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Arsenic removal of high-arsenic wastewater from gallium arsenide semiconductor production by enhanced two-stage treatment

Anfeng Li*, Jianping Luo, Wenjiang Xu, Tao Pan

State Environmental Protection Engineering (Beijing) Center for Industrial Wastewater Pollution Control, Beijing Municipal Research Institute of Environmental Protection, Beijing 100037, China, Tel. +86 010 88380895; Fax: +86 010 88362328; email: cee1219@hotmail.com (A. Li), Tel. +86 010 68351776; email: luo0409@163.com (J. Luo), Tel. +86 010 88362328; email: 15210029882@163.com (W. Xu), Tel. +86 010 88385869; email: pantao1112@263.net (T. Pan)

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ABSTRACT

High concentrations of arsenic and phosphate have been found in wastewater, from gallium arsenide (GaAs) semiconductor production facilities, which poses a threat to aquatic environments and human health in China. Arsenic removal by an enhanced two-stage process for this kind of high-arsenic wastewater was studied in this work. The process involves primary treatment, oxidation, secondary treatment, and post-treatment. Primary treatment was performed and enhanced with ferric chloride and polyacrylamide to effectively remove most of the arsenic, phosphate, and colloidal silica. The high-arsenic wastewater, which had an initial turbidity of 184 NTU and was milk-white, became clear and transparent with a turbidity of less than 10 NTU after the primary treatment. The bench-scale results showed that arsenic and phosphate concentrations were reduced dramatically from 63 mg/L and 270 mg/L to 0.08–0.13 mg/L, and 0.9–1.5 mg/L, respectively. Then, sodium hypochlorite was used to oxidize residual As(III) to As(V). In the secondary treatment, enhanced coagulation with powder bentonite and ferric chloride was applied and about 80% of residual arsenic could be removed. Based on the bench-scale results, a full-scale sequencing batch two-stage process followed by conventional sand filtration was conducted in a GaAs semiconductor production factory in Beijing. The combined process was successful in producing cleaned effluent with residual arsenic concentrations of below 0.02 mg/L, which met the permitted total discharge amount, and was of great demonstration significance for the high-arsenic wastewater treatment from the GaAs production industry.

Keywords: Arsenic wastewater; Enhanced coagulation; Ferric chloride; Gallium arsenide; Bentonite

1. Introduction

Gallium arsenide (GaAs) is the most widely used semiconductor material in the microelectronic and optoelectronic industries. Larger and larger amounts of high-arsenic (As) wastewater have been discharged in GaAs semiconductor manufacturing, etching, cutting, and grinding in recent years in China. Moreover, the wastewater components are considerably complex. In addition to arsenic, high concentrations of phosphate, silica, and other chemicals have also been found in the wastewater. Accordingly, untreated or

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*Corresponding author.

simply treated wastewater poses a great threat to aquatic systems and human health [1,2]. The wastewater must be treated to fully remove arsenic and other hazards to minimize the environment and health risks.

Ferric (Fe^{3+}) and aluminum (Al^{3+}) can hydrolyze, precipitate, and aggregate into highly porous and amorphous structures known as hydrous ferric oxide (HFO) and hydrous aluminum oxide (HAO), which provide active sites for arsenic sorption by surface complexation or ligand exchange. Therefore, coagulation with ferric (Fe^{3+}) or aluminum (Al^{3+}) and solid–liquid separation are considered to be very promising techniques for high-arsenic wastewater treatment with low cost and high efficiency [3–5]. Furthermore, it is generally found that HFO is more effective for arsenic removal than HAO, so ferric coagulants have been applied more widely in arsenic removal [6–8]. However, coagulation only by Fe^{3+} or Al^{3+} coagulant is often inadequate for treatment of high-arsenic-content wastewater to produce an effluent with very low arsenic concentrations, e.g. 0.02 mg/L, which is the discharge threshold based on the permitted total arsenic discharge amount for semiconductor companies in Beijing, China [9]. Some technologies such as reverse osmosis and ion exchange, which can lower arsenic concentrations to below 0.01 mg/L in drinking water treatments, are not suitable for high-arsenic wastewater because of the complex nature and high concentration of contaminants. As more stringent environmental discharge limits are being implemented for total control of hazardous heavy metals and metalloids in China, the best pathway for treatment of high-arsenic and complex wastewater is still coagulation processes that must be enhanced and optimized to further improve the removal efficiency.

