–17] Based on a similar mechanism and the results of some pretests in our research, we believe chitosan could potentially remove various arsenic compounds from water as well.

In the present work a promising method of arsenic removal using chitosan bead is investigated by batch and continuous experiments. Effects of pH, temperature, coexisting ions, and arsenic concentrations on arsenic adsorption by chitosan bead are also performed in our research. Finally, the chitosan bead column is also applied to the removal of arsenic from wastewater discharged from the manufacturing of GaAs supports. The overall objective of the present study is to ascertain the feasibility of using chitosan bead to remove arsenic from water in a one-step operation without any pretreatment.

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MATERIALS AND METHODS

Materials

Chitosan was derived from shrimp shells with a deacetylation degree of 90% from the Application Chemistry Company (Kaohsiung, Taiwan). Its characteristics were pKa = 5.6, and weight average molecular mass, $MW^w = 1.5 \times 10^6$ g/mol. Powdered chitosan was dissolved in 1 M acetic acid to give a final concentration of 1% (w/v), and the chitosan solution was stepwise dropped to 1 M NaOH solution by microsyringe. The reaction solution was stirred mildly for 16 hr at room temperature. After that, these chitosan beads were washed three times by deionized water. The average size of these beads was 2.5 mm (±5%). Stock solutions of As(III) and As(V) were prepared by dissolving analytical grade reagents $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ in deionized water. $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ were purchased from Merck Company (Germany). Other chemicals were purchased from Sigma Chemical Company (USA) unless otherwise specified.

Kinetic Adsorption

Batch adsorption experiments were conducted at 25 ± 2°C by agitating 1 g of chitosan bead with 200 mL of As(III) or As(V) solution (10 mg/L), and initial pH was 7.0 in a shaking thermostat machine. The mixture was shaken at 50 rpm for 72 hr. The 2 mL solution was sampled, filtrated through a 4.5 μm membrane, and analyzed by the hydride generation atomic absorption spectrophotometry method at a constant interval. All analyses were done in duplicate at least.

Effect of pH, Temperature, and Other Chemicals on Arsenic Adsorption

The experiments were performed in 300 mL flasks with 200 mL As(III) or As(V) solution and 1 g of chitosan bead. The initial arsenic concentration

was 0.1 mg/L or 10 mg/L to simulate different environmental conditions. The pH ranged from 4 to 9 and was adjusted using 0.1 M HNO_3 or 0.1 M NaOH. The solutions were shaken at 50 rpm in a shaker at 25 ± 2°C for 24 hr unless otherwise specified. To evaluate the effect of temperature on arsenic adsorption, the temperature ranged from 15°C to 60°C and pH was controlled at 5. Studies on the effect of coexisting chemicals (Ca^{+2}, Mg^{2+}, Cl^-, $SO_4^=$, $CO_3^=$) and their concentrations (10, 50, 100 mg/L) on arsenic adsorption were conducted to simulate actual water environments.

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Recovery of Arsenic and Reuse of Chitosan Bead

To evaluate the possibility of recycling the adsorbent, the desorption and regeneration process of chitosan bead were studied. Chitosan beads (5 g) with previously saturated adsorbed arsenic compounds were dried at room temperature and then were added to desorption solutions (HCl, H_2SO_4 or H_3PO_4) at various concentrations. The mixture was shaken at 50 rpm for various time (1–9 h) followed by a mild centrifugation for separation. The concentrations of arsenic compounds in the supernatant of the desorption solution were analyzed to obtain recovery efficiency in an interval. The chitosan bead was washed with deionized water and dried at 60°C for reuse.

Column Tests

The continuous column runs were carried out using a glass column 1.8 cm in diameter and 12 cm long with a water jacket. The column was maintained at 25 ± 2°C by circulating water in the column jacket. Then 20 grams of chitosan beads were loaded on the column, and the packing volume was 30.5 mL. An aqueous solution containing 10 mg/L of As(III) or As(V) at pH 5 was continuously fed at the flow rate of 8 mL/min to 32 mL/min (retention time: 3.8–0.95 min) into the column. The fraction of effluent was collected for the analysis of arsenic compounds every 0.5 hr until breakthrough occurred. To evaluate the arsenic removal efficiency from actual environmental conditions, the wastewater from the manufacturing of GaAs supports in Hsinchu Science Park (Hsinchu, Taiwan) was collected and treated by chitosan adsorption column at 32 mL/min. The wastewater characteristics are listed in Table 1.

