



A comparative study on stabilization of available As in highly contaminated hazardous solid waste

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ARTICLE INFO

Article history:

Received 4 May 2009

Received in revised form 14 August 2009

Accepted 8 September 2009

Available online 16 September 2009

Keywords:

As
Chemical fixation
Hazardous solid waste
Leaching
Speciation

ABSTRACT

The stabilization of available As was conducted by chemical fixation after Fenton process in a solid waste residual (SWR) from organic arsenic industry. Single as well as combined fixation treatments by using ferric sulfate (FS), magnesium chloride (MC) and calcium hydroxide (CH) were carried out to assess and to evaluate the fixation effect through toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP) and sequential extraction procedure (SEP). The effect of aging treatment on the fixation of available As in SWR was also investigated. Experimental result showed that the optimal molar ratios for Fe:As, Mg:As and Ca:As were 2:1, 3:1 and 2:1, respectively, and the combination fixation FS+MC+CH was found to be the optimal fixation treatment. With respect to the leaching behavior and the speciation migration of As in SWR after stabilization, TCLP, SPLP and SEP represent a pertinent and inseparable system for the fixation effect evaluation. The fixation treatment of available As in SWR could be evaluated directly after 3 days and the aging treatment is not needed though it can further enhance the fixation effect.

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1. Introduction

Organic arsenic, including arsanilic acid and roxarsone, has been widely used as feed additive for intensive poultry and swine farming in China. However, the solid waste residue (SWR) produced as by-product was identified as a hazardous waste (No. HW 02-275) since it contains a certain amount of As and aniline [1]. In fact, the SWR synthesis processes are based on arsenic trioxide and aniline, which have been considered as the first classes of toxic compounds with carcinogenic and mutagenic effects. Often, these chemicals are of concern in terms of environmental waste regulation because of their potential adverse effects on public health [2,3]. Therefore, there is an urgent need for a safe and environmentally sound process for the treatment and disposal of such hazardous solid waste.

Since both organic pollutants and metalloid toxicants are presented in SWR, it is hard to deal with them within a single technology. The current paradigm is that a combination of cleanup technologies and stabilization is the best choice for an efficient treatment of such hazardous solid waste [4]. In our previous studies [1], the SWR was at first pretreated by Fenton process, a promising cleanup technology [5], in which H₂O₂ and Fe(II) formed •OH rad-

icals at low pH to oxidize organic contaminants. To our surprise, As(III) was completely oxidized to As(V) accompanied the removal of the organics in the SWR. Those results are consistent with the findings of Hug and Leupin that As(III) could be oxidized by Fenton reagent [6]. These results are also important for the SWR stabilization that will be discussed later because As(III) is listed as 25–60 times more toxic and more mobile than As(V) in the environment [7].

The chemical fixation technologies using inorganic binders such as cement, lime, and pozzolanic materials, proved to be efficient in reducing the solubility of heavy metals in solid waste [8–11]. Recently, they also have been designed to promote the formation of more insoluble As-bearing phases in contaminated soils [12,13]. Chemical reagent such as magnesium, iron and calcic ions can be used as effective reagents in the stabilization of As [13–17]. In addition, many studies also have illustrated the potential for As attenuation via interaction with chemical reagents used and sorption on metal hydroxides [15,17,18]. The studies also confirmed that the contaminated soils were reacted with cooperating fixation solution (ferrous sulfate and/or potassium permanganate and/or calcium carbonate) to promote the formation of insoluble As-bearing phases and thereby decrease the As leachability [19].

However, most of the research works focused on a single chemical reagent, and hence the information on the differences among different chemical reagents and their combination effects are limited [13,20–22]. Furthermore, most of the previous research

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reported the stabilization of As in As-contaminated soil with low content, and none has focused on hazardous solid waste, especially with high As content. Moreover, the determination of total concentrations of metals established cannot give sufficient information to assess the environment impact of the studied substrates [23–25]. The distribution of metals in the various fractions determines their environmental behavior i.e. their mobility, bioavailability and toxicity [24,26,27]. Generally, the toxicity characteristic leaching procedure (TCLP) and the synthetic precipitation leaching procedure (SPLP) cannot provide detail information of the metal fractions in the SWR, especially the most active fraction. The real information of potential environmental risk may be masked. In order to evaluate the fixation treatment effect more precisely, it is necessary to carry out the sequential extraction procedure (SEP), which will help in the evaluation of the leaching behavior and environmental risks of As in SWR.

In this study, we present the remaining results of the As stabilization in the SWR after the pretreatment by Fenton process. Ferric sulfate (FS), magnesium chloride (MC) and calcium hydroxide (CH) were applied in a single or in a combination of fixation treatment to stabilize the available As in the SWR. Various types of analysis including TCLP, SPLP, and SEP were carried out to evaluate the effects and differences of the fixation treatments of As in SWR. In addition, the effect of aging treatment on the fixation of available As in SWR was also investigated. This research aimed at finding the best chemical reagent and/or a combination of reagents combination as well as the optimal parameters to be considered for industrial application. It also aimed to evaluate the fixation treatment more pertinently in long-term industrial application.

2. Experimental

2.1. Sampling and preparation

The SWR sample was collected from Zhejiang Ideal Nutrition Technology Company, one of the world largest arsenical feed additive factories in *Zhoushan, Zhejiang*, east China. The SWR was temporarily dumped in a hillside and covered with a rough cap without conventional pollution prevention facility, such as a watertight cover or an impermeable layer. The dumping volume was approximately $400\text{ m}^2 \times 2\text{ m}$. In order to get a representative SWR sample for this study, over 100 sampling points were selected. For each sampling point, two samples were collected at depths of 0.5 m and 1.5 m, respectively. Finally, samples from the different sampling points were mixed. The mixed SWR sample was separated with 40 mesh sieve firstly. The fraction pass through a sieve of 40 mesh was filled into a flask directly. While the fraction of size >40 mesh was ground by crusher (BB51, Retsch, Germany). The achievable final out-put fineness of the crusher was also set as 40 mesh. Then, the ground fraction was also filled into the flask. Finally, the SWR in the flask was rehomogenized thoroughly by shaking and shaking manually.

