Fish Sci
DOI 10.1007/s12562-008-0044-2

ORIGINAL ARTICLE

Environment

Shrimp shell as a potential sorbent for removal of arsenic from aqueous solution

Ming-Chao Lin · Chung-Min Liao · Ying-Cheng Chen

Received: 6 September 2007 / Accepted: 3 September 2008

Abstract This study examined the ability of shrimp shell to remove arsenic (As) from aqueous solutions. The shells of two species of shrimp, black tiger shrimp *Penaeus monodon* and white shrimp *Litopenaeus vannamei*, were chosen to be the sorbents. Laboratory exposure experiments estimated uptake and depuration rate constants (i.e., k_1 and k_2) as well as the bioconcentration factors (BCF) of the shells of the two shrimps. A first-order one-compartment model was presented to describe the uptake kinetics of As in shrimp shell. The resulting k_1, k_2, and BCF values of black tiger shrimp were 0.034–1.722 ml/g/day, 0.007–0.345 g/g/day, and 5.08 ± 1.56 ml/g, while those for white shrimp were 0.053–0.523 ml/g/day, 0.011–0.237 g/g/day, and 3.95 ± 1.88 ml/g, respectively. The sorption capacities of black tiger shrimp shell and white shrimp shell were 1.08×10^{-4}–6.66×10^{-3} and 1.04×10^{-4}–3.26×10^{-3} mmol/g, respectively. The sorption capacity of shrimp shell increased with the initial As concentration in water. Shrimp shell, as a waste material, could be potentially used for the removal of As from an aqueous medium. Although the As-removal capacity of shrimp shell was lower than those of natural and chemical sorbents, using shrimp shells as sorbents is less expensive and could increase the additional value of shrimp products.

M.-C. Lin (✉) · Y.-C. Chen
Department of Natural Biotechnology, General Education Center, Graduate Institute of Environmental Management, Nanhua University, Chiayi 622, Taiwan, ROC
e-mail: mingchaolin@mail.nhu.edu.tw

C.-M. Liao
Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei 106, Taiwan, ROC

Keywords Arsenic · Shell waste · Shrimp · Sorption capacity

Introduction

Arsenic (As) is ubiquitous in the environment and is an element notoriously toxic to the general population [1, 2]. Classified as a carcinogen, As is emitted into the environment, which poses risks to human health [3]. Contamination of As is globally a major public health issue. The main reason that people are exposed to As is because they come into contact with water, especially groundwater, which contains As. Arsenicosis is a serious disease mainly caused by drinking As-contaminated groundwater [4]. Many studies have shown that As can also be accumulated in seafood [5–7]. Chronic exposure of humans to high concentrations of arsenic is associated with skin lesions, peripheral vascular disease, hypertension, blackfoot disease, and high risk of cancers [8]. Several epidemiological studies have confirmed that there is an increased risk of cancer in case of exposure to As [9].

A wide range of physical and chemical treatment technologies have been applied for the removal of As from contaminated water, such as coagulation, ultrafiltration, ion exchange, lime softening, adsorption on iron oxides or activated alumina, and reverse osmosis [10]. These are two disadvantages of these treatments. First, there is always a deposited sludge of As compounds. Secondly, the operational costs of these treatments are high. Consequently there is growing interest in using low-cost materials to remove As from water [11]. The adsorption of As has been studied, using a variety of natural materials including sand, clay, kaolinite, bentonite, montmorillonite, goethite, spodic, and aquifer materials [12–15]. Among many other kinds

Published online: 28 January 2009

of identified low-cost natural sorbents, chitosan and chitin have the higher sorption capacities for As [16].

Chitosan is slightly soluble at low pHs, and poses problems because it has a tendency to agglomerate or form a gel in aqueous solutions. Chitosan could be obtained from chitin by a deacetylation process with a strong alkaline solution. Chitin is the main component of fungi, algae, molluscs, insects, and crustaceans [17–19]. Recently, chitin was recognized as an excellent sorbent; however, the processes of producing chitin require large amounts of acid and alkaline. Therefore, it is necessary to develop other kinds of techniques for As removal. Raw shrimp shell can be one of the choices among the potential materials [20].

Cultured shrimp is an important commercial crop in Taiwan. The total area of cultivating ponds is up to 9,000 ha. The total amount of supply and marketing of shrimp in Taiwan is 9,000 tons/year. Consumption of shrimp generates enormous amounts of shell waste. According to the stipulation of the Environmental Protection Administration in Taiwan, shrimp shells still remain solid offal at present. If these shrimp shells are thrown aside wantonly, they will cause pollution. In this study, we attempt to utilize shrimp shells as adsorbing materials.

Materials and methods

Among the cultured shrimps, black tiger shrimp (*Penaeus monodon*) and white shrimp (*Litopenaeus vannamei*) are two common species in Taiwan. The shrimp shells of these two species were chosen to obtain basic information on the use of shrimp shells for As removal. A total of 540 individuals of shrimp (commercial size, 20 ± 4 g wet weight, 15 ± 1 cm length), 270 individuals of black tiger shrimp and 270 individuals of white shrimp, were obtained from fish markets in Chiayi City, Taiwan, and placed on ice during transfer to the laboratory. The first shell from the abdominal segment of the shrimp was removed from its body and collected for laboratory exposure experiments. The shells were cleaned, rinsed, and then soaked in 1% NaOH at room temperature overnight to remove the bulk of the protein. After being rinsed with distilled water, the shells were dried in a convection oven (DO45, DENG YNG, Taiwan) at 40°C for 3 days.

Prior to the exposure experiment, the shells were placed into the oven at 105 ± 3°C for 1 day and dried to constant weight. The dry weight (g) of each shell was measured using an electronic balance (GT410, OHAUS, USA). Each dried shell was fixed between two glass slides and then photographed using a digital camera (DSC-N1, Sony, Japan). The photograph was traced and the surface area (cm^2) of shell was measured using a digitizer (Lab Visions LV-1, Bo-Seng, Taiwan) connected to a computer. The specific surface area (cm^2/g) of shell was calculated by dividing the surface area (cm^2) by the dry weight (g). The level of chitin in the shell was analyzed following the method of Juang et al. [21]. The chitin was obtained by immersing the shell in 5 wt.% NaOH for 18 h and later in 5 wt.% HCl (with a weight ratio of 1:10 for shell to solution) for 18 h.

Adsorption assays were conducted to determine the sorption capacities of the shells of the two shrimps. Equilibrium adsorption experiments were performed with varied As concentrations for a period of 14 days. The sorption capacity was examined by exposing the shells to the solutions with As concentrations of 0, 1, 2, 5, 10, 20, 40, 60, 80, and 100 mg/l, prepared from arsenite (Na_3AsO_3) at room temperature (25 ± 1°C). An amount of 270 dried shells from the same species was separated evenly into ten flasks, each with a volume of 500 ml; thus, every flask contained 27 pieces of shells. One by one the flasks were filled with 400 ml As solutions in the different concentrations as mentioned above. Three pieces of shells were taken from each flask at 0, 3, 6, 12, 24, 48, 96, 168, and 336 h and kept at −20°C before analysis. During the experiments, water samples were taken every 12 h from each flask, acidified by adding 5 ml 1 N HNO_3, and stored for analysis of As concentration. The pH values of solutions under various As concentrations were measured. After sampling, the water in flasks was renewed immediately to maintain the As concentration. The experiment was repeated twice.