Meanwhile, in recent years, more attention has been paid to adsorption onto a variety of adsorbent materials such as activated carbons, mineral oxides, treated slags, carbons developed from agricultural waste, and biosorbents for advanced arsenic removal [10–12]. In addition to the adsorption of arsenic, adsorbents used as powder particles could strongly enhance the coagulation process by increasing the coagulate size and reducing the particle concentration in suspensions [13]. Nevertheless, due to the high arsenic concentration and complexity of the wastewater, direct application of those adsorbent materials is not acknowledged to be suitable or feasible for GaAs wastewater purification.

Some improved coagulation and adsorption processes have been developed to thoroughly eliminate arsenic from high-arsenic wastewater [13–17]. It has been found that coagulation and adsorption are much more effective for the removal of As(V) than As(III). Generally, an oxidation step is required to convert As(III) to As(V) prior to coagulation and adsorption [14,15,18,19]. Enhanced ferric coagulation using coarse calcite was shown to achieve high arsenic removal and produce a cleaned effluent with residual arsenic concentration of 0.013 mg/L [13], but pre- and post-treatment membrane micro-filtration was required in the process. Adsorption on *in situ*-formed Fe–Mn binary oxides coupled with polyaluminium chloride (PACl) coagulation was shown to be effective in controlling arsenic concentrations to under 0.05 mg/L with an initial arsenic concentration of 5.8 mg/L [14]. In another study, in order to achieve the same treatment demand, an integrated process, including $KMnO_4$ pre-oxidation, lime and ferrous co-precipitation, Fe–Mn binary oxide adsorption, and PACl coagulation, was conducted to successfully treat high-arsenic industrial wastewater (423 mg/L) [15]. The two processes were successfully applied in practice with hydraulic retention times (HRTs) of more than 30 h. High HRTs allow for massive working volumes, which could become an important limiting factor for many companies in urban areas. Electro-coagulation using Fe or Al electrode pairs also exhibited a good capability to treat high-arsenic wastewater, but the process is very power- and material resource-intensive, and is still at a laboratory or pilot scale [16,17].

The objective of this study is to develop a new cost-effective process of high reliability for eliminating arsenic from high-arsenic wastewater produced in the GaAs semiconductor production industry. We attempted to apply primary process with ferric for removing the majority of arsenic and other interfering substances in the GaAs wastewater. Oxidant, sodium hypochlorite (NaClO) was then used to convert residual As(III) to As(V). Since bentonite, which consists mostly of montmorillonite, is cheap and readily available in China, and has been considered to be a useful adsorbent of ions in solution and complementary to arsenic removal [11,20,21], it was selected to enhance the secondary ferric coagulation to thoroughly remove residual arsenic. Furthermore, a full-scale system based on the combined process was constructed in a GaAs semiconductor factory in Beijing to evaluate the system's practical feasibility.

2. Materials and methods

2.1. Materials

$FeCl_3$ (99%), NaOH (99%), NaClO (30%), and polyacrylamide (99%, PAM, molecular weight: five million) of analytical purity were purchased from

Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China) and used in the experiment. Calcium bentonite powder (30–60 μm) of industrial grade was purchased from Kaibiyuan Co., Ltd (Beijing, China). In the full-scale treatment, all chemical reagents and solutions used were of industrial grade from Kaibiyuan Co., Ltd (Beijing, China).

The raw high-arsenic wastewater was sampled from a GaAs semiconductor factory in Beijing, and kept at 4℃. The composition was considerably complex, and there were many other chemicals in addition to arsenic in the wastewater (Table 1). The total arsenic concentration was 35–75 mg/L, of which less than 1% was As(III). The wastewater's pH value was 6.0–9.5 and was 7.5–9.0 in most of the time, and the pH of specific wastewater sample used in our experiment was 8.6. Turbidity, which was mainly due to silica (SiO_2), was 167–220 NTU, and the specific value for our wastewater sample was 184 NTU.