After homogenization, the SWR sample was first pretreated by Fenton process to remove the organics (aniline) and oxidize As(III) to As(V) [1]. Subsequently, the pretreated SWR sample was air-dried and ground to 40 mesh by BB51 crusher prior to the fixation tests.

2.2. Analytical methods

The pH of SWR was determined in a solution that was previously prepared by mixing 25 mL of de-ionized water and 5 g of SWR sample. The resulting solution was intermittently stirred for 1 h, and then left standing for 0.5 h. After digestion, the background metal contents in SWR were determined by standard methods described

in U.S. EPA Method 3050. TCLP (U.S. EPA Method 1311) and SPLP (U.S. EPA Method 1312) were conducted to evaluate the quantity of available As in the tailings, respectively. Moreover, the background speciation of As in SWR was conducted by SEP described by Wenzel et al. [28].

2.3. Chemical fixation

In a first step, a series of chemical batch experiments were carried out to study the effect of different kinds of single metal ion on the As immobility in SWR. FS, MC and CH were chosen with, respectively Fe, Mg, and Ca as chemical fixation ions to be evaluated. The molar ratios of each metal ion-to-As, namely Mg:As, Fe:As and Ca:As, were 1:1,2:1, and 3:1, respectively. Meanwhile, treatments without introduction of metal ions were carried out as controls (CK).

In a second step, combinations of fixation treatments were selected based on the effect of the single metal ions, considered in the first step, on the fixation of available As in SWR. Taking the FS as control treatment, three combination fixation treatments including (i) FS + CH; (ii) FS + MC; (iii) FS + MC + CH were examined to find the optimal combination fixation treatment.

Each of the experiments mentioned above was conducted in triplicate. The experimental procedure consists of (i) treating a 50 g weigh SWR sample with metal ion at liquid-to-solid ratio of 1:1.8 (m/v) in 250 mL glass reactors according to our previous semi-solid Fenton process pretreatment [1] to avoid introduction of excess water; (ii) adjust the pH to 6.0 by using concentrated NaOH solution; (iii) stoppering and shaking the glass reactors at 150 rpm under a constant temperature of $23 \pm 0.5^\circ\text{C}$ for 3 days; (iv) keeping the reactors for 1 month under intermittent shaking till the end of experiments.

2.4. Leaching test

In order to assess the fixation treatment effect, both the fixed SWR samples and the CK were subjected to sequential leaching. The leaching tests were conducted by two different methods, including the TCLP using acetic acid as reagent at pH 2.88, and SPLP using a mixture of sulfuric acid and nitric acid at pH 4.20. All the leachate collected after digestion were analyzed for As concentration by inductively coupled plasma-mass spectrometric (ICP-MS) (Agilent, 7500a).

2.5. SEP

To elucidate the distribution and migration of As speciation in the solid phase of fixed SWR, SEP was also carried in accordance with the methods described by Wenzel et al. [28]. Basing on the inherent limitations of chemical extraction, the adopted SEP is designed to target the As fractions primarily associated with (1) non-specifically sorbed; (2) specifically sorbed; (3) amorphous and poorly crystalline hydrous iron and aluminum oxides; (4) well-crystallized hydrous oxides of iron and aluminum; (5) residual phases [28]. The sequence and composition of extracting solutions of SEP are presented in Table 1. The extractants from each extraction step were separated from the solid residue by centrifugation ($5000 \times g$) and decantation of the supernatant liquid into a high density polyethylene container. The container was stoppered and the extractant either analyzed immediately or stored at 4°C . The residual fraction was digested with concentrated nitric and perchloric acids. The As concentration in each extractant was determined by ICP-MS (Agilent, 7500a).

In order to provide data against which the SEP results could be compared, each sample was handled in triplicate.

Table 1
As species in sequential extraction according to Wenzel et al. [25].

Fraction	Extractant	Extraction conditions	SSR ^a	Wash step
1	(NH ₄) ₂ SO ₄ (0.05 M)	4 h shaking, 20 °C	1:25	
2	NH ₄ H ₂ PO ₄ (0.05 M)	16 h shaking, 20 °C	1:25	
3	NH ₄ -oxalate buffer (0.2 M); pH 3.25	4 h shaking in the dark, 20 °C	1:25	NH ₄ -oxalate (0.2 M); pH 3.25; SSR 1:12.5; 10 min shaking in the dark
4	NH ₄ -oxalate buffer (0.2 M) + ascorbic acid (0.1 M); pH 3.25	30 min in a water basin at 96 °C in the light	1:25	NH ₄ -oxalate (0.2 M); pH 3.25; SSR 1:12.5; 10 min shaking in the dark
5	HNO ₃ /HClO ₄	Digestion		

^a SSR: solid solution ratio.

Table 2
Selected characteristics of SWR sample (mean ± S.D., n = 3).

Metals	Total content in SWR (mg/kg)	TCLP leachate concentration (mg/L)	SPLP leachate concentration (mg/L)
Al	32,580 ± 670	27.2 ± 1.6	30.2 ± 2.3
As	39,920 ± 783	1265 ± 10	1057 ± 11
Ca	6228 ± 314	219 ± 16	217 ± 20
Cd	5.9 ± 0.1	ND	0.01 ± 0.00
Cr	154.3 ± 5.8	0.1 ± 0.0	0.1 ± 0.0
Cu	26.2 ± 1.5	0.1 ± 0.0	0.1 ± 0.0
Fe	10,634 ± 890	1.6 ± 0.1	3.6 ± 0.2
Zn	3296 ± 129	0.1 ± 0.0	56.4 ± 2.8
Mg	303 ± 14	59.8 ± 4.2	1.0 ± 0.1
Pb	1366 ± 125	0.2 ± 0.0	83.9 ± 9.3
Sn	229 ± 21	0.1 ± 0.0	0.9 ± 0.1

3. Results and discussion

3.1. Characteristics of SWR

Table 2 lists the background metal contents in SWR as well as the metal concentrations in leachate after Fenton pretreatment from TCLP and SPLP. Overall, among all metals, As has the highest contents in the SWR which accounted for 39,920 mg/kg. The corresponding pH value of that SWR was 3.8, which represents the background value. Under this acidic condition, the As speciation in the SWR was considered as “moderately mobile” [29]. In this case, the SWR represents a hazardous solid waste highly contaminated by As, where the As has a high mobilization potential. Therefore, it is urgently needed to treat the SWR before the final disposal. One way to perform this treatment is by chemical fixation.

