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Experimental Study on the Removal of Arsenic in Waste Water from Semiconductor Manufacturing

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Abstract

An effective and economic process for removing arsenic in waste water which is acuminating in the process of etching, cutting and washing in semiconductor industry has been developed in this paper. The proposed technique of arsenic removal is as follows: first pretreatment step is to oxidize arsenite to arsenate by potassium permanganate, second key step is precipitation based on arsenic compound solubility with ferric sulfate and slaked lime under pH adjustment, and the last complementary step is followed by the adsorption of the bentonite with enhanced by activated carbon and organic adsorbent. Experimental results show that under the optimal condition the removal efficiency of arsenic in the waste water is better than 99.99%, or the concentration of arsenic is from its original 100mg/l reduced to less than 10μg/l accordingly.

1. Introduction

With the fast increasing requirements of the society and economy, the semiconductor industry is being under strong development. A major environment problem resulted by the compound semiconductor manufacturing is its waste water, which most commonly consist of elements such as arsenic, gallium, indium and phosphorous. These elements dissolve in water in the process of cutting, etching, grinding and lead risk to ecological system [1].

The main purpose of this study is to look for an effective process to reduce arsenic in waste water to level acceptable for water reuse or discharge. After comparing various techniques [2–4], i.e., precipitation, adsorption, ion exchange, reverse osmosis, distillation, evaporation, and electrolysis respectively, a combinative process of precipitation and adsorption has been chosen for its economics and convenience.

2. Materials and Methods

2.1. Materials

The waste water samples are collected at a local com-

pound semiconductor factory in September 2006. Several original major contents are: As of 100 mg/l, pH of 6, and a little of Ga (20mg/l) and In (5mg/l).

Arsenic and other heavy metals in water samples are analyzed by the atomic adsorption spectrometer (AA-70, HP, U. S.). The pH is detected by the pH instrument (PHS-25, Shanghai).

The bentonite is H-type come from Weifang, Shandong. The activated carbon is STR-type come from Shijiazhuang, Hebei. The organic adsorbent is unique made in this study which mainly consisted of vegetable protein. And all of the chemical reagents are of chemical analysis grade.

2.2. Methods

The procedure design for removal of arsenic in waste water is shown in Figure 1.

Because the removal efficiency of arsenate is 30% higher than that of arsenite, $KMnO_4$ has been selected to oxidize As(III) to As(V) at the beginning which guaranties As(V) is dominant in solution in the continues steps [2,3].

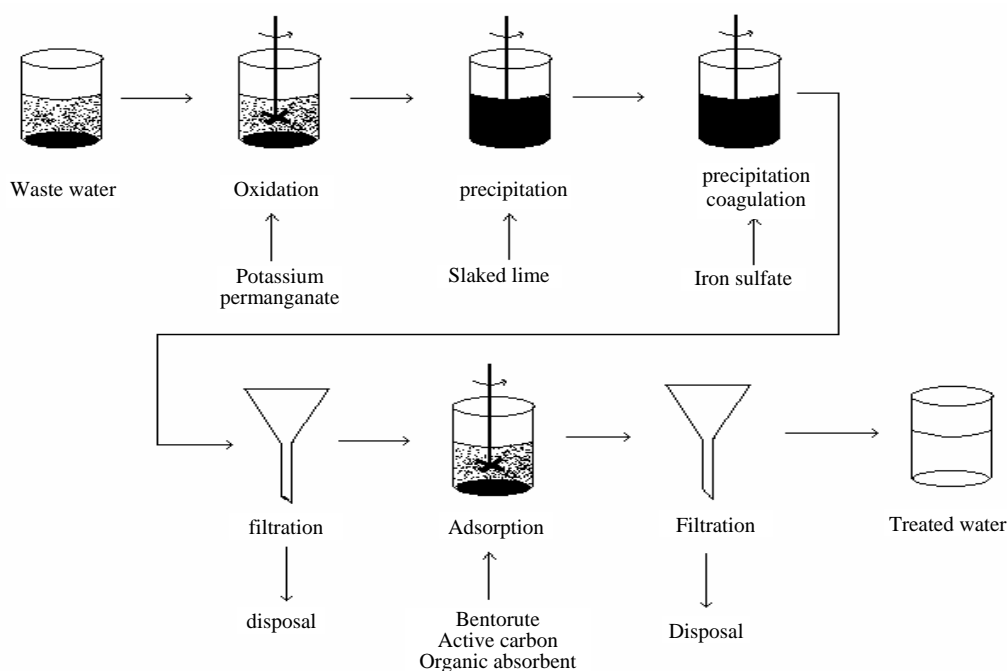Slaked lime ($Ca(OH)_2$) have been applied in pH adjustment and precipitation cooperated with ferric sulfate

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Figure 1. Treatment procedure design.