Samples were sent to the Super Micro Mass Research and Technology Center, Cheng Shiu Institute of Technology for analysis of total As. The shells were dehydrated in a dryer (40°C) for 96 h and ground into powder. Aliquots of dry shell powder weighing 0.5 g were placed into a 250-ml beaker. Nitric acid (65% 10 ml) was added and then covered with a glass for an overnight digestion.

After the initial digestion, the beaker covered with a watch glass was heated with a water bath at 70–80°C for 2–4 h to reduce the total volume to 1–2 ml. This volume of solution was transferred to a volumetric flask (50 ml). A mount of 5 ml 0.01 N HNO_3 was used to rinse the watch glass. The rinsed solution was added to the flask. The flask was then filled with 0.01 N HNO_3 to make a 50 ml final solution. After filtration, this 50 ml solution was transferred to test tubes for As analysis. Arsenic analysis was carried out by using an Agilent 7,500a ICP-MS. Analytical quality control was achieved by digesting and analyzing identical amounts of rehydrated (90% H_2O) standard reference materials (DORM-2, Dogfish Liver-2-organic matrix, NRC-CNRC, Canada). Recovery rates ranged from 95% to 97%.

The sorption capacity of shrimp shell can be calculated based on the following equation [19]:

$$Q = \frac{\left(C_{w,m}(t=0) - C_{w,m}(t)\right)V}{m}, \quad (1)$$

where Q is sorption capacity (mol/g); $C_{w,m}(t=0)$ is the initial concentration of pollutant in water (mol/ml); $C_{w,m}(t)$ is the residual concentration of pollutant in water (mol/ml) at time t; V is the volume of water (ml) and m is the weight of sorbent (g).

Since $C_{w,m}(t=0) - C_{w,m}(t) = (n_0 - n_1)/MV$, where n_0 is the initial weight of pollutant in water (g), n_1 is the residual weight of pollutant in water (g) and M is the molecular weight of pollutant, Eq. 1 can be modified as:

$$Q = \frac{\left(\frac{n_0-n_1}{MV}\right)V}{m} = \frac{\frac{n_0-n_1}{m}}{M}. \quad (2)$$

Under the equilibrium status, the amount of pollutant adsorbed by the sorbent is equal to the amount of pollutant reduced in water ($C_s(t=\infty) = (n_0 - n_1)/m$), Eq. 2 can be rewritten as:

$$Q = \frac{C_s(t=\infty)}{M}, \quad (3)$$

where $C_s(t=\infty)$ is the equilibrium level of pollutant in sorbent (g/g).

The equilibrium concentrations of these shells under varied pollutant concentrations in water were calculated using an iterative, nonlinear, least-squares curve-fitting technique, based on a first-order one-compartment model [22]:

$$C_s(t) = C_s(t=0) + C_w(t=\infty)\frac{k_1}{k_2}(1 - e^{-k_2 t}), \quad (4)$$

where $C_s(t)$ is the pollutant level in sorbent (μg/ml) at time t; $C_s(t)$ is the initial pollutant level in sorbent (g/g); $C_w(t=\infty)$ is the equilibrium concentration of pollutant in water (g/ml); k_1 is the uptake rate constant (ml/g/day) and k_2 is the depuration rate constant (g/g/day). The constants k_1 and k_2, indicate the inflow and outflow rates between the sorbent and its ambient water, respectively.

When under the equilibrium condition in which $C_s(t=0) = 0$ and $t = \infty$, then Eq. 4 can be calculated as

$$C_s(t=\infty) = C_w(t=\infty)\frac{k_1}{k_2}, \quad (5)$$

and the sorption capacity (Q) can be calculated as

$$Q = \frac{C_s(t=\infty)}{M} = \frac{C_w(t=\infty)}{M} \times \frac{k_1}{k_2}. \quad (6)$$

When steady-state pollutant concentrations of sorbent are attained, the equilibrium bioconcentration factor (BCF) of the sorbent can be calculated from the ratio of the pollutant concentration in sorbent to that in water.

The BCF can also be calculated from the ratio of the uptake rate constant to the depuration rate constant as

$$\mathrm{BCF} = \frac{C_s(t=\infty)}{C_w(t=\infty)} = \frac{k_1}{k_2}, \quad (7)$$

where BCF (ml/g) is the equilibrium bioconcentration factor of the sorbent. And therefore

$$Q = \frac{C_w(t=\infty)}{M} \times \mathrm{BCF}. \quad (8)$$

The curve fitting in this study was performed using the nonlinear regression option of the Statistica® software (StatSoft, Tulsa, OK, USA) to simulate the values of k_1 and k_2, based on Eq. 4 and the data of $C_s(t=\infty)$ and $C_w(t=\infty)$. The BCF value was then calculated by dividing k_1 by k_2.

Results

The wet weight, dry weight, and length of black tiger shrimp were 21.51 ± 1.64 g, 4.89 ± 0.42 g, and 15.49 ± 0.55 cm, respectively, while those of white shrimp were 17.93 ± 1.58 g, 4.34 ± 0.39 g, and 14.61 ± 0.36 cm, respectively. The wet weight, dry weight, surface area, and specific surface area of shells of black tiger shrimp were 0.126 ± 0.015 g, 0.065 ± 0.012 g, 7.08 ± 1.31 cm^2, and 0.011 m^2/g, respectively, while those of shells of white shrimp were 0.093 ± 0.015 g, 0.050 ± 0.006 g, 11.59 ± 1.38 cm^2, and 0.023 m^2/g, respectively. The shell of black tiger shrimp contained 46.09 ± 11.39% water of the total wet weight. The water in the shell of white shrimp was 44.62 ± 6.40% of total wet weight. The protein and chitin in the shell of black tiger were 22.83 ± 5.64% and 32.13 ± 7.94% of dry weight, respectively, while those in the shell of white shrimp were 25.85 ± 3.71% and 41.41 ± 5.94% dry weight.

Analysis of variance (ANOVA) on the resulting data showed that the As concentration in water did not change significantly during the exposure experiments for black tiger shrimp ($F = 903.56$, $n = 90$, $P < 0.05$) or for white shrimp ($F = 1010.71$, $n = 90$, $P < 0.05$) (Tables 1 and 2). The As level in shrimp shell, however, increased significantly compared with the initial As level. The As level in the shell of black tiger shrimp showed a significant positive relation to exposure time (Fig. 1). A similar phenomenon was also found in white shrimp (Fig. 2). The uptake of As in shrimp shell was higher initially, reducing with increasing time, and reached an equilibrium level. The shrimp shells exposed to the solutions with As concentrations 20–100 mg/l reached an equilibrium status within 96 h, while they did not reach an equilibrium status under 0–10 mg/l during the 96-h period. The pH values of the solutions remained between 6.03 and 7.02.