Generally, the TCLP is used to determine whether a substance should be considered as a hazardous waste, whereas the SPLP is used to determine if a potentially contaminated material would leach out toxic substances when it is exposed to a normal environment. In our study, the metal concentrations in the leachates analyzed by TCLP and SPLP marked below the limitation of environmental standards except for As with values of 1265 mg/L and 1057 mg/L, respectively. This latter results confirmed that the As was the most dangerous element in the SWR. Therefore, a more effective fixation strategy is needed to weaken its pollution potential.

SEP was also conducted on the SWR in order to compensate for the insufficient information provided by the total metal content. As shown by the results presented above, the SWR was an As-contaminated hazardous solid waste. Therefore, only the SEP results of As were herein investigated. The experimental results showed that the cumulative As concentration from SEP was 38,571 ± 536 mg/kg. As for the recovery i.e. the quotient of the sum of As content in SEP to the total As content determined directly after digestion directly, it was 96.6%. The most abundant fraction of As in SWR was fraction 3, which was bound to the amorphous and poorly crystalline oxides of Fe and Al. This fraction accounted for 11,830 mg/kg, corresponding to 30.7% of the total As. This result suggested that much more As in the SWR was associated with Fe

and Al oxides. The second abundant fraction in terms of As concentration was fraction 5, which is made up of the residual As. This fraction amounts for 9900 mg/kg, or 25.7% of the total As. The contents of the other three fractions were: 5886 mg/kg or 15.2% of the total As for fraction 4, which represents the well-crystallized hydrous oxides of iron and aluminum; 6596 mg/kg or 17.1% of the total As for fraction 1, which is the fraction of non-specifically sorbed; 4359 mg/kg or 11.3% of the total As for fraction 2 of the specifically sorbed As. Fraction 5 representing the residual is always not easy to be separated from the SWR matrix and is thus considered as beneficial from the standpoint of environmental risk. Overall, 74.3% of the total As in the SWR showed mobility potential. Importantly, 28.4% of total As in fraction 1 and fraction 2 was weakly bounded and easily releasable. Generally, fraction 1 and fraction 2 are considered as the available fractions, called available As in this study, due to their high mobility. More attention should be paid to this fraction. The available As content in the SWR was 10,955 mg/kg or 28.4% of the total As. The latter result shows that the SWR was a hazardous solid waste with a high content of available As.

3.2. Effect of single fixation on available As in the SWR

3.2.1. TCLP and SPLP

The effects of single metal ion on the fixation of available As were at first evaluated by the As concentration in leachates from TCLP and SPLP. As shown in Fig. 1, comparing with the CK, the As concentrations in the leachates from TCLP and SPLP were 1265 mg/L and 1057 mg/L, respectively. For the three fixation treatments, Fig. 1 clearly shows a significant attenuation of As leachability in SWR after 3 days, especially in FS treatment. However, the fixation effect for available As varied greatly with the types of metal ions and the ratios of metal ion-to-As. The As concentrations in TCLP leachates were higher than the SPLP leachates concentrations after MC and CH treatment. However, a reverse trend was observed in FS treatment. Overall, the FS treatment resulted in the lowest As concentration in leachates both from TCLP and SPLP. The MC treatment had the worst fixation effect. It can also be confirmed by the differences on the final pH values of leaching solution of TCLP and SPLP. As shown in Table 3, the pH values of MC are always lower

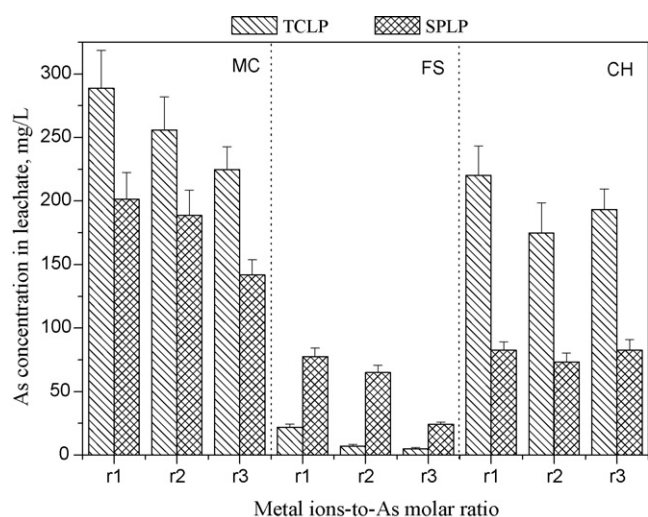


Fig. 1. As concentrations in TCLP and SPLP leachates of SWR after different single fixation treatments (r1 = 1, r2 = 2, and r3 = 3).

than FS and CH. As(V) anions exhibit better adsorption results in acid ranges [30]. At higher pH values, lower competition by protons for the same binding sites stimulates the adsorption of As(V) to the adsorbent. The higher the pH of the bulk phase, the higher the degree of de-protonation of the substrate. It was well consistent with Seidel et al. [31].

Moreover, the As concentration in TCLP and SPLP leachates decreased with the increase of metal ion-to-As molar ratio in all treatments except for the CH treatment. In the MC treatment, the As concentrations of TCLP and SPLP leachates were 288.8 mg/L and 201.4 mg/L at Mg:As molar ratio of 1:1, and 224.7 mg/L and 141.8 mg/L at Mg:As molar ratio of 3:1, respectively. The optimal Mg:As molar ratio was 3:1. A similar phenomenon was observed in the FS treatment. However, no significant difference ($P > 0.05$) could be obtained between the As concentrations in TCLP and SPLP leachates when considering Fe:As molar ratios of 2:1 and 3:1. From the standpoint of treatment cost effectiveness, an optimal Fe:As molar ratio of 2:1 was chosen. In the CH treatment, the As concentrations in TCLP and SPLP leachates were kept at the lowest levels, respectively 174.7 mg/L and 73.3 mg/L at the Ca:As molar ratio of 2:1. In summary, with regard to the As concentration in TCLP and SPLP leachates, the order of strength of the fixation effect among the three treatments was FS > CH > MC, and the optimal ion-to-As molar ratios were 2:1 for (Fe:As), 2:1 for (Ca:As) and 3:1 for (Mg:As).

