Study on the Purification Process of Arsenic High Iron Wastewater from Zinc Smelter

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Abstract: Arsenic high iron wastewater was produced by sulfated roasting-water leaching process from the zinc smelting industry, high contents of total iron, zinc ion and sulfate ion, were contained, a certain amount of arsenic ion, copper ion and cadmium ion were also involved. With strict environmental protection, the comprehensive utilization of wastewater has great economic significance, it is one of the most important direction that the preparation of iron-salt flocculant with wastewater. It is necessary to pretreat and purify firstly. In this paper, the sample comes from Chihong Inner Mongolia, China. The concentrations of total iron, sulfate ion and zinc ion are 24.18 g/L, 91.31 g/L and 5.54 g/L, respectively. The effect of reducing agent proportion, temperature, stirring speed on the purification of arsenic ion, copper ion, cadmium ion was researched. The optimal conditions are: reducing agent proportion of 1% of iron powder, 2% of zinc powder, temperature of 60 ℃, and stirring speed of 800 rpm. Under the conditions, the efficiency of arsenic ion, copper ion and cadmium ion all reached 99.99%. The concentrations of total iron, sulfate ion and zinc ion in the wastewater after purification are 55.23 g/L, 126.25 g/L and 39.00 g/L, respectively, which provided the precondition for the subsequent preparation of iron-salt flocculant.

1 INTRODUCTION

Arsenic high iron wastewater was produced by sulfated roasting-water leaching process from the zinc smelting industry(Fu and Wang, 2011)(Zhao et al., 2012). The main features of this type of wastewater was high iron content, which was generally up to 30-60 g/L; strong acidity, pH value between 1-4; sulfate ion mass concentration up to thousands of milligrams per liter; at the same time, contains trace amounts of arsenic ion, copper ion, cadmium ion and so on(Ozverdi, 2006)(Tang, 2010). Arsenic high iron wastewater treatment methods were neutralization precipitation method, sulfide precipitation method, ion exchange method, iron reduction method and biological flocculation method(He et al., 2013; Huisman, 2006; Yang et al., 2014; Huo et al., 2009; Greenleaf et al., 2006; Liu, 2016). Among them, the industrial application was still extensively used in the neutralization precipitation method, which has the advantages of low cost and simple process The main problem was the large amount of slag, secondary pollution problem(Meng and Geng, 2013)(Gao and Sheng, 2015).

The use of arsenic high iron wastewater for preparation of iron and zinc complex salt flocculant has good industrial application prospects(Busetti et al., 2005; Jong and Parry, 2003; Song, 2016). However, the resource utilization of the kind of wastewater was limited for arsenic ion, copper ion, cadmium ion. To prepare iron and zinc complex salt flocculant by using the wastewater, firstly, it was necessary to purificate(He et al., 2012)(Li et al., 2010). In this paper, arsenic high iron wastewater was used as research object, which come from Chihong Smelting Plant in In Nei Mongol Province, China. Iron powder and zinc powder were used as reduing agent, arsenic ion, copper ion, cadmium ion and other impurities were purified. Different factors on the efficiency of arsenic ion, copper ion, cadmium ion were researched, which included adding proportion of reducing agent, reaction temperature and stirring speed.

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2 MATERIAL AND METHODS

2.1 Material

The arsenic high iron wastewater was obtained from Chihong Smelting Plant in In Nei Mongol Province, China. The chemical multi-elemental analysis was detected by ICP-OES, the product model is Agilent 725-ES. The results are shown in Table 1. The sample contains 46.35 mg/L cadmium ion, 453.74 mg/L arsenic ion, 260.5 mg/L copper ion, 91310 mg/L sulfate ion, 5540 mg/L zinc ion, 24180 mg/L total iron.

2.2 Experimental Method

Purification experiment was performed in 500 mL beaker containing 200 mL solution. The content of arsenic ion, cadmium ion, copper ion, total iron, zinc ion, and sulfate ion in the solution was measured by ICP-OES.

(1) Effect of reducing agent proportion

The reactor was set to temperature 60 ℃, time 4 h, stirring speed 800 rpm. The addition amount of the reducing agent was 3%(ω/ν) of iron, 2%(ω/ν) of iron and 1%(ω/ν) of zinc, 1.5%(ω/ν) of iron and zinc, 1%(ω/ν) of iron and 2%(ω/ν) of zinc, 3% (ω/ν) of zinc.

(2) Effect of stirring speed

The reactor was set to temperature 60 ℃, time 4 h, iron 2% (ω/ν) and zinc 1% (ω/ ν). The stirring speed was 400 rpm, 600 rpm, 800 rpm, 1000 rpm.

(3) Effect of temperature

The reactor was set to time 4 h, stirring speed 800 rpm, reducing agent iron 2%(ω/ν) and zinc 1%(ω/ν). The temperature was 20 ℃, 40 ℃, 60 ℃, 80 ℃.