2.2. Bench-scale experiment

A bench-scale experiment was performed in a six-paddle stirrer with 1,000-mL glass beakers at a room temperature of 26 ± 1℃. In the primary step, the high-arsenic wastewater was first mixed with a given amount of $FeCl_3$ and stirred at 90 rpm for 5 min. Then, the mixture was adjusted for pH with NaOH. Coagulates were formed during pH adjustment. After that, coagulates were flocculated with PAM and settled within 15 min. The supernatants were transferred, mixed, and oxidized with NaClO to convert residual As(III) to As(V). In the secondary coagulation, the oxidized supernatant was first mixed with bentonite for 15 min and was then coagulated and flocculated similarly with the primary step. Finally, the supernatant was filtered through filter paper (aperture 30–50 μm). Each bench-scale test was conducted in duplicate.

Table 1
Constituents of the high-arsenic wastewater

Constituents[a]	Concentration (mg/L)
Arsenic (III and V)	35–75 (63)[b]
Phosphate (PO_4^{3-})	225–306 (270)[b]
Bicarbonate (HCO_3^-)	124–187 (162)[b]
Sulfate (SO_4^{2-})	185–258 (196)[b]
Chloride (Cl^-)	220–266 (247)[b]
Silica (SiO_2)	128–154 (145)[b]
Sodium (Na^+)	485–672 mg/L

[a] Only major chemicals in the wastewater are listed.

[b] Concentrations of each species in the sample wastewater used in the bench-scale experiment are shown in brackets.

2.3. Full-scale operation description

A full-scale treatment system for the high-arsenic wastewater was constructed based on the results of the bench-scale experiments. The system was operated as sequencing batch reactors, which mainly included primary treatment, secondary treatment, buffer, and sand filter tanks (Fig. 1). In every treatment batch, arsenic concentration of the final effluent was detected using online analysis.

2.4. Analytical methods

All samples were prepared in triplicate and average values were reported in this paper. Arsenic concentration was analyzed by hydride generation atomic fluorescence spectrometry (AF 610B, Ruili Instrument Co., Ltd). The zeta-potential of coagulates was directly determined with a Zetasizer 2000 (Malvern Instruments Ltd, UK). Turbidity was measured with a turbidimeter (WGZ-2000A). Total phosphorus was analyzed by the ammonium molybdate spectrophotometer method.

3. Results and discussion

3.1. Primary treatment

The total arsenic removal from high-arsenic wastewater by primary treatment with different $FeCl_3$ dosages is shown in Fig. 2. The total arsenic removal was obviously improved with increasing $FeCl_3$ dosage from 2,000 to 4,000 mg/L, but there was no significant difference between dosages of 4,000 and 5,000 mg/L. Removal efficiency was also closely related with pH; detailed analyses about pH are discussed below. Additionally, the extent of turbidity and phosphate removal followed the arsenic trends. Only a few settleable flocs were formed with 2,000 mg/L $FeCl_3$ at a pH of 6.0, which was a good pH value for coagulation (detailed analyses of pH are discussed below). The turbidity was not reduced, and even increased, and the residual phosphate concentration remained at 178 mg/L (about only 30% removal). Larger quantities of settleable flocs were observed with 3,000 mg/L $FeCl_3$ at a pH of 6.0. However, turbidity and phosphate were not thoroughly eliminated, as residual turbidity and phosphate values of 80 NTU and 30 mg/L were seen, respectively. With 4,000 and 5,000 mg/L at a pH of 6.0, the removal rates of both phosphate and turbidity were seen to reach more than 99%, and the supernatant was very clear with a phosphate concentration of 0.9–1.5 mg/L and a turbidity of less than 10 NTU. It was noteworthy that the flocs had also a very good settling performance and could precipitate completely