It is worth noticing that the results of TCLP and SPLP were not always in accordance to each other though both can provide important information on the evaluation of As fixation effect. For example, the As concentration in TCLP leachate was not significant different ($P > 0.05$) when the Fe:As molar ratio were 2:1 and 3:1 in the FS treatment. However, that was not the case in SPLP leachate where $P < 0.01$. The same phenomenon could also be observed for CH treatment with Ca:As molar ratios of 2:1 and 3:1. Therefore, the real fixation effect of As in SWR might be masked if only TCLP was introduced in the evaluation. Generally, TCLP is an evaluation standard of hazardous solid waste, while SPLP is used for the determination of potential leachability when the tested substance is exposed to normal environment. Taking into consideration the hazardous nature of SWR, the final disposal by landfilling should be carried out after the fixation treatment of As after all. The long-term behavior of As in SWR after fixation and landfill will still be of concerns in the future. Once the fixation treatment has been underestimated during the stabilization process, there might be a high potential risk of secondary pollution to the surrounding environment due to the As leachability. Therefore, the SPLP is also an important evaluation standard to accompany the TCLP in the fixation treatment of As in SWR.

3.2.2. SEP

3.2.2.1. Non-specifically sorbed (NSS). This fraction includes weakly adsorbed metals retained on the matrix surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes, etc. Changes in the ionic composition, influencing adsorption-desorption reactions, or lowering of pH could cause remobilization of metals from this fraction. The NSS is the most dangerous fraction for the environment. Therefore, the As content in NSS can directly demonstrate the effectiveness of the fixation of available As. As shown in Fig. 2, the NSS As in the SWR was significantly reduced after fixation treatments. Among the three fixation treatments, the FS treatment could greatly reduce the NSS As content, while the MC treatment had the worst effect. As discussion above, it can also be explained by the difference on the pH values of leaching solutions. As shown in Table 3, the pH values of the leaching solutions after the NSS fraction in MC treatment are always lower than the other treatment.

For MC treatment, the NSS As content varied slightly for different Mg:As molar ratios. Compared with the CK where the NSS As fraction amount for 6596 mg/kg, the decreases observed in the NSS As concentrations for Mg:As molar ratio of 1:1, 2:1 and 3:1 were, respectively 3452 mg/kg or 47.7% reduction, 3053 mg/kg or 53.7% reduction, and 3230 mg/kg or 51.0% reduction. As Fig. 1 shows, the

Table 3

Final pH values of leaching solution in TCLP, SPLP and each steps of SEP from different fixation treatments.

Treatments		TCLP	SPLP	SEP			
				Step 1	Step 2	Step 3	Step 4
Single fixation	CK	3.33 ± 0.02	4.70 ± 0.04	4.92 ± 0.11	4.73 ± 0.11	3.44 ± 0.07	3.44 ± 0.06
	Mg/As = 1	3.36 ± 0.00	4.54 ± 0.10	4.82 ± 0.08	3.99 ± 0.02	3.45 ± 0.11	3.31 ± 0.11
	Mg/As = 2	3.27 ± 0.03	4.65 ± 0.05	4.07 ± 0.20	4.60 ± 0.10	3.37 ± 0.10	3.38 ± 0.08
	Mg/As = 3	3.27 ± 0.01	4.60 ± 0.11	4.07 ± 0.14	4.69 ± 0.13	3.42 ± 0.09	3.36 ± 0.10
	Fe/As = 1	3.34 ± 0.10	4.81 ± 0.09	4.02 ± 0.11	4.69 ± 0.05	3.48 ± 0.12	3.40 ± 0.06
	Fe/As = 2	3.41 ± 0.05	4.79 ± 0.11	4.84 ± 0.04	4.75 ± 0.11	3.45 ± 0.04	3.39 ± 0.11
	Fe/As = 3	3.40 ± 0.02	4.74 ± 0.01	4.83 ± 0.10	4.85 ± 0.12	3.55 ± 0.11	3.44 ± 0.04
	Ca/As = 1	3.65 ± 0.03	5.67 ± 0.01	5.89 ± 0.11	5.30 ± 0.16	3.48 ± 0.08	3.42 ± 0.10
	Ca/As = 2	3.74 ± 0.02	6.18 ± 0.02	6.45 ± 0.09	5.54 ± 0.19	3.49 ± 0.10	3.44 ± 0.12
	Ca/As = 3	3.71 ± 0.12	6.52 ± 0.05	6.69 ± 0.12	5.68 ± 0.08	3.49 ± 0.04	3.44 ± 0.09
Combination fixation	CK ^a	3.41 ± 0.05	4.79 ± 0.11	4.84 ± 0.04	4.75 ± 0.11	3.45 ± 0.04	3.39 ± 0.11
	FS + CH	3.42 ± 0.04	4.70 ± 0.03	5.04 ± 0.11	4.60 ± 0.01	3.56 ± 0.13	3.42 ± 0.11
	FS + MC	3.50 ± 0.11	4.90 ± 0.01	5.11 ± 0.11	4.93 ± 0.02	3.49 ± 0.02	3.46 ± 0.08
	FS + MC + CH	3.48 ± 0.08	5.04 ± 0.10	4.10 ± 0.08	4.49 ± 0.07	3.58 ± 0.11	3.46 ± 0.15

^a The CK of combination fixation is the FS treatment with the Fe/As = 2.