3 RESULTS AND DISCUSSION

3.1 Effect of Reducing Agent Proportion

Figure 1 shows the efficiency of arsenic ion, copper ion, and cadmium ion under different reducing agent proportion. As shown in Figure 1(a)(b)(c)(d)(e), the efficiency of arsenic ion, copper ion and cadmium ion increase firstly then remain stable. Under the condition of iron powder 3%, copper ion efficiency was 98.03% in the first hour, finnaly, arsenic ion and cadmium ion efficiency were 95.64%, 34.81%. Adding 3%(ω/ν) iron powder has good removal effect on copper ion and arsenic ion, however removal effect on cadmium ion was poor with efficiency of only 34.81%. Under the condition of 2% (ω/ν), iron powder added with 1% (ω/ν) zinc powder, the copper ion efficiency was less affected, and the copper ion efficiency reached 99.24% in first hour, it increased by 1.21 percentage points compared to iron 3%, and the addition of zinc powder accelerated the efficiency of arsenic ion, the efficiency of arsenic ion was basically identical, the efficiency of cadmium ion was 42.23%, which was obviously higher than that without zinc powder, Zinc have a good impact on the removal of cadmium ion.

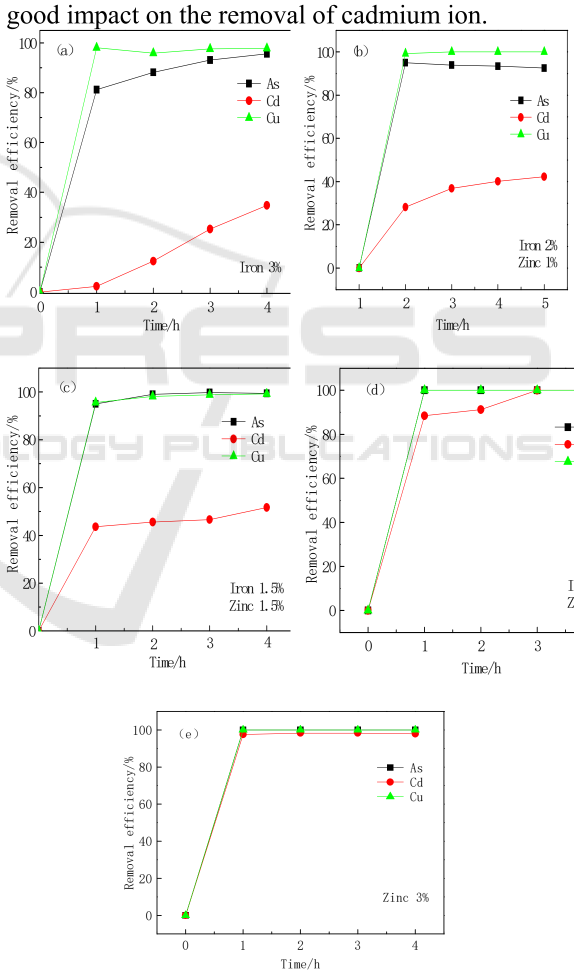

Figure 1: Arsenic ion, copper ion and cadmium ion efficiency with different iron and zinc addition ratios. (a) iron powder 3% (b) iron powder 2%, zinc powder 1% (c) iron powder, zinc powder 1.5%d) iron powder 1%, zinc powder 2% e) zinc powder 3%.

Table 1: Chemical multi-elemental analysis of arsenic high iron wastewater (concentration, mg/L).

As^{3+}	Ca^{2+}	Cd^{2+}	Cu^{2+}	TFe	K^{+}	Mg^{2+}	Na^{+}	SO_4^{2-}	Zn^{2+}
453.74	0.48	46.35	260.5	24180	0.07	0.05	0.02	91310	5540

As shown in Figure 1 (c)(d)(e), the efficiency of copper ion and arsenic ion have little impact with the increase of zinc powder addition, copper ion and arsenic ion efficiency reached 99.99% in first hour, and the efficiency of cadmium ion was shown an increasing trend. While the amount of zinc powder added was 1.5% (ω/v), the efficiency of cadmium ion was 51.67%. The addition of 2%(ω/v) zinc powder of cadmium ion efficiency reached 99.99% in the third hour. Cadmium ion efficiency got faster under the condition of 3% zinc, it reached 99.99% in the first hour.

As a result, while reducing agent was only iron powder, arsenic ion and copper ion efficiency was good, cadmium ion efficiency was poor. With the increase addition of zinc powder, copper ion efficiency was less effected, arsenic ion efficiency can be accelerated to a certain extent. However, cadmium ion efficiency was effected greatly, the final efficiency reached 99.99%.

In the selection of addition of iron and zinc powder, due to the industrial price of zinc is much more expensive than iron, and combined with the follow-up preparation of iron-zinc composite salt flocculant, the agent proportion was iron 2% (ω/v), zinc 1% (ω/ v), the reaction time was 3 h

3.2 Effect of Stirring Speed

The effect of stirring speed on the efficiency of cadmium ion was shown in Figure 2. As can be seen from Figure 2, with the increase of stirring speed, the efficiency of cadmium ion was gradually increased. After the stirring speed was increased to 800 rpm, the cadmium ion efficiency reached 99.99%. The effect of stirring speed on the efficiency of copper ion and arsenic ion was shown in Table 2. It can be seen from that the stirring speed has little effect on the efficiency of copper ion and arsenic ion. The increase of stirring speed increased the removal of cadmium ion, but had no obvious effect on the efficiency of copper ion and arsenic ion. In summary, stirring speed was 800 rpm.