Table 1 The values of pH, the As level in the shell of black tiger shrimp, and the actual As concentration of water at different exposure time under various As concentrations (C_w)

C_w (mg/l)	pH	Time (h)								
		0	3	6	12	24	48	96	168	336
0	6.98 ± 0.17	0.23 ± 0.07[a]	0.28 ± 0.20[a]	0.22 ± 0.07[a]	0.23 ± 0.16[a]	0.17 ± 0.07[a]	0.21 ± 0.06[a]	0.31 ± 0.41[a]	0.30 ± 0.30[a]	0.25 ± 0.28[a]
		0.04 ± 0.02[b]	0.02 ± 0.01[b]	0.01 ± 0.01[b]	0.00 ± 0.00[b]	0.02 ± 0.02[b]	0.04 ± 0.01[b]	0.02 ± 0.01[b]	0.01 ± 0.00[b]	0.01 ± 0.00[b]
1	6.03 ± 0.14	0.78 ± 0.04[a]	0.46 ± 0.04[a]	0.58 ± 0.07[a]	1.62 ± 1.26[a]	3.38 ± 2.28[a]	4.32 ± 1.53[a]	6.56 ± 3.96[a]	5.30 ± 1.49[a]	9.35 ± 3.02[a]
		1.16 ± 0.90[b]	0.96 ± 0.28[b]	1.14 ± 0.35[b]	0.79 ± 0.59[b]	1.02 ± 0.30[b]	1.26 ± 0.61[b]	0.87 ± 0.50[b]	0.98 ± 0.35[b]	1.29 ± 0.54[b]
2	6.03 ± 0.25	0.52 ± 0.27[a]	0.69 ± 0.34[a]	1.06 ± 0.49[a]	1.25 ± 0.47[a]	1.90 ± 0.94[a]	3.92 ± 1.41[a]	4.04 ± 0.67[a]	5.62 ± 1.21[a]	8.90 ± 0.65[a]
		1.84 ± 0.81[b]	2.10 ± 0.47[b]	2.12 ± 1.54[b]	1.78 ± 0.38[b]	1.89 ± 0.68[b]	2.24 ± 0.54[b]	2.12 ± 1.08[b]	1.74 ± 1.01[b]	2.19 ± 0.85[b]
5	6.30 ± 0.27	0.95 ± 0.27[a]	1.56 ± 0.19[a]	1.59 ± 0.51[a]	4.26 ± 1.36[a]	6.01 ± 3.42[a]	8.42 ± 3.02[a]	10.34 ± 3.45[a]	13.28 ± 19.24[a]	19.24 ± 8.02[a]
		5.26 ± 2.78[b]	5.11 ± 0.97[b]	4.88 ± 2.00[b]	4.80 ± 1.54[b]	5.31 ± 1.47[b]	5.20 ± 0.80[b]	4.67 ± 2.72[b]	5.48 ± 1.56[b]	5.05 ± 1.12[b]
10	6.17 ± 0.11	1.01 ± 0.62[a]	5.10 ± 2.11[a]	5.04 ± 2.45[a]	17.40 ± 3.81[a]	13.09 ± 3.55[a]	25.40 ± 6.61[a]	30.38 ± 18.74[a]	41.07 ± 7.48[a]	53.68 ± 14.94[a]
		9.68 ± 6.50[b]	9.74 ± 6.11[b]	11.45 ± 3.40[b]	11.64 ± 3.84[b]	9.15 ± 4.57[b]	9.48 ± 3.95[b]	10.85 ± 6.96[b]	11.15 ± 3.87[b]	10.33 ± 4.57[b]
20	6.15 ± 0.09	0.10 ± 0.04[a]	23.07 ± 9.21[a]	34.87 ± 13.25[a]	55.83 ± 27.14[a]	65.33 ± 18.29[a]	71.17 ± 20.01[a]	77.50 ± 11.82[a]	76.75 ± 19.64[a]	77.08 ± 17.98[a]
		21.45 ± 7.32[b]	20.10 ± 3.2[b]	19.41 ± 5.52[b]	21.37 ± 8.77[b]	18.27 ± 8.45[b]	19.78 ± 5.84[b]	22.50 ± 2.64[b]	17.87 ± 8.40[b]	19.78 ± 11.92[b]
40	6.37 ± 0.18	0.80 ± 0.55[a]	41.00 ± 25.71[a]	68.26 ± 29.86[a]	89.47 ± 14.05[a]	93.66 ± 39.51[a]	115.83 ± 32.07[a]	123.85 ± 50.23[a]	120.98 ± 44.91[a]	118.02 ± 88.43[a]
		43.54 ± 13.08[b]	38.69 ± 4.98[b]	39.71 ± 11.91[b]	37.58 ± 14.07[b]	44.45 ± 19.82[b]	41.69 ± 18.14[b]	38.10 ± 21.18[b]	40.84 ± 12.05[b]	45.52 ± 19.82[b]
60	6.41 ± 0.18	0.39 ± 0.17[a]	194.50 ± 89.07[a]	276.67 ± 92.84[a]	347.67 ± 118.24[a]	407.80 ± 139.99[a]	352.42 ± 210.69[a]	452.33 ± 161.02[a]	386.06 ± 143.5[a]	400.38 ± 256.12[a]
		64.85 ± 21.04[b]	58.54 ± 15.67[b]	60.88 ± 21.41[b]	65.78 ± 12.51[b]	57.57 ± 20.31[b]	54.32 ± 21.01[b]	59.70 ± 4.89[b]	62.88 ± 15.87[b]	64.32 ± 27.15[b]
80	6.70 ± 0.53	0.64 ± 0.11[a]	266.67 ± 107.72[a]	288.33 ± 207.58[a]	399.67 ± 179.61[a]	269.08 ± 126.89[a]	447.78 ± 229.81[a]	628.33 ± 259.91[a]	490.56 ± 389.01[a]	408.92 ± 210.67[a]
		78.39 ± 32.01[b]	81.89 ± 12.84[b]	85.76 ± 8.04[b]	76.89 ± 23.32[b]	73.04 ± 19.25[b]	87.08 ± 8.10[b]	77.56 ± 17.14[b]	84.37 ± 21.01[b]	80.87 ± 24.15[b]
100	6.60 ± 0.08	0.34 ± 0.31[a]	337.67 ± 21.89[a]	407.33 ± 245.68[a]	517.33 ± 184.95[a]	529.67 ± 410.51[a]	430.56 ± 267.58[a]	586.57 ± 127.13[a]	510.58 ± 294.51[a]	490.01 ± 263.47[a]
		111.56 ± 15.10[b]	107.84 ± 11.44[b]	104.51 ± 11.47[b]	94.41 ± 25.56[b]	89.45 ± 27.40[b]	104.57 ± 28.45[b]	119.10 ± 27.45[b]	94.47 ± 24.75[b]	97.45 ± 25.36[b]

[a] The As level in the shell (μg/g)

[b] The actual As concentration in water (mg/l)

Table 2 The values of pH, the As level in the shell of white shrimp, and the actual As concentration in water measured at different exposure time under various As concentrations (C_w)