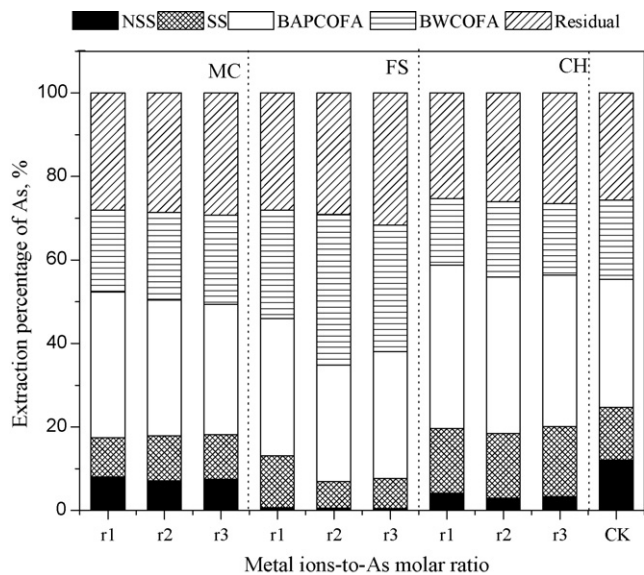


Fig. 2. Comparison of As fractions after different fixation treatments (r1 = 1, r2 = 2, and r3 = 3).

lowest As concentrations in TCLP and SPLP leachates were observed at Mg:As molar ratio of 3:1, while the lowest NSS As content was observed at Mg:As molar ratio of 2:1. Therefore, the evaluation of MC treatment may be misguided if only TCLP or SPLP results were to be considered. With respect to fraction 1 which is the most dangerous in its nature, there is a need to assess its distribution more accurately. Therefore, the introduction of SEP is an important supplement to TCLP and SPLP results when the fixation treatment of As in SWR was carried out.

The experimental results show a similarity between CH and MC treatments in the variation trend of NSS As content for various Ca:As molar ratios. However, the NSS As contents were much lower in the CH treatment as compared to the MC treatment. The NSS As content decreased from 6596 mg/kg to 1816 mg/kg, 1198 mg/kg and 1392 mg/kg at CH/As molar ratios of 1:1, 2:1 and 3:1, respectively. Namely, the reductions were 72.3%, 81.8%, and 78.9%, respectively.

For FS treatment, the NSS As content decreased with increasing Fe:As molar ratios. For FS treatment, the variation trend of NSS As content was different from the one observed in MC and CH treatments. The NSS As content showed the lowest values in the FS treatment, ranging from 267 mg/kg to 187 mg/kg. Namely, the reductions were 95.9% and 97.2%, respectively. This latter result suggests that the ranking of NSS As fixation efficiency was FS > CH > MC. Thus among the three fixation treatments, the FS treatment has the highest effectiveness on the fixation of the NSS As in SWR.

3.2.2.2. Specifically sorbed (SS). The SS fraction referred to the amount of surface-bound As species and inner-sphere surface complexes. Metal oxides surface is capable of forming inner-sphere adsorption configurations and has proved to have a high affinity for As [19]. Hence, the SS fraction was more stable than the first fraction (NSS). As Fig. 2 shows, the SS As contents were significantly reduced in all the fixation treatments but in CH treatment, where the SS As content increased with increasing Ca/As molar ratios and was even higher than that in CK. Previous investigation showed that the As immobilization was mainly controlled by Ca–As precipitates in lime–As(V) slurries [13]; that might be the same reason in our study. Much of the SS As were formed by secondary enrichment in lime–As(V) precipitation.

The SS As contents in the FS and MC treatment differed greatly with those in the CH treatment. Though the SS As content in the MC treatment was slightly higher than that in the FS treatment, there was no significant difference between them. In the FS treatment, the SS As content decreased from 4359 mg/kg to 2534 mg/kg corresponding to an observed reduction of 41.9%, which is the lowest value observed in this treatment.

The discussion above suggests that the FS treatment had also the highest effect on the fixation of the SS As in SWR among the three fixation treatments. With respect to the fixation of available As (the NSS and the SS fraction) in SWR, the FS is the best choice.

3.2.2.3. Bound to amorphous and poorly crystalline oxides of Fe and Al (BAPCOFA). This fraction shows the amount of As associated with amorphous and poorly crystalline oxides of Fe and Al. Therefore, As was apparently sequestered through the stable forms of metal–As compound or co-precipitation.

Fig. 2 shows that the CH treatment resulted in large increases of the BAPCOFA As content. Compared with the CK (30.7%), the highest percentage of BAPCOFA As was observed at Ca:As molar ratio of 1:1 (39.3%). However, there were no significant differences on the BAPCOFA As contents among the MC treatment, the FS treatment and the CK. Importantly, this fraction decreased as the Ca:As molar ratio increased. This latter result implied that higher Ca:As molar ratio increased the step 3 fraction but also contributed to the following fractions. Similar trends were found for the Mg and Fe treatments, although there were no significant transformations on this fraction. To a certain extent, the latter finding meant that the percentages of the following step fractions, relatively more stable, were much higher in MC and FS treatment than in CH treatment.

3.2.2.4. Bound to well-crystalline oxides of Fe and Al (BWCOFA). This fraction showed the amount of As associated with well-crystalline oxides of Fe and Al. Compared with BAPCOFA fraction, BWCOFA fraction is more stable and presents less environmental risk. As shown in Fig. 2, the BWCOFA As contents were all higher than those in the CK and differed significantly from each other among the three kinds of treatments. When subject to the MC and CH treatments, the BWCOFA As contents were slightly higher in the MC treatment than in the CH treatment which was close to the CK treatment. However, for different Mg:As or Ca:As molar ratios, the differences in the BWCOFA As fractions were not significant ($P > 0.05$). For FS treatment, the BWCOFA As contents increased with increasing FS/As molar ratios and were much higher in the CH and MC treatments. The highest content was observed at Fe/As molar ratio of 3:1 in which BWCOFA As increased from 9900 mg/kg to 12,093 mg/kg with 22.2% increment. This could be explained by the desorption processes of As intensified by the dissolution of Fe hydroxides and their transformation into easily soluble forms of Fe(II) in the extracted solution under reducing conditions. The main extractant component of fraction 4 in SEP was the ascorbic acid.