RESULTS AND DISCUSSION

Kinetic Adsorption Tests

To understand the feasibility of chitosan beads on arsenic adsorption, bath kinetic studies were conducted. Two parameters including removal efficiency and adsorption capacity of chitosan beads were evaluated. The adsorption capacity (mg As/g bead) of chitosan bead was defined as the adsorbed arsenic

Table 1: Characteristics of wastewater discharged from the manufacturing of GaAs supports.

Constituents	Concentration
Temperature	32 ± 0.5°C
Turbidity	28 ± 2 NTU
pH	4.8 ± 0.2
TOC	6.6 ± 0.4 mg/L
$SO_4^{=}$	56 ± 1.2 mg/L
$CO_3^{=}$	3.6 ± 0.3 mg/L
SiO_2	420 ± 10 mg/L
Al(III)	154 ± 8 mg/L
As(III)	2.5 ± 0.2 mg/L
As(V)	35 ± 1.3 mg/L

amount per weight of chitosan bead. Figure 1 shows the change versus time in removal efficiency and adsorption capacity of chitosan bead for As(III) and As(V). The results indicated 24 hr was the minimum required to reach an adsorption balance. The chitosan beads favored adsorption of As(V) over As(III). After 24 hr of reaction time, 91.5% As(III) removal and 96.8% As(V) removal were achieved, respectively. Under these conditions, the adsorption capacities of As(III) and As(V) were 1.83 and 1.94 mg As/g bead, better than the results (0.04 mg As/g FMO and 0.068 mg As/g FMO) obtained by treating with FMO (ferruginous manganese ore) adsorbent under similar conditions.[18] If these data were calculated by various kinetic analyses (zero-, first-, and second-order kinetics), we found the arsenic adsorption rate of chitosan beads could be described by a first-order equation. Similar results were observed by using coconut husk carbon, mineral adsorbent, and chrome wastes.[19–21]The adsorption kinetic constants of chitosan beads for As(III) and As(V) were calculated as 0.352 hr^{-1} and 0.492 hr^{-1}, respectively. Based on the results of the removal efficiency and adsorption rate, we suggest that the chitosan bead favors adsorption of As(V) over As(III).

Effect of pH on Arsenic Adsorption

Dominant arsenic species are a function of pH and redox potential. Moreover, pH value also affects the charged property (negative, positive, or neutral charge) of chitosan bead. Thus, the effect of pH on arsenic adsorption by chitosan bead requires investigation. In this experiment, the adsorption behavior of low arsenic concentrations (0.1 mg/L) was also examined. The experimental result is shown in (Fig. 2). Results indicated different effects for As(III) and As(V) adsorption. Insignificant differences in As(III) removal were found at pH 4–9, but pH 5–6 seemed to be the optimal range for chitosan bead to remove As(V). As for concentration effect, chitosan bead was less efficient at adsorbing diluted arsenic whether it was As(III) or As(V). Both As(III) and As(V) occur in several protonate forms: at near-neutral pH, the predominant species are