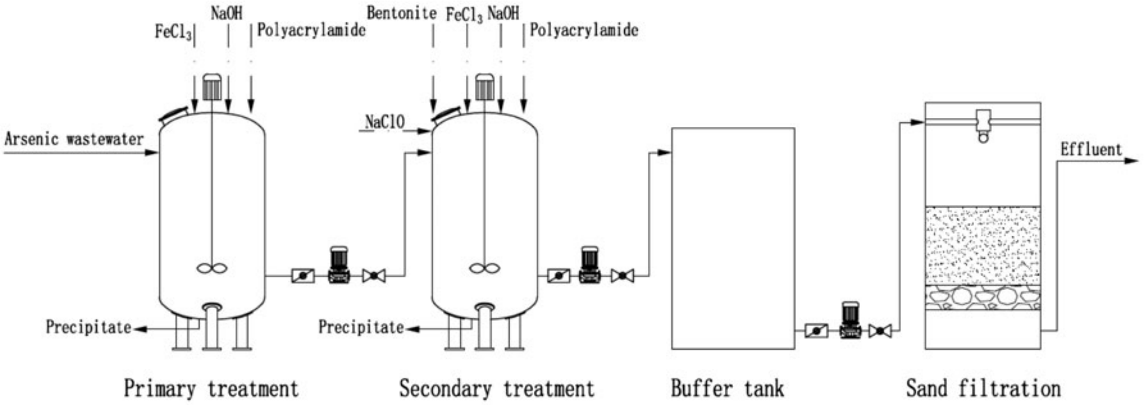

Fig. 1. Schematic diagram of enhanced two-stage treatment for the arsenic wastewater.

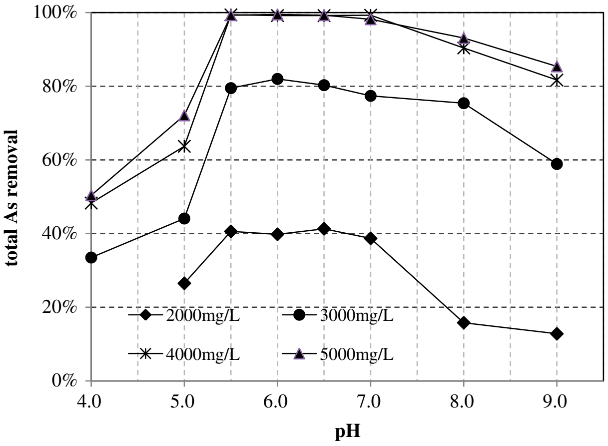

Fig. 2. Arsenic removal by $FeCl_3$ coagulation as a function of pH.

within 15 min. Therefore, for the high-arsenic wastewater in this study, a $FeCl_3$ dosage of more than 4,000 mg/L was appropriate, which was much higher than those used in other studies (usually less than 1,000 mg/L) [4,18,22].

Two reasons may explain the high demand of $FeCl_3$. One was that the high SiO_2 concentration in the wastewater interfered with the Fe^{3+} coagulation process. Because the main removal pathway of SiO_2 colloids and other particulates in the wastewater is enmeshment or entrapment by HFO [6], a large amount of Fe^{3+} was necessary to form a sufficient concentration of HFO *in situ* for charge neutralization and sweep coagulation of the colloid, and to fully reduce the SiO_2 colloids and other particulates. The other reason for the large $FeCl_3$ requirement was the existence of many anions such as phosphate, bicarbonate, and sulfate in the wastewater. These anions—especially the phosphate—could compete with arsenic for active HFO surface sites, and negatively impact arsenic adsorption during coprecipitation with Fe^{3+} [23].