3.2.2.5. Residual. The residual fraction of metals has the strongest bond with the crystalline structures of the minerals. It is always not easy to separate the material extracted from the matrix. Digestion in strong acids such as nitric acid or perchloric acid that do not dissolve the silicate matrix can give an estimate of the maximum amounts of elements that are potentially mobilizable with changing environmental conditions. Therefore, the results of this fraction are pseudo-total contents. The terms pseudo-total analysis and pseudototal contents are useful in expressing the environmental role of such strong acid digestion procedures. Overall, the residual As contents were higher than in the CK to different extents (Fig. 2) and increased with increasing molar ratios in the three treatments. The highest residual content was showed in FS treat-

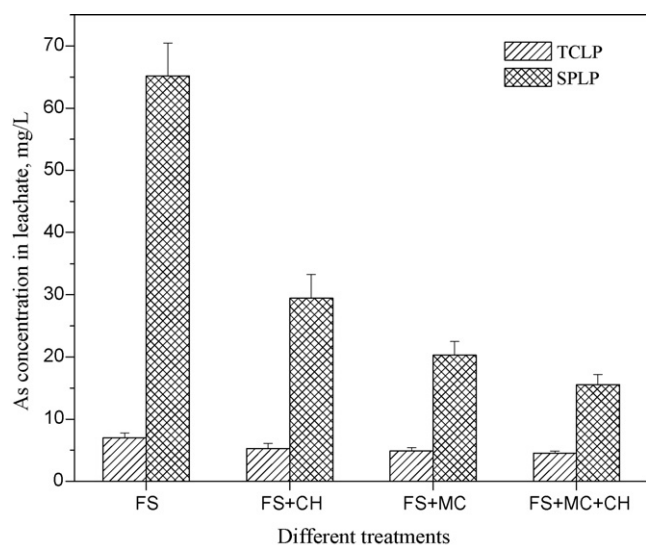


Fig. 3. As concentrations in TCLP and SPLP leachates of SWR after different combination fixation treatments.

ment with the Fe:As molar ratio of 3:1 (30.9%) and the lowest one was in MC treatment with the Mg:As molar ratio of 3:1 (29.3%), respectively.

In conclusion, the high contribution of the last two fractions in SWR should undoubtedly be considered as beneficial from the standpoint of environmental risk. The cumulative As contents of the last two fractions were 54.0%, 60.6% and 62.9% at Fe:As molar ratio of 1:1, 2:1 and 3:1, respectively. The FS treatment was again confirmed to be the most efficient one among the three treatments.

From the SEP results, in which the As speciation variation under each treatment can be determined clearly, the fixation effect on As in SWR was understood more comprehensively, especially on the available As fixation. SEP results can also provide important information on how to avoid the speciation migration during the fixation treatment such as the CH treatment. Therefore, SEP is another important indicator in the evaluation of available As fixation effect in SWR besides the TCLP and SPLP.

3.3. Effect of combination fixation on available As in the SWR

3.3.1. TCLP and SPLP

Based on the results of single treatments presented above, FS (Fe:As = 2:1) was chosen as the basic treatment in the combination fixation. Results of TCLP and SPLP leaching in the three combination fixation treatments were shown in Fig. 3, which were lower in the CK. When subjected to SPLP As, the difference in the three combination fixation treatments was obvious. The lowest As concentration in SPLP leachate was observed in the FS+MC+CH treatment (15 mg/L), and the highest one was found in the FS+CH treatment (29.5 mg/L). However, the effect of combination fixation treatments on available As was significant with respect to the As concentration in CK (65.2 mg/L). Therefore, the combination of

FS+MC+CH treatments was chosen as the optimal treatment in the fixation of available As in SWR.

3.3.2. SEP

As the SEP results in Table 4 show, the available As in the step 1 transferred to relatively stable phases in the three combination fixation treatments. For the NSS fraction in step 1, the ranking was CK (FS treatment, 0.61%) > FS+CH (0.56%) > FS+MC (0.51%) > FS+MC+CH (0.47%). In addition, there were similar trends for the SS fraction in step 2 and the BAPCOFA fraction in step 3. Correspondingly, the variation trends for the contents of the last two SEP fractions were opposite to those of the first three fractions above. Noticeably, there were no significant differences ($P > 0.05$) on the last three fractions in the three combination treatments and the CK, while for the first two fractions the difference was found significant ($P < 0.01$). This has been explained by the As speciation transformation from available fractions into more stable fractions in the combination treatments. In other words, the available As in SWR was stabilized obviously after the combination fixation treatments. The combination fixation treatment could enhance the binding strength of available As to precipitates. Especially, a significant decrease in the contribution of the potentially mobile fraction was realized, as mentioned above. Therefore, the combination fixation treatment for the stabilization of available As in SWR was more efficient than the single fixation treatment, and the combination of FS+MC+CH was the best choice.

3.4. Effect of aging treatment on fixation of available As in SWR

The results of single and combination fixation treatments mentioned above were all evaluated after 3 days. In order to assess their long-term effect on the stabilization of available As, we also investigate the effects of aging on the treated SWR. TCLP, SPLP and SEP were also carried out for the evaluation of the same samples mentioned above.

After a month's aging, the As concentrations in TCLP and SPLP leachates for the different fixation treatments were all lower than those of treatment after 3 days except for the CH treatment (Figs. 4 and 5). However, such differences on As concentrations were not significant ($P > 0.05$). The As concentration in SPLP leachate showed a slight increase in the CH treatment after the aging. That can be explained by the buffer effect of the surplus calcium hydroxide in the CH fixation treatment. During the aging, the surplus CH would react with the atmospheric carbon dioxide to form calcium carbonate, which can weaken the buffering as compared to the calcium hydroxide. Subsequently, much more As could be extracted in TCLP and SPLP leaching test, especially in SPLP. Therefore, in terms of time saving in the industrial process, the effect of fixation treatment of available As in SWR could be directly evaluated after 3 days and the aging is not needed.

However, as Fig. 5 clearly shows, the As speciation has experienced a redistribution during the month's aging. For example, fraction 1 decreased slightly, except for the CH treatment, because of the buffer effect of CH. Moreover, both of the less stable frac-

Table 4

Extraction percentage of As in SWR by SEP after different fixation treatments (Mean \pm S.D., $n = 3$).