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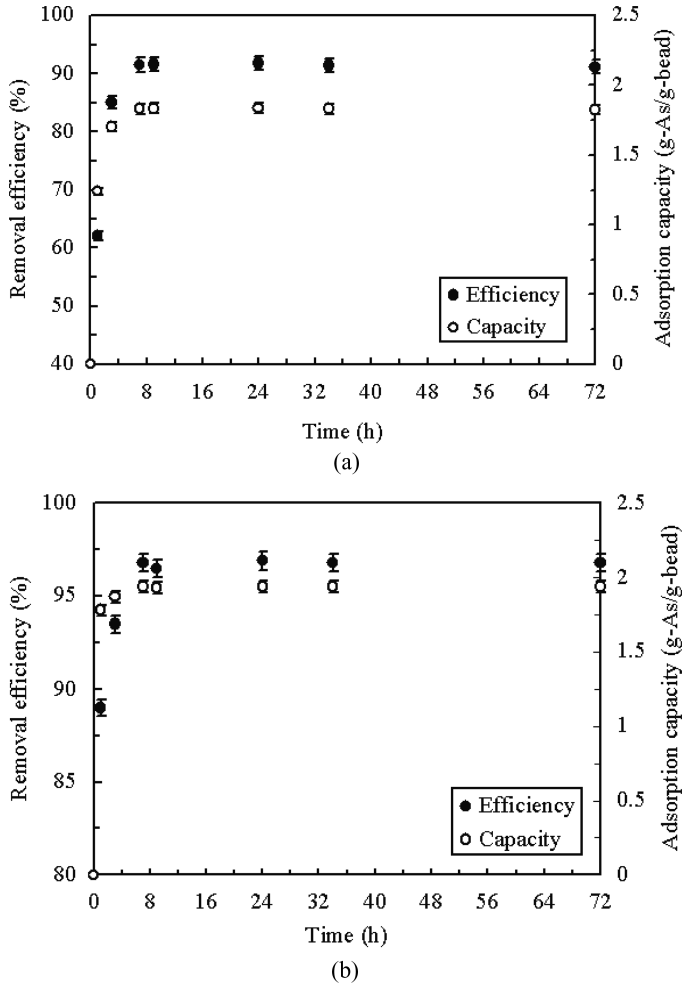

Figure 1: Change versus time in removal efficiency and adsorption capacity of chitosan bead for (A) trivalent arsenite and (B) pentavalent arsenate at 25 ± 2°C.

$HAsO_2$ for As(III), and $H_2AsO_4^-$ and $HAsO_4^{2-}$ for As(V). It means that As(V) exists as an anion at pH 4–9, while As(III) remains as a neutral molecule in the same pH range.[22] Due to the charge properties and the chemical structures of individual arsenic compounds, As(V) should be more easily removed from waters than As(III).

Because the pKa of chitosan was 5.6 in this study, chitosan bead was restricted from removing As(III) in nature by charge neutralization. As(III) removal by chitosan bead may be a function of hydrogen bond formation or van der Waals force between both at pH 4–9. On the other hand, when pH was lower than 5.6, As(V) with a negative charge was easily and closely adsorbed by positively charged chitosan. Conversely, when pH was higher than 5.6, efficient

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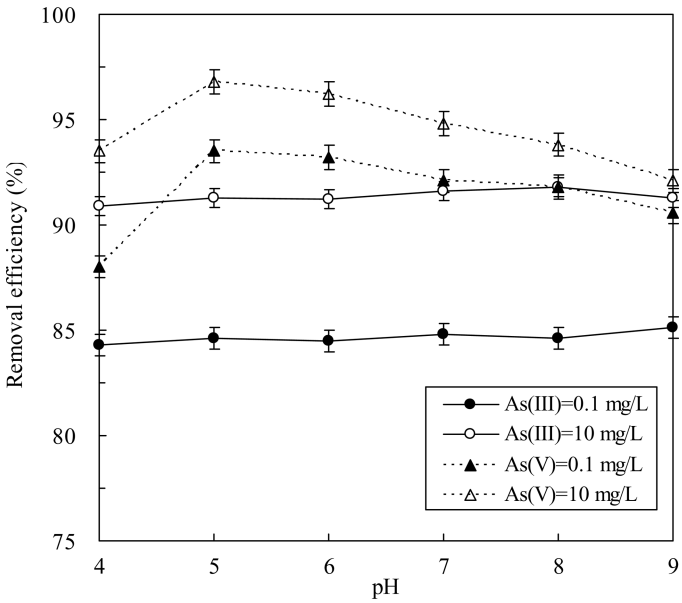

Figure 2: Effect of pH(4–9) on removal efficiency of chitosan bead for AS(III) and As(V) at 25 ± 2°C.