It could be also seen that, in addition to $FeCl_3$ dosage, the pH was an important factor for arsenic removal from the high-arsenic wastewater. The total arsenic removal was dependent on the pH value, and the highest removal efficiencies were obtained in a pH range of 5.5–7.0 (Fig. 2). The average removal efficiencies of total arsenic in the best pH range (e.g. pH 6.0) were 40.1, 79.8, 99.8, and 99.9% for $FeCl_3$ dosages of 2,000, 3,000, 4,000, and 5,000 mg/L, respectively. Arsenic concentrations in the 4,000 and 5,000 mg/L $FeCl_3$-dosed supernatants varied between 0.08 and 0.13 mg/L. However, these residual arsenic concentrations could not meet the permitted discharge limit, so a secondary treatment was required to further reduce the residual arsenic concentration.

Fig. 2 also shows that arsenic could not be removed efficiently in strongly acidic pH (lower than 5.0) or alkaline pH (higher than 8.0). After dosing with $FeCl_3$, the pH value of the mixed liquor decreased sharply from 8.6 to 4.8 (2,000 mg/L), 3.6 (3,000 mg/L), 2.7 (4,000 mg/L), and 2.2 (5,000 mg/L), respectively. During coagulation, as the pH increased, Fe^{3+} hydrolyzed and formed different cationic complexes *in situ* at acidic pH values of 2.2–5.0, according to a pH-dependent equilibrium distribution of ferric species. Between weakly acidic to neutral pH values (5.5–7.0), the hydrolyzed Fe^{3+} species precipitated and aggregated to form structurally amorphous, high-porosity HFO *in situ*. Arsenic and other pollutants could be effectively adsorbed on active sites of HFO by surface complexation or ligand exchange. At alkaline pH, anionic complexes with OH^-, such as $Fe(OH)^{4-}$, would increase and the number of positively charged active sites on the HFO surfaces would decrease. Accordingly, pollutants, especially anions such as arsenate, adsorbed by HFO at weakly acidic pH, would be displaced by OH– [24]. This phenomenon was verified by zeta potential analysis. The zeta potentials of colloids in raw wastewater were consistently negatively charged at pH values of higher than 5.0, and increased significantly due to charge neutralization of $FeCl_3$ in the 5.0–8.0 pH range (Fig. 3). As the pH increased from 5.0 to 8.0, the zeta potential of the HFO particles in the supernatant declined and became negative; and in a pH range of 5.5–6.0, the zeta potential was very close to the isoelectric point. Because As (V) would exist as anionic species ($HAsO_4^{2-}$ and $H_2AsO_4^-$) at pH values higher than 2.0, its removal would not be favored as the pH increases and HFO becomes negatively charged.

Furthermore, As(III) could not be removed as effectively as As(V), since the As(III) contribution to the total arsenic content was dramatically increased from less than 1% in the raw wastewater to about 20% in the primary coagulation supernatants with dosages of 4,000 and 5,000 mg/L in the 5.5–7.0 pH range. As(III) accumulated in the supernatant relative to As (V). Thereby, oxidation was required prior to further purification of the primary supernatant to convert As (III) to As(V) to improve the arsenic removal in the secondary treatment.

3.2. Secondary treatment

Fig. 4 shows that about 70% of As(III) could be oxidized to As(V) with an NaClO concentration of 300 mg/L, and that As(III), as a percentage of the total arsenic content, could be decreased to lower than 5%. Fig. 5 shows that the arsenic removal efficiencies of secondary treatment could be improved by about 40% after oxidization with NaClO in comparison with the non-oxidized case. Like primary treatment, arsenic removal from the oxidized supernatant depended on the number of active sites on HFO, and consequently the ferric dose. Nevertheless, the filtrate arsenic concentrations after oxidization, coagulation, settlement, and filtration could not be consistently reduced below the 0.02 (0.014–0.027 mg/L), the permitted total discharge threshold (Fig. 5). The residual arsenic could exist in both freely dissolved and filterable particle-bound forms [14].