C_w (mg/l)	pH	Time (h)								
		0	3	6	12	24	48	96	168	336
0	7.04 ± 0.21	0.17 ± 0.08[a]	0.21 ± 0.04[a]	0.24 ± 0.17[a]	0.20 ± 0.11[a]	0.15 ± 0.04[a]	0.21 ± 0.10[a]	0.25 ± 0.17[a]	0.17 ± 0.04[a]	0.21 ± 0.13[a]
		0.01 ± 0.01[b]	0.02 ± 0.01[b]	0.02 ± 0.01[b]	0.02 ± 0.00[b]	0.05 ± 0.01[b]	0.10 ± 0.07[b]	0.05 ± 0.01[b]	0.02 ± 0.01[b]	0.01 ± 0.01[b]
1	6.18 ± 0.50	0.26 ± 0.05[a]	0.65 ± 0.23[a]	0.95 ± 0.30[a]	1.90 ± 1.08[a]	2.84 ± 0.65[a]	2.91 ± 1.40[a]	4.38 ± 1.27[a]	7.41 ± 1.67[a]	7.79 ± 0.65[a]
		1.08 ± 0.77[b]	1.05 ± 0.39[b]	1.22 ± 0.13[b]	1.20 ± 0.80[b]	1.13 ± 0.41[b]	0.99 ± 0.62[b]	0.94 ± 0.36[b]	1.09 ± 0.18[b]	0.95 ± 0.57[b]
2	6.22 ± 0.50	0.37 ± 0.06[a]	1.79 ± 0.15[a]	2.65 ± 0.24[a]	3.54 ± 0.21[a]	5.57 ± 0.64[a]	7.27 ± 1.03[a]	9.44 ± 1.77[a]	11.47 ± 3.76[a]	13.08 ± 2.83[a]
		2.04 ± 0.78[b]	2.06 ± 0.65[b]	1.86 ± 0.46[b]	2.13 ± 1.00[b]	2.10 ± 1.11[b]	1.81 ± 1.24[b]	1.88 ± 0.51[b]	2.03 ± 0.78[b]	1.94 ± 0.66[b]
5	6.27 ± 0.49	0.98 ± 0.62[a]	1.62 ± 1.11[a]	1.58 ± 1.45[a]	4.18 ± 3.81[a]	5.15 ± 3.55	10.54 ± 6.61[a]	12.60 ± 8.74	15.88 ± 7.48[a]	19.55 ± 15.41[a]
		4.85 ± 1.48[b]	5.27 ± 1.55[b]	4.10 ± 1.04[b]	4.91 ± 2.36[b]	4.97 ± 0.98[b]	5.17 ± 1.92[b]	5.30 ± 2.44[b]	4.86 ± 1.34[b]	4.88 ± 2.31[b]
10	6.37 ± 0.50	0.24 ± 0.04[a]	6.79 ± 0.51[a]	20.91 ± 0.48[a]	19.99 ± 1.74[a]	27.90 ± 4.24[a]	25.38 ± 1.83[a]	35.15 ± 4.11	42.78 ± 6.49[a]	50.09 ± 29.05[a]
		11.94 ± 3.94[b]	12.64 ± 7.11[b]	9.48 ± 4.41[b]	9.84 ± 7.20[b]	10.68 ± 3.20[b]	11.04 ± 0.54[b]	9.76 ± 6.10[b]	10.45 ± 3.65[b]	10.78 ± 6.66[b]
20	6.42 ± 0.55	0.10 ± 0.04[a]	23.40 ± 14.33[a]	48.10 ± 15.58[a]	60.27 ± 35.01[a]	79.65 ± 33.65[a]	63.91 ± 18.79[a]	73.31 ± 31.42[a]	75.69 ± 23.21[a]	70.36 ± 7.35[a]
		19.78 ± 8.91[b]	18.98 ± 6.65[b]	21.87 ± 5.55[b]	19.44 ± 8.26[b]	23.66 ± 10.63[b]	21.65 ± 8.12[b]	23.15 ± 3.94[b]	19.56 ± 9.49[b]	19.97 ± 8.99[b]
40	6.51 ± 0.62	0.28 ± 0.55[a]	31.48 ± 22.64[a]	66.51 ± 29.65[a]	88.69 ± 24.04[a]	95.49 ± 4.68[a]	104.98 ± 33.15[a]	106.32 ± 48.27[a]	105.66 ± 72.08[a]	97.08 ± 27.80[a]
		46.02 ± 15.62[b]	40.20 ± 13.64[b]	35.65 ± 12.25[b]	41.36 ± 18.39[b]	38.91 ± 11.25[b]	39.65 ± 11.94[b]	42.01 ± 20.03[b]	44.62 ± 13.65[b]	37.15 ± 7.95[b]
60	6.70 ± 0.53	0.37 ± 0.09[a]	106.34 ± 49.58[a]	128.45 ± 65.25[a]	149.77 ± 55.25[a]	169.42 ± 98.56[a]	160.26 ± 35.98[a]	165.95 ± 71.15[a]	152.94 ± 26.35[a]	171.65 ± 105.21[a]
		59.65 ± 11.03[b]	57.32 ± 20.30[b]	64.38 ± 1.65[b]	61.25 ± 22.01[b]	62.35 ± 5.14[b]	59.24 ± 16.25[b]	54.95 ± 17.68[b]	58.47 ± 26.23[b]	62.37 ± 5.64[b]
80	6.85 ± 0.69	0.29 ± 0.15[a]	114.67 ± 80.15[a]	118.54 ± 38.94[a]	147.67 ± 88.51[a]	167.21 ± 100.26[a]	180.95 ± 29.15[a]	194.77 ± 68.24[a]	215.32 ± 118.54[a]	189.54 ± 36.87[a]
		85.25 ± 9.25[b]	78.01 ± 18.25[b]	74.69 ± 12.15[b]	88.35 ± 21.32[b]	81.27 ± 21.45[b]	79.62 ± 15.24[b]	88.47 ± 15.30[b]	75.68 ± 26.82[b]	84.26 ± 13.15[b]
100	7.02 ± 0.92	0.32 ± 0.18[a]	152.67 ± 97.25[a]	168.64 ± 78.24[a]	233.54 ± 139.54[a]	229.61 ± 120.49[a]	226.67 ± 103.25[a]	270.65 ± 127.13[a]	278.69 ± 88.95[a]	286.91 ± 201.63[a]
		106.54 ± 12.56[b]	98.67 ± 3.64[b]	113.02 ± 14.09[b]	101.26 ± 23.64[b]	98.04 ± 12.37[b]	99.57 ± 21.75[b]	118.62 ± 22.27[b]	111.14 ± 16.98[b]	94.25 ± 23.10[b]

[a] The As level in the shell (μg/g)

[b] The actual As concentration in water (mg/l)