As(V) removal may be attributed to the hydrogen bond formation or van der Waals force between As(V) and chitosan, not the mechanism of charge neutralization. However, more complicated adsorption mechanisms or considerations (for example: the strength of hydrogen bond, steric hindrance, the strength electrostatic force) need to be clarified in the future. Based on these results, pH 5 seemed the right operating condition for removing coexisting As(III) and As(V) from wastewater. Results of the optimal pH value for arsenic removal by chitosan bead were similar to the case of arsenic removal by Zr resin, activated alumina, and Ce-Fe adsorbent,[23,24] but differed from other adsorbents (iron-oxide-coated polymeric material or coconut husk carbon), which efficiently removed As(III) under slightly alkaline conditions.[19,25] It showed that chitosan could be applied to the removal of As(III) in the wider pH range.

Effect of Temperature on Arsenic Adsorption

Groundwater often keeps a lower temperature and industrial effluents a higher one in comparison with surface water. To investigate the effect of temperature on arsenic adsorption by chitosan bead, experiments were conducted at 15°C, 25°C, 40°C, and 60°C, respectively. The results are shown in Figure 3. Arsenic adsorption decreased as temperature increased with both As(III) and As(V). However, the adsorption difference between 25°C and 40°C was insignificant ($p > 0.05$). This indicates arsenic adsorption on chitosan bead should be an

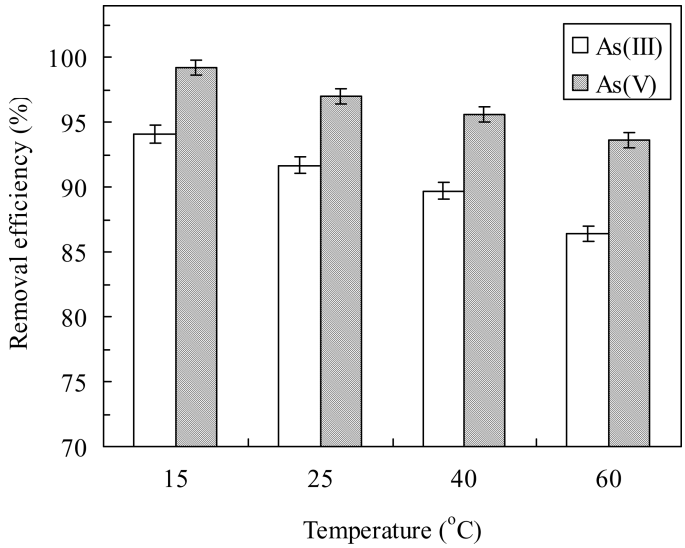

Figure 3: Effect of temperature (15–60°C) on removal efficiency of chitosan bead for As(III) and As(V) at pH 5.

exothermic reaction: higher temperature results in lower amounts of saturated adsorption. Thus, relatively high removal efficiencies, such as 94.1% for As(III) and 99.2% for As(V), were achieved at 15°C. If these data were calculated by the linear regression method, the equations $y = -2.57x + 96.8$ for As(III) and $y = -1.82x + 100.9$ for As(V) were obtained. Obviously, the effect of temperature on arsenic adsorption was higher for As(III) than As(V), judging from the slope of the equation. In Taiwan, the temperature of groundwater, surface water, and wastewater containing arsenic generally remains below 40°C throughout the year. We suggest that chitosan beads could be applied to removing arsenic from water based on temperature considerations.

Effect of Ion Coexistence on Arsenic Adsorption

In southwest Taiwan, groundwater is a major source of arsenic pollution. Since groundwater is harder than surface water, we utilized Ca^{+2} and Mg^{2+} (the main components of hardness) as indicators to evaluate the effect of hardness on arsenic adsorption. A synthetic solution containing 0, 10, 50 or 100 mg/L of Ca^{+2} or Mg^{2+} was prepared to evaluate the effect on removal efficiency of chitosan bead for arsenic by the batch adsorption tests. Additionally, the effect of some anions including Cl^-, $SO_4^=$, and $CO_3^=$ on arsenic removal were respectively examined. These results are listed in Table 2. In respect of cations, high concentrations of Ca^{+2} and Mg^{2+} favored As(V) removal, but the coexisting Ca^{+2} or Mg^{2+} did not significantly affect As(III) adsorbed by chitosan beads. As for anions, their impacts were more complicated. 10 or 50 mg/L Cl^- and $SO_4^=$ did

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Table 2: Effect of ion coexistence on arsenic removal efficiency.