$(Fe_2(SO_4)_3)$, because of the high efficiency of the removal of arsenic based on the low solubility of $Ca_3(AsO_4)_2.3H_2O$ (solubility of 0.013), $Ca_3(AsO_4)_2.Ca(OH)_2$ (solubility of 0.0023-0.0048), and $FeAsO_4. 2H_2O$ (insoluble) [4].

Bentonite has been considered to complement removal of arsenic, which enhanced by activated carbon and organic adsorbent [2,5,6]. Bentonite can reach its absorbing equilibrium quickly with good saturated adsorption amount, and the most important is that it is cost-efficient and easy to obtain. Activated carbon is a classical kind of adsorbent with better saturated adsorption amount, and it is used in a broad way presently. The unique organic absorbent is more effective in the removal of arsenic, and it is easy to produce but a little expensive compared to the two adsorbents above mentioned.
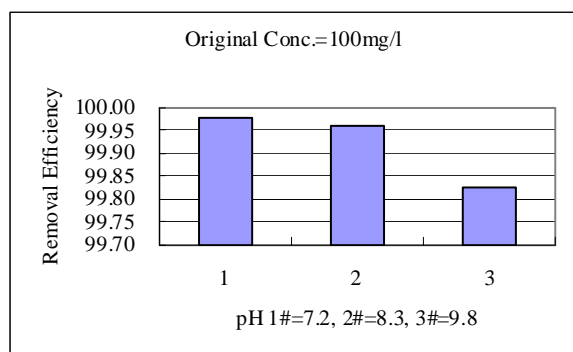
3. Results and Discussion

3.1. The Removal Efficiency of $Ca(OH)_2$ and $Fe_2(SO_4)_3$

After pre-treatment of oxidation, a batch experiment has been taken on the composition of $Ca(OH)_2$ and $Fe_2(SO_4)_3$. The results are shown in Table 1.

From the results (Figure 2) it indicates that pH is a controlled element in this step. If the $Ca(OH)_2$ is over added the excessive OH^- can replace AsO_4^{3-} and make AsO_4^{3-} dissolve out from the sludge and adsorbent. From the experiment it shows the suitable composition is 0.2g of $Ca(OH)_2$ and 1ml of $Fe_2(SO_4)$ (30%) for 100ml of waste water as well as keeping the pH at neutrality.

Table 1. The batch test of $Ca(OH)_2$ and $Fe_2(SO_4)_3$.

Original As (mg/l)	$Ca(OH)_2$ (g/100ml)	$Fe_2(SO_4)_3$(30%) (ml/100ml)	Remaining As (μg/l)
100	0.025	0.125	154.3
100	0.05	0.25	119.4
100	0.075	0.375	90.2
100	0.1	0.5	56.6
100	0.125	0.625	37.8
100	0.15	0.75	24.3
100	0.175	0.875	15.9
100	0.2	1.0	13.7
100	0.225	1.125	13.8

Figure 2. As removal efficiency under different pH.

The arsenic in waste water can be reduced from 100mg/l to 13.7 µg/l under the optimal precipitation condition, which is quite close to the final requirement.

3.2. The Removal Capacity of Bentonite

A batch experiment has been taken to test the adsorption capacity of bentonite. Twelve samples of 100ml solution which contain arsenic from 5 mg/l to 60 mg/l are added by 1g of bentonite separately. After stirring for 60 minutes under room temperature, the remaining arsenic in water of each sample is detected. The results are shown in Table 2 and Figure 3.

Based on Figure 3 it can be summarized that the saturated arsenic adsorption amount of bentonite is about 5.1mg/g.

Based on the same method, the saturated arsenic adsorption amount of activated carbon (18.3mg/g) and organic adsorbent (21.2mg/g) are also obtained.