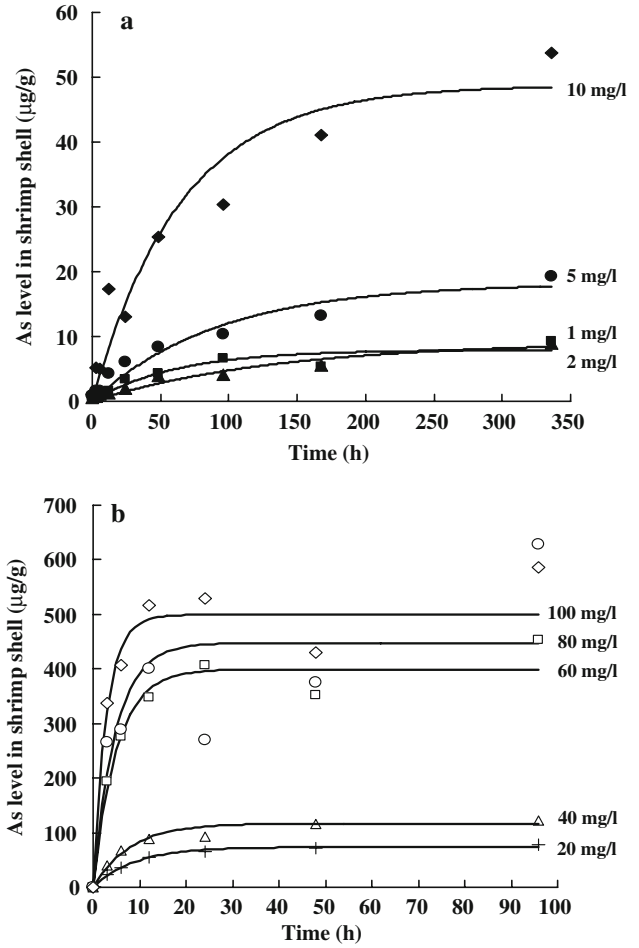

Fig. 1 Plot of the relation between the As level of black tiger shrimp shell and the exposure time under various As concentrations in water (**a** 1–10 mg/l; **b** 20–100 mg/l)

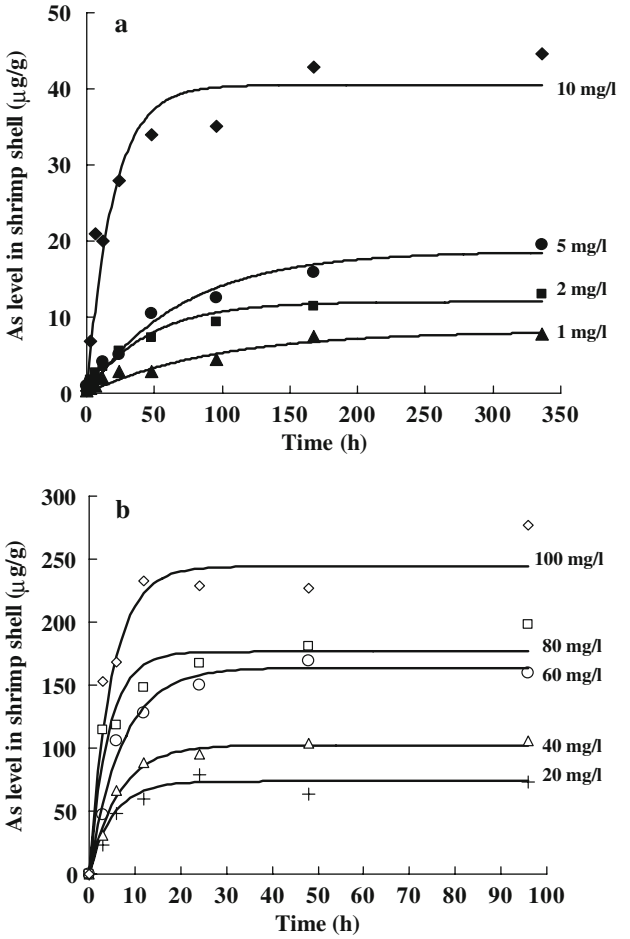

Fig. 2 Plot of the relation between the As level of white shrimp shell and the exposure time under various As concentrations in water (**a** 1–10 mg/l; **b** 20–100 mg/l)

The kinetic uptake data were successfully modeled using the first-order one-compartment model incorporating nonlinear adsorption, with high R^2 values of 0.67–0.99. The k_1, k_2, and BCF values of black tiger shrimp were 0.034–1.722 ml/g/day, 0.007–0.345 g/g/day, and 5.08 ± 1.56 ml/g (Table 3), while those of white shrimp were 0.053–0.523 ml/g/day, 0.011–0.237 g/g/day, and 3.95 ± 1.88 ml/g, respectively (Table 4). The values of BCF showed that the shrimp shells can accumulate a high level of waterborne As. The sorption capacities of these shells were calculated based on Eq. 5. The sorption capacities of black tiger shrimp shell and white shrimp shell were 1.08×10^{-4}–6.66×10^{-3}, and 1.04×10^{-4}–3.26×10^{-3} mmol/g, respectively (Table 5). ANOVA of the resulting data showed that the sorption capacities of the shell of black tiger shrimp did not significantly differ from those of white shrimp ($F = 1.50$, $n = 18$, $P > 0.05$).

A time needed to reach equilibrium status, i.e., equilibrium time, of longer than 336 h was calculated using the first-order one-compartment model (Eq. 4) and the nonlinear regression option of the Statistica® software. The resulting data for equilibrium time under various As concentrations are shown in Fig. 3. The equilibrium time

Table 3 Values of uptake rate constant (k_1), depuration rate constant (k_2), BCF, and R^2 of black tiger shrimp shell under various As concentrations

C_w (mg/l)	k_1 (ml/g per day)	k_2 (g/g per day)	BCF (ml/g)	R^2
1	0.129	0.016	8.06	0.98
2	0.034	0.007	4.86	0.97
5	0.040	0.011	4.00	0.99
10	0.075	0.015	5.00	0.90
20	0.411	0.112	3.67	0.99
40	0.366	0.125	2.93	0.91
60	1.310	0.197	6.65	0.99
80	1.168	0.209	5.59	0.67
100	1.722	0.345	4.99	0.88
Mean			5.08 ± 1.56	

Table 4 Values of uptake rate constant (k_1), depuration rate constant (k_2), BCF, and R^2 of white shrimp shell under various As concentrations

C_w (mg/l)	k_1 (ml/g per day)	k_2 (g/g per day)	BCF (ml/g)	R^2
1	0.086	0.011	7.82	0.96
2	0.134	0.022	6.09	0.95
5	0.053	0.014	3.79	0.97
10	0.207	0.051	4.06	0.82
20	0.445	0.118	3.77	0.91
40	0.399	0.152	2.63	0.99
60	0.379	0.139	2.73	0.99
80	0.523	0.237	2.21	0.99
100	0.501	0.205	2.44	0.95
Mean			3.95 ± 1.88	

Table 5 Sorption capacities of the shells of black tiger shrimp and white shrimp under various As concentration in water

As concentration (mg/l)	Black tiger shrimp (mmol/g)	White shrimp (mmol/g)
1	1.08×10^{-4}	1.04×10^{-4}
2	1.30×10^{-4}	2.47×10^{-4}
5	2.67×10^{-4}	2.53×10^{-4}
10	6.67×10^{-4}	5.42×10^{-4}
20	9.80×10^{-4}	1.01×10^{-4}
40	1.56×10^{-3}	1.40×10^{-3}
60	5.33×10^{-3}	2.18×10^{-3}
80	5.97×10^{-3}	2.36×10^{-3}
100	6.66×10^{-3}	3.26×10^{-3}