	As(III)				As(V)			
	0 mg/L	10 mg/L	50 mg/L	100 mg/L	0 mg/L	10 mg/L	50 mg/L	100 mg/L
Ca^{2+}	91.3%	91.4%	91.6%	91.5%	96.4%	96.2%	96.3%	98.2%
Mg^{2+}	91.4%	91.3%	91.5%	91.7%	96.5%	96.3%	96.4%	97.8%
Cl^-	91.4%	91.3%	91.5%	89.5%	96.6%	94.1%	92.3%	89.8%
$SO_4^=$	91.5%	91.4%	91.5%	83.6%	96.4%	94.6%	92.1%	89.4%
$CO_3^=$	91.3%	91.3%	91.2%	91.3%	96.5%	96.4%	96.3%	96.3%

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not interfere with the As(III) adsorbed by chitosan beads, but 100 mg/L of these coexisting ions reduced the efficiency with which As(III) was removed. The impact of $SO_4^=$ was more significant than Cl^- on As(III) removal. Surprisingly, even low concentrations of coexisting Cl^- or $SO_4^=$ affected As(V) removal. As for $CO_3^=$, it did not affect As(III) or As(V) removal because the dominant species of $CO_3^=$ in solution was neutral H_2CO_3 molecule.

Since about 80% of the chitosan surface is positively charged and As(III) remained a neutral molecule at pH 5, the As(III) adsorbed by chitosan bead resulted from the formation of a hydrogen bond or hydrophobic bond. By contrast, positively charged chitosan and negatively charged As(V) were mainly bound by charge neutralization. Thus, the effect of cations on As(III) were negligible. However, high concentrations of cations would easily react with As(V) ($H_2AsO_4^-$) and result in the occurrence of precipitation, which brought about high As(V) removal from the supernatant of the tested solution. Because anions react with chitosan at pH 5, they completed the functional group (NH_3^+) of chitosan with As(V). Thus, anions, excepting $CO_3^=$, had a deep effect on the As(V) adsorbed by chitosan beads. As for the effect of high concentrations of Cl^- and $SO_4^=$ on As(III) removal, we ascribed it to a intermolecular steric hindrance between As(III) and chitosan. Thus, the effect of $SO_4^=$ was more significant than Cl^- on As(III) adsorption. Based on the results, we believe the effect of coexisting ions was slight for As(III) adsorption compared to As(V) adsorption.

Recovery of Arsenic and Recycling of Chitosan Beads

In an effort to reduce both costs and waste production, a practical method of recovering arsenic while simultaneously recycling chitosan bead was developed. Chitosan bead, previously saturated with arsenic, was immersed for 9 hr with 100 mL of desorption solution to desorb the arsenic from it. The recovery efficiencies using various solvents are calculated based on the ratio of the recovered arsenic amount relative to the arsenic amount previously adsorbed on the chitosan bead. The recovery efficiency depended on the kind and concentration of the solvent and is listed in Table 3. The HCl solvent with different concentrations and 1 M H_2SO_4 made achieving our goals difficult because it resulted in chitosan bead disfigurement (data not shown). The chitosan bead,

Table 3: Recovery efficiency of As(III) and As(V) by various desorption solutions for various treatment times.

	As(III)					As(V)				
	H_2SO_4		H_3PO_4			H_2SO_4		H_3PO_4		
	0.1 M	0.5 M	0.1 M	0.5 M	1 M	0.1 M	0.5 M	0.1 M	0.5 M	1 M
1 hr	12%	14%	10%	15%	26%	26%	32%	20%	36%	42%
3 hr	21%	26%	—	—	—	71%	70%	—	—	—
5 hr	31%	38%	—	—	—	70%	71%	—	—	—
7 hr	32%	37%	—	—	—	69%	72%	—	—	—
9 hr	31%	37%	—	—	—	70%	70%	—	—	—

treated by H_3PO_4 solvent over 1 hr produced a similar result. Considering the recovery efficiency and treatment time, H_2SO_4 was the optimal desorption solution.