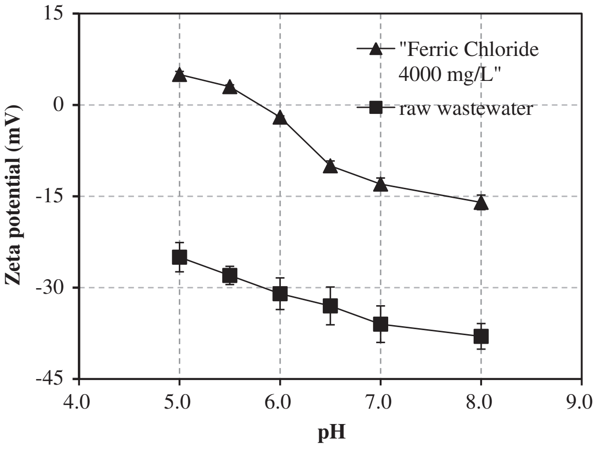

Fig. 3. Zeta potential of raw wastewater and coagulation supernatant as a function of pH.

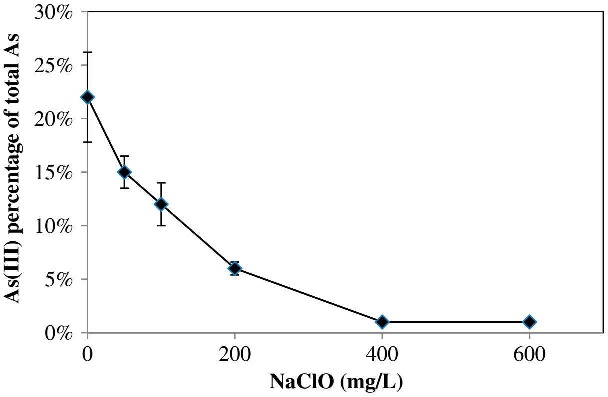

Fig. 4. As(III) oxidized by NaClO.

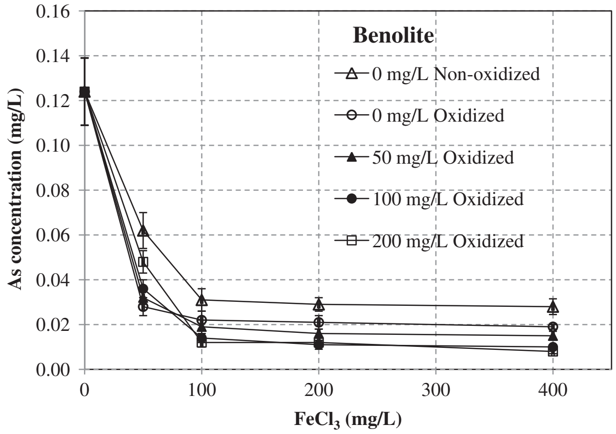

Fig. 5. Enhanced coagulation with NaClO and bentonite for the primary treatment supernatant (pH 6.0).

Therefore, enhanced coagulation with bentonite was used to remove the arsenic from supernatant. With increasing bentonite content, arsenic removal is enhanced and the residual arsenic concentration could decline to nearly 0.012 mg/L. The mechanism of the bentonite enhancement effect might be attributed to adsorption and aggregation acceleration. Arsenic adsorption by bentonite has previously been shown in our laboratory and other studies [20,21]. We found that arsenic adsorption on bentonite was very quick and could reach a steady state within 15 min, but that the maximum adsorption capacity was lower than 0.5 mg/g at a pH of 6.0. Similar results were also seen by Mar et al. [20], who reported a maximum adsorption capacity of As(V) on bentonite of 0.33 mg/g. In addition, bentonite powder particles could increase the collision rate between the powder and colloid particles, compared with the collision frequency between colloid particles themselves [25]. Then, the suspended colloid particles would form multilayer coatings on the powder particles, which would increase the coagulate size and reduce the particle numbers in suspensions.

It is noted that $FeCl_3$ dosages of more than 100 mg/L were necessary for efficient coagulation and flocculation after bentonite addition. The zeta potential of bentonite particles in deionized water with 100 mg/L was −29 mV at a pH of 6.0. This meant that more Fe^{3+} was needed to neutralize the negative charge and enhance aggregation and sedimentation. Otherwise, the powder bentonite (more than 100 mg/L) might impact arsenic removal with $FeCl_3$ dosages of less than 50 mg/L, in comparison with that without bentonite (Fig. 5).