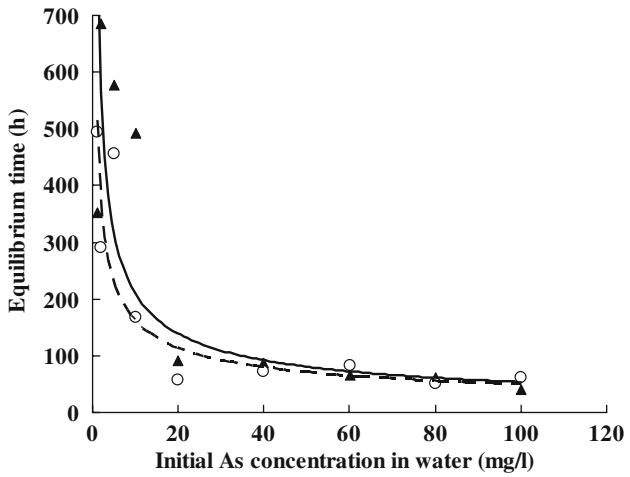

Fig. 3 Plot of the relation between the equilibrium time for shells of the two shrimp species, black tiger shrimp (*filled triangle*) and white shrimp (*open circle*), and the As concentration in water

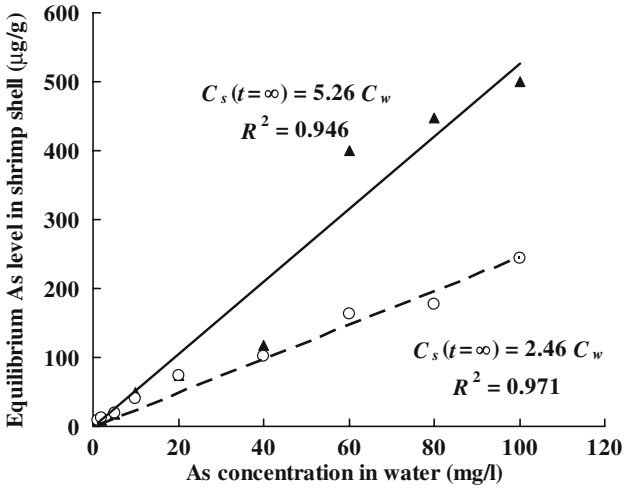

Fig. 4 Plot of the relation between the equilibrium As level in shells of the two shrimp species, black tiger shrimp (*filled triangle*) and white shrimp (*open circle*), and the As concentration in water. C_s is the equilibrium level of pollutant in sorbent (μg/g); $C_w(t = \infty)$ is the concentration of pollutant in water (mg/l)

showed a significant negative relation to the initial As concentration in water (Fig. 3). The shrimp shells of the two species had higher equilibrium As levels under higher initial As concentrations in water (Fig. 4). This showed that the shrimp shells have different sorption capacities under various initial As concentrations in ambient water. When the initial As concentration in water is higher, the shrimp shell showed a higher sorption capacity.

Figures 5 and 6 show that the As levels in shrimp shell changed under various As exposure concentrations in water at different times. Both the data obtained from the actual measurements (Fig. 5) and the data obtained based on the As level in shrimp shell (Fig. 6) showed that the decrease of As concentration in water could be neglected compared with the increase of the As level in shrimp shell.

Discussion

The BCF of the shell of black tiger shrimp did not significantly differ from that of white shrimp. The sorption capacity also did not show a significant difference between the two shrimp species. The first-order one-compartment model (Eq. 4) was successfully fitted to the uptake curve of As levels in shrimp shell. The high R^2 values (generally higher than 0.9) indicated that this model is appropriate to predict the As level in shrimp shell at different time points under a certain concentration. In this study, the exposure experiment was conducted under a condition of high As concentrations (1–100 mg/l) in a large quantity of water (400 ml) and low quantity of shrimp shells (approximately

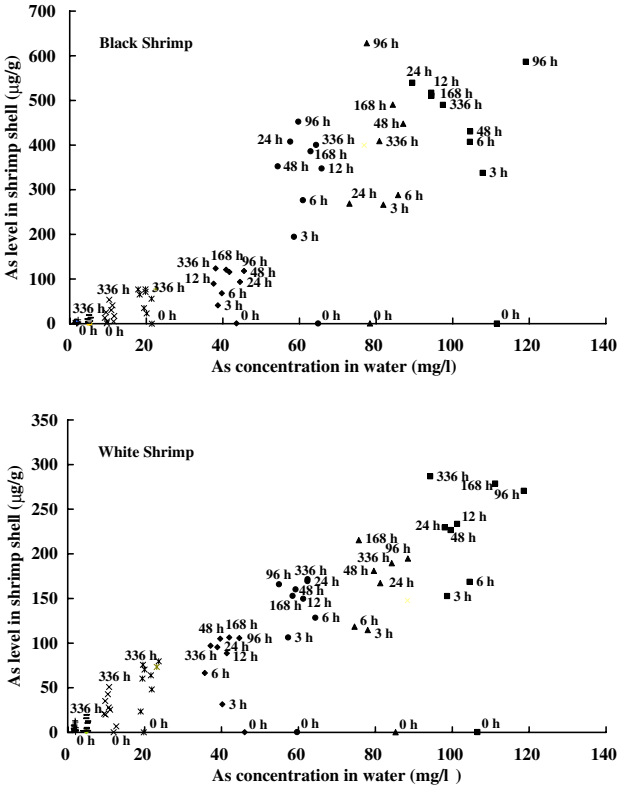

Fig. 5 Plot of the As level of shrimp shell and the As concentration in water, based on the actual measurement, at various exposure times. Symbols indicating the original As concentrations in water: *filled square* 100 mg/l, *filled triangle* 80 mg/l, *filled circle* 60 mg/l, *filled diamond* 40 mg/l, *asterisk* 20 mg/l, *times* 10 mg/l, *minus* 5 mg/l, *plus* 3 mg/l, *hyphen* 1 mg/l