Table 2: Effect of stirring speed on copper ion and arsenic ion efficiency (efficiency/%).

	400 rpm	600 rpm	800 rpm	1000 rpm
Cu^{2+}	99.99	99.99	99.99	99.99
As^{3+}	99.99	99.99	99.99	99.99

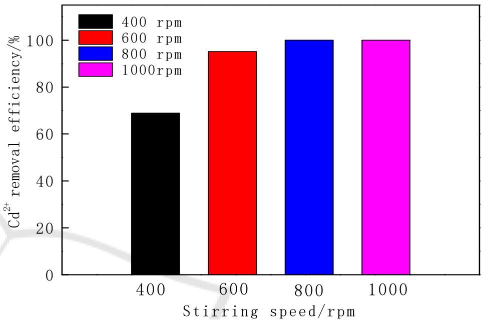

Figure 2: cadmium ion efficiency with different stirring speed.

The chemical elemental analysis of the purified solution was shown in Table 3. It can be seen from Table 3 that the total iron concentration of the purified solution was significantly increased from initial iron concentration of 24.18 g/L to final of 45.25 g/L. And the concentration of zinc ion was 31.07 g/L, which was significantly higher than the initial 5.54 g/L. It was worth noting that the content of arsenic ion, copper ion, and cadmium ion was lower after purifying, which meets the National standards.

Table 3: Chemical multi-element analysis of the purified solution (concentration, mg/L).

	TFe	SO_4^{2-}	Zn^{2+}	Cu^{2+}	As^{3+}	Cd^{2+}
Initial	24180	91310	5540	260.5	453.73	46.35
Final	45250	120090	31070	0.0001	0.0001	0.0001

3.3 Effect of Temperature

The effect of reaction temperature on cadmium ion removal rate was shown in Figure 3. As was seen from Figure 3, cadmium ion efficiency increased with the increase of reaction temperature. When the reaction temperature was 20 ℃, the efficiency of cadmium ion was only 76.49%. When the temperature was increased to 40 ℃, the efficiency of cadmium ion was increased to 98.12%. After the temperature was increased to 60 ℃, the efficiency of cadmium ion reached 99.99%.

The influence of reaction temperature on copper ion and arsenic ion efficiency was shown in Table 4. It can be seen from Table 4 that the reaction temperature has little effect on the efficiency of copper ion and arsenic ion. The increase of reaction temperature increased the removal of cadmium ion by iron powder and zinc powder, but had no obvious effect on the removal of copper ion and arsenic ion. In summary, the reaction temperature was selected 60

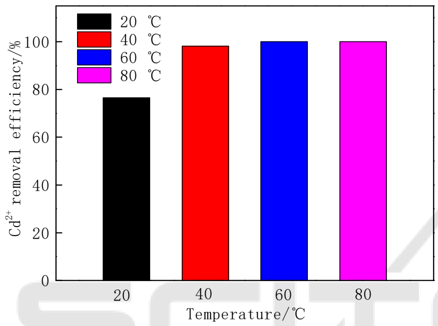

Figure 3: Cadmium ion efficiency with different temperature.

Table 4: Effect of temperature on copper ion and arsenic ion efficiency (efficiency/%).

	20 ℃	40 ℃	60 ℃	80 ℃
Cu^{2+}	99.99	99.99	99.99	99.99
As^{3+}	99.99	99.99	99.99	99.99

The chemical multi-elemental analysis of the solution after purification at 60 °C was shown in Table 5. It can be seen from Table 3 that the concentration of total iron, zinc ion and sulfate ion in purified solution were respectively 55.23 g/L, 39.0 g/L and 126.25 g/L. It was worth noting that the content of arsenic ion, copper ion and cadmium ion in the purified solution was relatively low, which also meets the National standards.

Table 5: Chemical multi-element analysis of the purified solution(concentration, mg/L).

	TFe	SO_4^{2-}	Zn^{2+}	Cu^{2+}	As^{3+}	Cd^{2+}
Initial	24180	91310	5540	260.5	453.73	46.35
Final	55230	126250	39000	0.0001	0.0001	0.0001

4 CONCLUSIONS

Adding iron powder as reductant without zinc, arsenic ion, copper ion efficiency was good, the removal rate reached 99.37%、99.17%, however, cadmium ion removal rate was poor, the removal rate of only 51.67%. cadmium ion removal rate can be greatly improved by adding zinc powder , which reached 99.99% under the condition of 1% zinc;

The best purification conditions are: iron powder 1%, zinc powder 2%, reaction temperature 60 ℃, stirring speed 800 rpm. Under this condition, arsenic ion, copper ion, cadmium ion content comply with national emission standards;

After purification, the concentrations of total iron, sulfate ion and zinc ion were 55.23 g/L, 126.25 g/L and 39.00 g/L, respectively, which provided the precondition for the subsequent preparation of iron and zinc complex salt flocculant.

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