Table 2
Main parameters of the full-scale sequencing batch treatment system

Process	Parameters	
Primary treatment	$FeCl_3$ dosage	4,000–5,000 mg/L
	PAM	8–10 mg/L
	pH	5.5–6.0
Secondary treatment	NaClO dosage	300–400 mg/L
	Bentonite dosage	100–200 mg/L
	$FeCl_3$ dosage	200–300 mg/L
	PAM	4–5 mg/L
	pH	5.5–6.0
Sand filtering	Filtering velocity	5 m/h

3.3. Full-scale application

The main parameters of the full-scale system (Fig. 1), which were based on the bench-scale experimental results, are listed in Table 2. Sand filtering instead of paper filtration was introduced in the full-scale system to eliminate unsettled particles in the secondary coagulation supernatant and guarantee final effluent water quality. The velocity gradient (*G* value) for mixing the wastewater with $FeCl_3$ was 500 s in both first and secondary stages, and *G* value for flocculation after PAM addition was 90 s. The *G* value for bentonite mixing was also 500 s. pH adjustment, flocs settlement, and accumulative times in primary treatment were 7–10, 10–15, and 40–45 min, respectively. The arsenic concentration in the primary supernatant varied between 0.08 and 0.15 mg/L. Times for NaClO oxidization and bentonite adsorption were 5–10 and 15–20 min, respectively, and the accumulative time was 60–80 min in secondary treatment. The arsenic concentration in the secondary supernatant varied between 0.015 and 0.025 mg/L. The final effluent arsenic concentration after sand filtration was 0.009–0.018 mg/L, which met the permitted discharge threshold. The whole process was completed within 125 min, which was significantly shorter than other coagulation processes for arsenic wastewater [14,15].

Cost analysis showed that total cost of the combined process used for arsenic removal varied between 3.50 and 4.34 USD (Table 3). The cost of $FeCl_3$ contributed more than 60% for the total cost due to its high demand, and cost of NaClO contributed about 15%. Labor and power costs only took over 12–15%. It seemed that the enhanced two-stage process was a little expensive. However, the process could effectively reduce the arsenic concentration from 35 to 75 mg/L to less than 0.02 mg/L, and the total cost is far lower than that of the process using ultrafiltration and reverse osmosis to achieve the same arsenic concentration target in our another test.

Table 3
Economic evaluation of the full-scale process

Items		Price[a]	Process cost (USD/m^3)
Labor		20 USD/(day person)	0.30
Power consumption		0.13 USD/(kwh)	0.21
Chemical reagents or solutions	$FeCl_3$ (38%)	0.20 USD/kg	2.19–2.77
	PAM	3.64 USD/kg	0.04–0.05
	NaOH	0.41 USD/kg	0.25–0.33
	NaClO (10%)	0.17 USD/kg	0.50–0.66
	Bentonite	0.08 USD/kg	0.01–0.02
Total cost			3.50–4.34

[a] Price was calculated by exchange rate.

4. Conclusion

High-arsenic wastewater from GaAs semiconductor production was effectively purified by a combined process including primary treatment by $FeCl_3$ and PAM, oxidization by NaClO, enhanced secondary treatment with bentonite, and sand filtering, giving a residual arsenic concentration of lower than 0.02 mg/L. Primary treatment with large quantities of $FeCl_3$ (more than 4,000 mg/L) was essential, effectively eliminating most arsenic, phosphate, silica, and other interferents. Oxidization was necessary to convert residual As(III) to As (V) before secondary treatment. Bentonite powder (30–60 μm) could be used to enhance secondary treatment for arsenic removal by its adsorption of arsenic and coagulation improvement. Conventional sand filtration was adequate and suitable to produce a final effluent with very low arsenic concentrations, which met the permitted total discharge limit. The successful full-scale case demonstrated that the proposed process in this study could be used to treat high-arsenic wastewater from GaAs production facilities with the advantages of high reliability, effectiveness, and ease of operation.

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