The optimal recovery efficiency of As(III) was 38% desorbed by 0.5 M H_2SO_4 for 5 hr, and it was 71% for As(V) desorbed by 0.1 M H_2SO_4 for 3 hr. Since the application of acid desorption solution would lower system pH value, it made negatively charged As(V) convert to neutral-charged As(V) (i.e., $H_2AsO_4^-$ to H_3AsO_4). Thus, it destroyed the chemical bond between the As(V) molecule and chitosan bead, resulting in the molecule's desorption. The chitosan bead was recycled 20 times by cycling the adsorption and desorption of arsenic by an adequate desorption solution. The results showed that recovery efficiency maintained its initial values after 15 recycling tests. This was far preferable to the mere three cycles afforded by coconut husk carbon in arsenic recovery.[18] The results showed the application of chitosan bead in removing arsenic, especially As(V), was a feasible method.

Column Adsorption Test

For a practical application of chitosan bead to the continuous removal of arsenic from water, the column adsorption test was conducted, and the result is shown in Figure 4. The breakthrough time (i.e., $C_e/C_o = 0.2$)(C_e and C_o are the effluent and influent concentrations of arsenic) decreased as flow rate increased, and the curve showed an S-type mode. The effect of flow rate was more significant for As(III) than As(V), meaning that the breakthrough time is highly related to the adsorption capacity of chitosan bead. About 5 hr was required to reach 100% breakthrough of As(V) at 8 mL/min (retention time: 3.8 min). When we calculated the saturated adsorbed amount of As(III) and As(V) by chitosan bead after the experimental end, it was 1.78 and 1.90 mg As/g bead, respectively, which approximates the results of kinetic adsorption tests. Besides, if we converted the unit of treated time to the breakthrough volume, the chitosan bead column clearly had a higher capacity than the Zr resin column but was equivalent to the Al-SZP_1 column under same retention time.[9,23]

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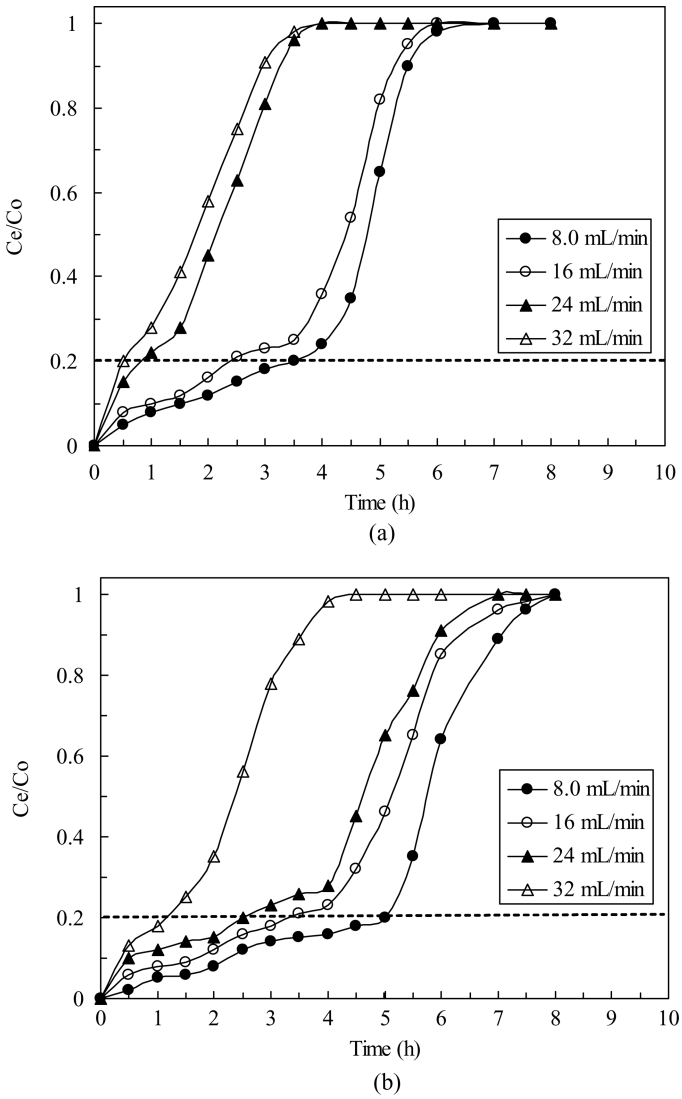

Figure 4: Effect of different flow rates (8–32 mL/min)on As adsorption by chitosan bead packed column for (A) trivalent arsenite and (B) pentavalent arsenate.