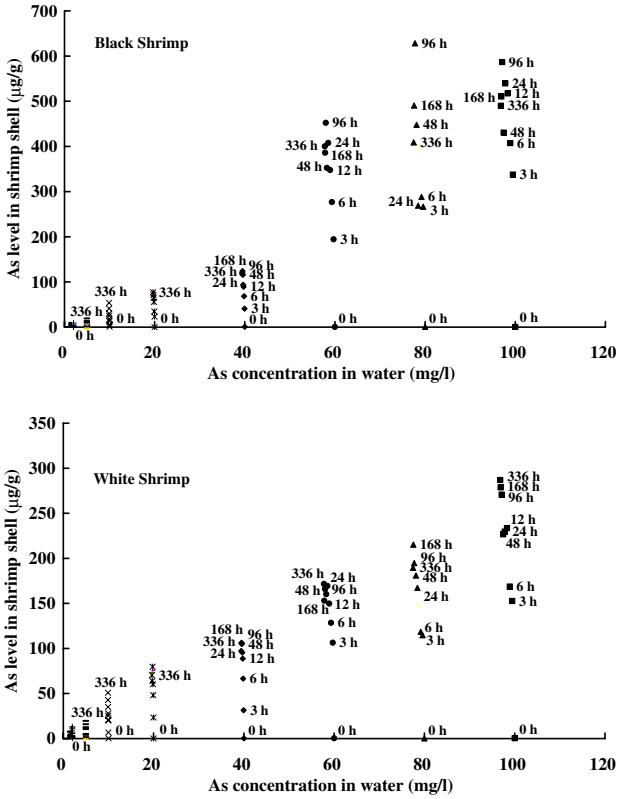

Fig. 6 Plot of the As level of shrimp shell and the As concentration in water, calculated based on the As level of shrimp shell, at various exposure times. Symbols indicating the original As concentrations in water: *filled square* 100 mg/l, *filled triangle* 80 mg/l, *filled circle* 60 mg/l, *filled diamond* 40 mg/l, *asterisk* 20 mg/l, *times* 10 mg/l, *minus* 5 mg/l, *plus* 3 mg/l, *hyphen* 1 mg/l

0.05 g dry weight per piece). In this case the decrease of As in water can be neglected because of the large quantity of water and high As concentrations in water, but the increase of As in shrimp shells cannot be neglected because of the small quantity of shrimp shells. Under this condition of high pollutant concentration in a large quantity of water and small quantity of sorbents, Eq. 8 can simply be used to calculate the sorption capacity of sorbent, based on the equilibrium concentration of pollutant in water, the molecular weight of pollutant, and the BCF of the sorbent.

The first-order one-compartment model is usually used to simulate the bioaccumulation, including bioconcentration and/or biomagnification, of pollutants in living organisms. The uptake rate (k_1) and depuration rate (k_2) could be influenced by the active intake/elimination behaviors of organisms and/or be influenced passively by the concentration gradients. Since shrimp shell is a non-living matter, k_1 and k_2 are only passively influenced by the concentration gradients. Under this situation, the first-order one-compartment model should still be suitable to simulate the As level in shrimp shell based on k_1 and k_2 of the shrimp shell.

Dambies et al. [17] have shown that the sorption capacity of raw chitosan beads for As(III) removal remained constant, independently of the pH. The influence of pH change (6.03–7.02) on the sorption capacity of shrimp shell in this study can be neglected. Many previous studies have shown that pollutant uptake in a sorbent decreases with increasing time. Evans et al. [23] indicated that, following the stage of initial adsorption at the surface of sorbent, the uptake rate is controlled by intraparticle diffusion in the sorbent. In our study, we found that the uptake rate is influenced simultaneously by k_1 and k_2 of the sorbent. Normally the sorption capacity of a sorbent should be a constant. Our study showed that the sorption capacity can be influenced by the initial pollutant concentration in water. Shrimp shells exposed to higher As concentrations can reach equilibrium status within a shorter period, indicting that the shrimp shells have higher sorption capacities under higher As concentrations in water. The exposure experiments in this study took place in static water without any agitation. Under this condition, a greater concentration gradient on the interface between water and

shrimp shell, which remains undisturbed around the shell, forms a concentration boundary layer (i.e., diffusion layer) between the shell surface and the bulk solution. The higher the As concentration in water, the more it enhances the absorption of As on shrimp shell and the earlier the As level on shrimp shell reaches the equilibrium status.

The BCF of the shell of black tiger shrimp did not significantly differ from that of white shrimp. The sorption capacity also did not show a significant difference between the two shrimp species. Dambies et al. [17] noted that the sorption capacities of activated carbon, activated alumina, activated mineral surfaces, silica, bauxite, coral limestone, and chitin were commonly lower than 0.1–0.2 mmol/g. Among these sorbents, activated carbon, and activated alumina, currently regarded as advantageous sorbents, have sorption capacities of 0.60 and 0.27 mmol/g, respectively [24, 25]. The As-removal capacity of shrimp shell was lower than those of natural and chemical sorbents. A large amount of shrimp shells might be needed to remove a small amount of As from a solution. Besides circulating the solution to stream over the shrimp shells, renewing the shrimp shells after a certain expose period will be helpful to compensate for the low As sorption capacity of shrimp shell. Since shrimp shell is a waste product, the cost of this sorbent may be lower than that of the other mentioned sorbents.

The sorption capacities (1–2 mmol/g for Pb, Cd, Cu, and Cr removal) of pulverized crab shell [19] were higher than the sorption capacity (1.04×10^{-4}–6.66×10^{-3} mmol/g for As(III) removal) of raw shrimp shell (this study). Compared with the sorption capacities (2.52–6.2 mmol/g for Cu(II) removal and 1.9×10^{-2} mmol/g for As(III) removal) of prepared chitosan bead [17, 21] the sorption capacity of raw shrimp shell (this study) was also relatively low. The specific surface areas of raw shrimp shell were 0.011–0.023 m^2/g, while those of the crab shell particle and the chitosan bead were 13.35 and 12.50 m^2/g, respectively. This difference in specific surface area could be the main reason for the significant difference in sorption capacity. Compared with the chitin level (26.65% dry weight) in crab shell, the two species of shrimp contained higher chitin levels (32.13 ± 7.94% dry weight for black tiger shrimp and 41.41 ± 5.94% dry weight for white shrimp) in the shell. This indicates that shrimp shell can be an ideal material as a potential sorbent for pollutants removal.

High concentrations of As were found in cultured fish from southwest Taiwan since As-contaminated groundwater was used for aquaculture in this area [5–7]. Several studies have been conducted to demonstrate that use of As-contaminated groundwater for aquaculture may cause overexposure of As in fish [5, 6, 26]. Ingestion of As-contaminated fish could result in As accumulation in inhabitants and lead to adverse health effects [7, 27]. Many cultured stocks, such as eel, carp, and shrimp, from this area may also be contaminated by As. Public health experts are concerned since it has been known for years that using groundwater for aquaculture is a common situation in the As-contaminated area in Taiwan [28] but few As-removal techniques have been developed. With a capacity of removing As from aqueous solution, shrimp shells may have the potential to remove As from As-contaminated pond water.

From the results of our study it can be concluded that, even when not much As is removed from the water because of the small amount and low absorption capacity of shrimp shell, the shrimp shell is still helpful to remove As because it is cheap and can therefore be used in large quantities. Because the absorption capacity of raw shrimp shell is rather low, a large amount of shells needs to be used for the removal of As from the aqueous solution. After the shells are chemically satiated by As, the shell scrap may cause environmental problems. Dambies et al. [17] have provided useful information to solve these problems. They have noted that phosphate anion can strongly reduce As sorption, and this property is useful for the desorption of As-saturated sorbents. Phosphoric acid at an intermediary concentration (0.1–0.2 M) was suggested to be used for the recovery of As and the regeneration of the sorbents. It is necessary in further studies to research the suitability of using phosphate acid for the desorption of As from shrimp shell.