3.3. The Optimal Condition for Removal of Arsenic

To find the optimal condition for removal of arsenic in waste water, a batch experiment has been taken on the proportions of chemicals and adsorbents added. Suppose 1 unit of $Ca(OH)_2$ is represented by 0.10g, 1 unit of $Fe_2(SO_4)_3$ (30%) is represented by 0.50ml, 1 unit of bentonite is represented by 0.175g, 1 unit of activated carbon

Table 2. The batch test of bentonite.

Original As (mg/l)	Remain As (µg/l)	Original As (mg/l)	Remaining As (µg/l)
5	4.7	35	30.5
10	8.8	40	35.1
15	12.9	45	40.02
20	17.1	50	44.97
25	21.4	55	49.9
30	25.9	60	54.89
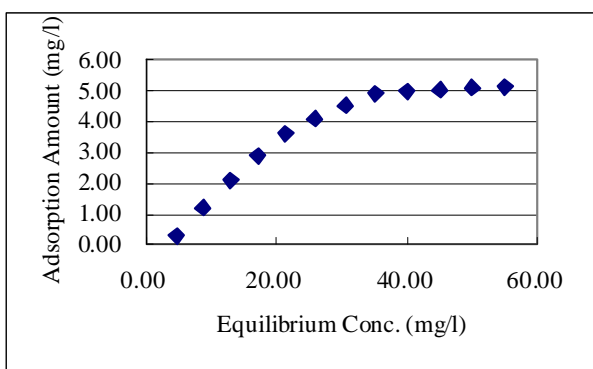
Figure 3. The adsorption equilibrium curve of bentonite.

is represented by 0.100g, and 1unit of organic adsorbent is represented by 0.025g. The results are shown in Table 3.

It can be concluded that fourteen composition (No.2, 3, 5, 6, 8, 9, 12, 13, 14, 15, 18, 19, 20, and 21) can meet the requirement of arsenic in treated water should be reduced to less than 10 µg/l. After consideration both of the economic and technique factors, No.2 is chosen to be the optimal composition for our procedure.

In addition, the process is also efficient to remove gallium and indium in the waste water. After treated the concentrations of gallium and indium are from original 20 mg/l and 5 mg/l respectively reduced to lower than the detecting limit of AA analysis.

4. Conclusions

For removing arsenic from waste water which is acuminating in the process of etching, cutting and washing in semiconductor manufacturing, a proposed technique is designed based on technique and economic efficiency. The procedure includes: first pretreatment step is to oxidize arsenite to arsenate by potassium permanganate, second key step is precipitation based on arsenic compound solubility with ferric sulfate and slaked lime under pH adjustment, and the last complementary step is followed by the adsorption of bentonite with enhanced by activated carbon and organic adsorbent.

Table 3. The batch test of removal of arsenic.

Number	$Ca(OH)_2$ (unit)	$Fe_2(SO_4)_3$ (unit)	Bentonite (unit)	Activated carbon (unit)	Organic adsorbent (unit)	Remaining As (µg/l)
1	1	1	1	1	1	30.8
2	2	2	1	1	1	9.8
3	3	3	1	1	1	6.2
4	1	1	2	2	2	28.7
5	2	2	2	2	2	9.2
6	3	3	2	2	2	5.8
7	1	1	3	3	3	24.2
8	2	2	3	3	3	8.9
9	3	3	3	3	3	4.6
10	1	1	2	1	1	29.0
11	1	1	3	1	1	24.3
12	2	2	1	2	2	9.3
13	2	2	3	2	2	9.0
14	3	3	1	3	3	5.0
15	3	3	2	3	3	4.8
16	1	1	1	2	2	29.3
17	1	1	1	3	3	26.5
18	2	2	2	1	1	9.6
19	2	2	2	3	3	8.9
20	3	3	3	1	1	5.5
21	3	3	3	2	2	5.3

The optimal composition of reagents for removal of arsenic from 100 mg/l to 10 µg/l in 100ml solution can be concluded as 0.2g of $Ca(OH)_2$, 0.1ml of $Fe_2(SO_4)_3$ (30%), 0.175g of bentonite, 0.1g of activated carbon, and 0.025g of organic adsorbent.

5. Acknowledgement

6. References

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