Treatment	As proportions in individual fractions (%)				
	Step 1	Step 2	Step 3	Step 4	Step 5
FS (CK)	0.61 \pm 0.07Aa	6.47 \pm 0.32Aa	32.31 \pm 2.73Aa	30.82 \pm 3.10Aa	29.79 \pm 2.48Aa
FS+CH	0.56 \pm 0.04ABab	5.88 \pm 0.39ACa	30.92 \pm 3.24Aa	32.60 \pm 1.86Aa	30.05 \pm 2.67Aa
FS+MC	0.51 \pm 0.04ABbc	5.14 \pm 0.47BCb	30.81 \pm 2.84Aa	31.61 \pm 3.07Aa	31.93 \pm 1.57Aa
FS+MC+CH	0.47 \pm 0.03Bc	4.57 \pm 0.33Bb	30.98 \pm 2.66Aa	30.98 \pm 2.80Aa	32.99 \pm 1.93Aa

Means with the same small letter(s) and capital letter(s) are not significantly different at $P < 0.05$ or $P < 0.01$ based on LSD comparisons, respectively.

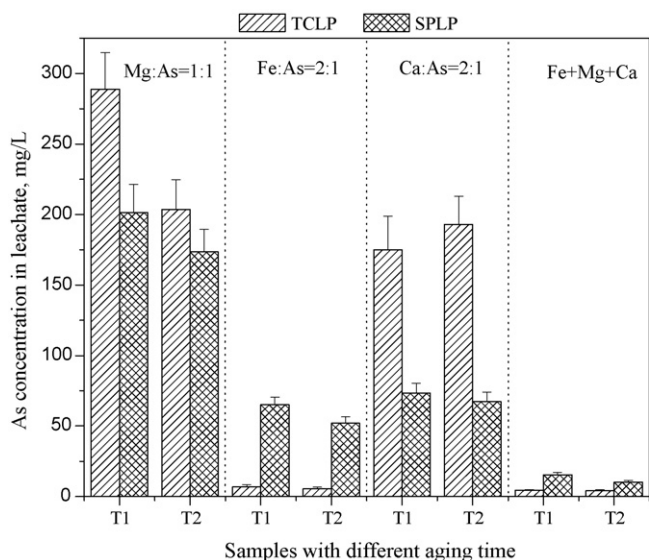


Fig. 4. As concentrations in leachate from TCLP and SPLP after aging (T1, 3 days after treatment and T2, 1 month after treatment).

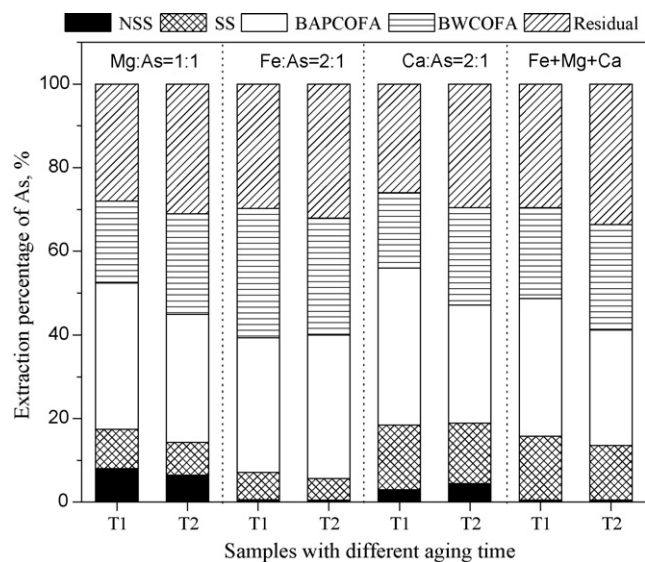


Fig. 5. As fractions in different treatments after aging (T1, 3 days after treatment and T2, 1 month after treatment).

tions of As i.e. fraction 2 and fraction 3 decreased in all treatments including in the CH treatment. Accordingly, the proportions of As in the last two fractions generally increased during the aging. The phenomenon of As speciation redistribution during the aging was defined here as a further stabilization. It may be ascribed to the transformation of the thermodynamically unstable amorphous metal hydroxides, to the stable anhydrous oxides, to the binding strength of available As to the metal-As precipitate, or to increased occluding of As within the metal oxide structure. This represents an interesting result for the final disposal of such SWR. Once the SWR after fixation and aging treatment of available As was disposed in a landfill, the environmental risk of As could be abated greatly.

In summary, the aging treatment enhanced the fixation effectiveness in both the single and the combined treatments. This treatment is also favorable to landfill disposal. However, the effect of the fixation treatment of available As in the SWR could be directly evaluated after 3 days and the aging treatment is not essential.

4. Conclusions

Chemical fixation treatments including FS, MC and CH represent effective strategies in the treatment of available As in SWR from organic acid industrial after Fenton process pretreatment. The optimal molar ratios of Fe:As, Mg:As and Ca:As were 2:1, 3:1 and 2:1, respectively. The combination fixation can further enhance the effect of available As fixation in SWR and the optimal combination fixation was the FS + MC + CH treatment. The effect of fixation can be evaluated more pertinently by analyzing the leaching (TCLP and SPLP) and the inherent speciation (SEP) together. With respect to the leaching behavior and the speciation migration of As in SWR after stabilization, TCLP, SPLP and SEP are inseparable indicators for the evaluation of the fixation effect. The fixation treatment of available As in SWR could be directly evaluated after 3 days and the aging treatment is not needed though it can further enhance the fixation effect.

Acknowledgements

This work was carried out under the auspices of '811' Momentous Treatment Project of Zhejiang, China. We are thankful to the 985-Institute of Agrobiological and Environmental Sciences of Zhejiang University, for providing convinces in using the experimental equipments.