The removal of shells from shrimps, as well as other shellfish, crabs, and krill creates a large amount of waste [29]. Using these shell wastes could also increase the additional value of fishery and aquaculture products. It has been shown that the use of shrimp shell for As removal appears to be technically feasible. Shrimp shell, as a natural material, is ideally available with low cost and is environmentally friendly. Moreover, being composed entirely of aquacultural and fishing industry waste, it helps in reduction of waste generation. Because shrimp shells can be easily obtained, employed, and disposed of with little cost, they could be good candidates for adsorption of As in wastewater streams. The use of shrimp shells as sorbents should be investigated as a replacement for current costly methods of removing heavy metals from solution. The mechanism of As adsorption in shrimp shells should be revealed. To make the As removal more efficient, the use of a significant amount of shells of shrimp shell is required, which implies that more research should be done on the desorption of As from the shells. Furthermore, studies concerning As as well as the other metals adsorbed by shrimp shells need to be undertaken to provide more information on shrimp shells as low-cost sorbents.

Acknowledgments This work was financially supported by the National Science Council of the Republic of China (NSC 93-2313-B-343-001). The authors thank Dr. G.P. Chang-Chien for providing analysis facilities and Miss W.C. Wu for deploying experimental assistance. An earlier draft of this manuscript benefited from the comments of Mr. R. Regout.

References

1. Mandal BK, Suzuki KT (2002) Arsenic round the world: a review. Talanta 58:201–235
2. Ng JC, Wang JP, Shraim A (2003) A global health problem caused by arsenic from natural sources. Chemosphere 52:1353–1359
3. Wu MM, Kuo TL, Hwang YH, Chen CJ (1989) Dose-response relation between As concentration in well water and mortality from cancers and vascular disease. Am J Epidemiol 130:1123–1131
4. Chen CJ, Hsu LI, Tesng CH, Hsueh YM, Chiou HY (1999) Emerging epidemics of arseniasis in Asia. In: Chappell WR, Abernathy CO, Calderon RL (eds) Arsenic exposure and health effects. Elsevier, Amsterdam, pp 113–121
5. Lin MC, Liao CM, Liu CW, Singh S (2001) Bioaccumulation of arsenic in aquacultural large-scale mullet *Liza macrolepis* from the blackfoot disease area in Taiwan. Bull Environ Contam Toxicol 67:91–97
6. Lin MC, Cheng HH, Lin HY, Chen YC, Chen YP, Liao CM, Chang-Chien GP, Dai CF, Han BC, Liu CW (2004) Arsenic accumulation and acute toxicity in milkfish (*Chanos chanos*) from blackfoot disease area in Taiwan. Bull Environ Contam Toxicol 72:248–254
7. Lin MC, Lin HY, Cheng HH, Chen YC, Liao CM, Shao KT (2005) Risk assessment of arsenic exposure from consumption of cultured milkfish, *Chanos chanos* (Forsskål), from the arsenic-contaminated area in southwestern Taiwan. Bull Environ Contamin Toxicol 75:637–644
8. Chen CJ, Wu MM, Kuo TL (1988) Arsenic and cancers. Lancet 1:414–415
9. Chiou HY, Hsueh YM, Liaw KF, Horng SF, Chiang MH, Pu YS, Lin JSN, Huang CH, Chen CJ (1995) Incidence of internal cancers and ingested inorganic As: a seven-year follow-up study in Taiwan. Cancer Res 55:1296–1300
10. Kartinen EO, Martin CJ (1995) An overview of arsenic removal processes. Desalination 103:79–88
11. Chakravarty S, Dureja V, Bhattacharyya G, Maity S, Bhattacharjee S (2002) Removal of arsenic from groundwater using low cost ferruginous manganese ore. Water Res 36:625–632
12. Deans JR, Dixon BG (1992) Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers. Water Res 26:469–472
13. Veglio F, Beolchini F (1997) Removal of heavy metals by biosorption: a review. Hydrometallurgy 44:301–316
14. Elizalde-González MP, Mattusch J, Einicke W-D, Wennrich R (2003) Sorption on natural solids for arsenic removal. Chem Eng J 81:187–195
15. Katsoyiannis IA, Zouboulis AI (2004) Application of biological processes for the removal of arsenic from groundwaters. Water Res 38:17–26
16. Bailey SE, Olin TJ, Bricka RM, Adrian DD (1999) A review of potentially low costs sorbents for heavy metals. Water Res 33:2469–2479
17. Dambies L, Vincent T, Guiba E (2002) Treatment of arsenic-containing solutions using chitosan derivatives: uptake mechanism and sorption performances. Water Res 36:3699–3710
18. Ilyina AV, Tikhonov VE, Varlamov VP, Radigina LA, Tatarinova NY, Yamskov IA (1995) Preparation of affinity sorbents and isolation of individual chitinases from a crude supernatant produced by *Streptomyces kurssanovii* by a one-step affinity chromatographic system. Biotech Appl Biochem 21:139–148
19. An HK, Park BY, Kim DS (2001) Crab shell for the removal of heavy metals from aqueous solution. Water Res 35:3551–3556
20. Modak JM, Natarajan KA (1995) Biosorption of metals using nonliving biomass: a review. Miner Metallurgy Proc 12:189–196
21. Juang RS, Wu FC, Tseng RL (2001) Solute adsorption and enzyme immobilization on chitosan beads prepared from shrimp shell wastes. Bioresour Technol 80:187–193
22. Lin MC, Liao CM (1999) $^{65}Zn(II)$ accumulation in soft tissue and shell of abalone *Haliotis divesicolor supertexta* via the alga *Gracilaria tenuistipitata* var liui and the ambient water. Aquaculture 178:89–101
23. Evans JR, Davids WG, MacRae JD, Amirbahman A (2002) Kinetics of cadmium uptake by chitosan-based crab shells. Water Res 36:3219–3226
24. Pattanayak J, Mondal K, Mathew S, Lalvani SB (2000) A parametric evaluation of the removal of As (V) and As (III) by carbon-based adsorbents. Carbon 38:589–596
25. Yuan T, Hu JY, Ong SL, Luo QF, Ng WJJ (2002) Arsenic removal from household drinking water by adsorption. Environ Sci Health A 37:1721–1736
26. Liao CM, Ling MP (2003) Assessment of human health risks for arsenic bioaccumulation in tilapia (*Oreochromis mossambicus*) and large-scale mullet (*Liza macrolepis*) from blackfoot disease area in Taiwan. Arch Environ Contam Toxicol 45:264–272
27. Liao CM, Chen BC, Singh S, Lin MC, Liu CW, Han BC (2003) Acute toxicity and bioaccumulation of arsenic in tilapia (*Oreochromis mossambicus*) from a blackfoot disease area in Taiwan. Environ Toxicol 18:252–259
28. Chou BYH, Liao CM, Lin MC, Cheng HH (2006) Toxicokinetics/toxicodynamics of arsenic for farmed juvenile milkfish *Chanos chanos* and human consumption risk in BFD-endemic area of Taiwan. Environ Int 32:545–553
29. Yang TC, Zall RR (1984) Adsorption of metals by natural polymers generated from sea food processing wastes. Ind Eng Chem Prod Res Dev 23:168–172