Figure 5 indicates the results of actual wastewater containing arsenic from the manufacturing of GaAs supports treatment by chitosan bead packed column. Native chitosan bead and recycled chitosan bead (15 times) were simultaneously evaluated. Obviously, a minor difference ($p > 0.05$) was found between native chitosan bead and recycled chitosan bead with both As(III) and As(V). A longer adsorption time required for As(III) removal than As(V) removal from wastewater by chitosan bead column was found, which seemed discordant with previous results. Since the wastewater contained different concentrations of

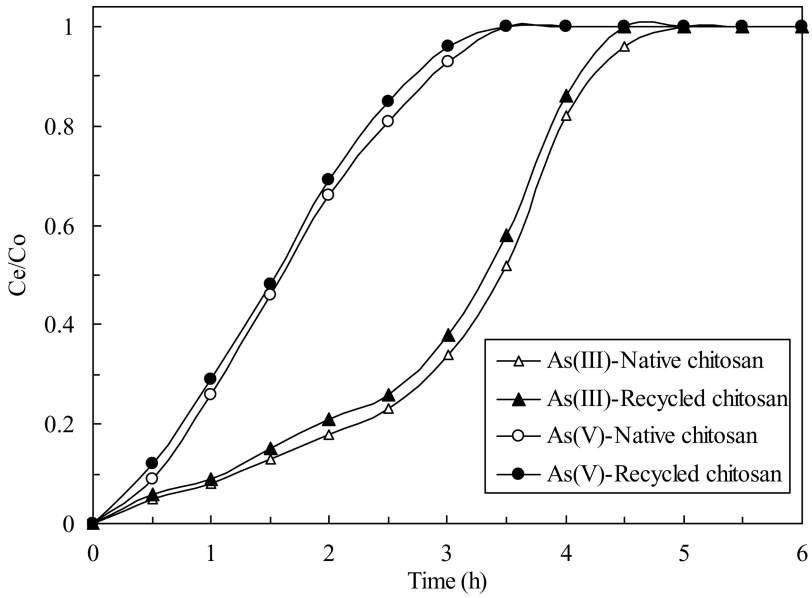

Figure 5: Effect of native and recycled chitosan bead column on As adsorption. The wastewater containing arsenic discharged from the manufacturing of GaAs supports was introduced at 32 mL/min.

As(V) and As(III), the result was reasonable. The similar solution containing As(V) or As(III) alone prepared by deionized water was examined. The adsorption curve for As(V) alone was similar, but not As(III) (data not shown). This suggested that competitive adsorption occurred between As(III) and As(V). However, further study should clarify this. In the literature, some adsorbents (e.g., iron-oxide-coated polymeric material and Ce-Fe adsorbent) for arsenic removal were deeply affected by the chemical composition of treated water.[24,25] Thus, using chitosan bead to remove arsenic was at an advantage.

CONCLUSION

Overall, chitosan bead exhibited efficient arsenic removal in the batch and continuous tests. Furthermore, chitosan bead itself and arsenic adsorbed by chitosan bead can be reused and recycled. The chitosan bead favored adsorption of As(V) over As(III), and the adsorption capacities of As(III) and As(V) were 1.83 and 1.94 mg As/g bead, respectively. The effect of temperature on arsenic adsorption was more significant for As(III) than As(V), but the pH effect was the inverse. The effect of existing ions was varied and depended on their concentrations and species. The synthetic wastewater and actual wastewater containing arsenic were examined and achieved an acceptable level using the chitosan bead column. From these results, we suggest that chitosan beads are a promising adsorbent in actual water environments.

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