References

- [1] L.-F. Hu, Y.-Y. Long, H.-J. Feng, D.-S. Shen, Evaluation of a novel semi-solid Fenton process: case study on a kinetic model of o-nitroaniline degradation in hazardous solid waste, *J. Environ. Sci. Health A* 44 (2009) 1127–1135.
- [2] F. Sanchez, A.C. Garrabrants, C. Vandecasteele, P. Moszkowicz, D.S. Kosson, Environmental assessment of waste matrices contaminated with arsenic, *J. Hazard. Mater.* 96 (2003) 229–257.
- [3] E. Brillas, E. Mur, R. Saulea, L. Sanchez, J. Peral, X. Domenech, J. Casado, Aniline mineralization by AOPs: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes, *Appl. Catal. B: Environ.* 16 (1998) 31–42.
- [4] L. Mater, R.M. Sperb, L.A.S. Madureira, A.P. Rosin, A.X.R. Correa, C.M. Radetski, Proposal of a sequential treatment methodology for the safe reuse of oil sludge-contaminated soil, *J. Hazard. Mater.* 136 (2006) 967–971.
- [5] R.D. Villa, A.G. Trovo, R.F.P. Nogueira, Environmental implications of soil remediation using the Fenton process, *Chemosphere* 71 (2008) 43–50.
- [6] S.J. Hug, O. Leupin, Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction, *Environ. Sci. Technol.* 37 (2003) 2734–2742.
- [7] S.R. Poulson, Y. Chikaraishi, H. Naraoka, Carbon isotope fractionation of monoaromatic hydrocarbons and chlorinated ethylenes during oxidation by Fenton's reagent, *Geochim. Cosmochim. Acta* 67 (2003) A382–A1382.
- [8] S. Kundu, A.K. Gupta, Immobilization and leaching characteristics of arsenic from cement and/or lime solidified/stabilized spent adsorbent containing arsenic, *J. Hazard. Mater.* 153 (2008) 434–443.
- [9] G.R. Qian, J. Shi, Y.L. Cao, Y.F. Xu, P.C. Chui, Properties of MSW fly ash-calcium sulfoaluminate cement matrix and stabilization/solidification on heavy metals, *J. Hazard. Mater.* 152 (2008) 196–203.
- [10] T. Zhou, Y. Li, F.-S. Wong, X. Lu, Enhanced degradation of 2,4-dichlorophenol by ultrasound in a new Fenton like system (Fe/EDTA) at ambient circumstance, *Ultrason. Sonochem.* 15 (2008) 782–790.
- [11] T.S. Singh, K.K. Pant, Solidification/stabilization of arsenic containing solid wastes using portland cement, fly ash and polymeric materials, *J. Hazard. Mater.* 131 (2006) 29–36.
- [12] P. Palfy, E. Vircikova, L. Molnar, Processing of arsenic waste by precipitation and solidification, *Waste Manage.* 19 (1999) 55–59.
- [13] D.H. Moon, D. Dermatas, N. Menounou, Arsenic immobilization by calcium-arsenic precipitates in lime treated soils, *Sci. Total Environ.* 330 (2004) 171–185.
- [14] J.Y. Kim, A.P. Davis, K.W. Kim, Stabilization of available arsenic in highly contaminated mine tailings using iron, *Environ. Sci. Technol.* 37 (2003) 189–195.
- [15] J.V. Bothe, P.W. Brown, Arsenic immobilization by calcium arsenate formation, *Environ. Sci. Technol.* 33 (1999) 3806–3811.
- [16] G. Román-Ross, G.J. Cuervo, X. Turrillas, A. Fernández-Martínez, L. Charlet, Arsenite sorption and co-precipitation with calcite, *Chem. Geol.* 233 (2006) 328–336.
- [17] M.A. Garcia, J.M. Chimenos, A.I. Fernandez, L. Miralles, M. Segarra, F. Espiell, Low-grade MgO used to stabilize heavy metals in highly contaminated soils, *Chemosphere* 56 (2004) 481–491.

- [18] B.D. Kocar, M.J. Herbel, K.J. Tufano, S. Fendorf, Contrasting effects of dissimilatory iron(III) and arsenic(V) reduction on arsenic retention and transport, *Environ. Sci. Technol.* 40 (2006) 6715–6721.
- [19] Y. Li, R.J. Donahoe, C. James, In situ chemical fixation of arsenic-contaminated soils: an experimental study, *Sci. Total Environ.* 387 (2007) 28–41.
- [20] D. Burghardt, E. Simon, K. Knöller, A. Kassahun, Immobilization of uranium and arsenic by injectible iron and hydrogen stimulated autotrophic sulphate reduction, *J. Contam. Hydrol.* 94 (2007) 305–314.
- [21] D. Sarkar, K.C. Makris, V. Vandanapu, R. Datta, Arsenic immobilization in soils amended with drinking-water treatment residuals, *Environ. Pollut.* 146 (2007) 414–419.
- [22] H. Seidel, K. Görsch, K. Amstätter, J. Mattusch, Immobilization of arsenic in a tailings material by ferrous iron treatment, *Water Res.* 39 (2005) 4073–4082.
- [23] M. Zemberyova, J. Bartekova, I. Hagarova, The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins, *Talanta* 70 (2006) 973–978.
- [24] J. Usero, M. Gamero, J. Morillo, I. Gracia, Comparative study of three sequential extraction procedures for metals in marine sediments, *Environ. Int.* 24 (1998) 487–496.
- [25] L. Campanella, D. D'Orazio, B.M. Petronio, E. Pietrantonio, Proposal for a metal speciation study in sediments, *Anal. Chim. Acta* 309 (1995) 387–393.
- [26] G. Rauret, R. Rubio, J.F. López-Sánchez, E. Casassas, Determination and speciation of copper and lead in sediments of a Mediterranean river (River Tenes, Catalonia Spain), *Water Res.* 22 (1988) 449–455.
- [27] P. Szefer, G.P. Glasby, H. Kunzendorf, E.A. Gorlich, K. Latka, K. Ikuta, A. Ali, The distribution of rare earth and other elements and the mineralogy of the iron oxyhydroxide phase in marine ferromanganese concretions from within Slupsk Furrow in the southern Baltic, *Appl. Geochem.* 13 (1998) 305–312.
- [28] W.W. Wenzel, N. Kirchbaumer, T. Prohaska, G. Stingeder, E. Lombi, D.C. Adriano, Arsenic fractionation in soils using an improved sequential extraction procedure, *Anal. Chim. Acta* 436 (2001) 309–323.
- [29] X. Meng, G.P. Korfiatis, C. Jing, C. Christodoulatos, Redox transformations of arsenic and iron in water treatment sludge during aging and TCLP extraction, *Environ. Sci. Technol.* 35 (2001) 3476–3481.
- [30] S. Schiewer, B. Volesky, Modeling multi-metal ion exchange in biosorption, *Environ. Sci. Technol.* 30 (1996) 2921–2927.
- [31] A. Seidel, J. Waypa, M. Elimelech, Role of charge exclusion in removal of arsenic from water by a negatively charged porous nanofiltration membrane, *Environ. Eng. Sci.* 18 (2001) 105–113.