

A novel strategy for arsenic removal from dirty acid wastewater via CaCO_3 - $\text{Ca}(\text{OH})_2$ -Fe(III) processing



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ABSTRACT

To solve the environmental problems caused by dirty acid wastewater discharging from sulfuric acid plant, this study developed an efficient and economical method to remove arsenic from dirty wastewater through a continuous three-stage co-precipitation processing, which includes (1) formation of gypsum by addition of calcium carbonate, (2) neutralization of the filtrate with lime, and (3) adsorption of residual arsenic by ferric sulfate. In the 1st stage, the gypsum formed from using CaCO_3 showed higher crystal purity than those using traditional neutralizers such as CaO and $\text{Ca}(\text{OH})_2$, and the precipitates are recyclable due to the fact that carbon dioxide (CO_2) emitted in neutralization could prevent gypsum from shielding the surface of the neutralizer. In the 2nd stage, $\text{Ca}(\text{OH})_2$ was used to get a pH of 11.9 for arsenic removal. CO_3^{2-} shows little effect on arsenic removal rate and stability of precipitates. In the 3rd stage, $\text{Fe}_2(\text{SO}_4)_3$ was utilized to further remove arsenic to make its concentration below than 0.2 mg/L by adsorption at pH 9.0. Using this novel 3-stage processing, the gross weight of As-containing hazardous waste was sharply reduced to as high as 50%. The high purity of the obtained As-containing solid waste makes it possible to be reused as a raw material.

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1. Introduction

Sulfuric acid is widely used in agriculture, metallurgy industry, national defense, and textile industry, which also plays an important role in producing raw chemical materials. It was estimated that sulfuric acid-containing wastewater in China amounted to 100 billion tons in 2015, and 30% of them was from smelting off-gas. During the production process, wastewater, known as *dirty acid wastewater* (DAW), is the main by-product. DAW typically contains 0.5–1.0 M sulfuric acid, high-concentrated arsenic and some extremely toxic heavy metals. In general, the concentration of arsenic in DAW ranges from 0.5 to 3 g/L⁻¹, which mainly exists in forms of trivalent arsenic [1]. In some cases, the concentration of arsenic in DAW could be as high as 10 g/L⁻¹. A direct discharge without effective removal of arsenic from DAW could cause serious damages to the ecological environment [2].

It is widely known that toxicity of arsenic, even at low concentrations, can cause cancer [3,4]. Therefore, arsenic removal from dirty acid wastewater is a global critical issue. Removal of arsenic with chemical precipitation is currently the most common meth-

ods. Traditional precipitants like ferric salt [5], lime [6] and sulfide [7] show good performance. Combination of lime neutralization with ferric iron coagulation is also commonly used for removing As in industrial applications [1]. However, traditional chemical precipitation methods have some disadvantages. For example, the typical weight content of arsenic in precipitates is as high as 5%–15%, which results in another problem to disposal of the formed dangerous solid waste. When the concentration of arsenic in the solution is higher than 1 mg/L⁻¹, lime neutralization is also not preferred [8,9]. Recent researches have focused on the following main ways to optimize this process: removing arsenic efficiently, reducing the weight of sludge, improving the stability of solid wastes, and increasing utilization of resources.

A combination of lime and ferric chloride were able to remove more than 99% of the original arsenic concentration [10]. Iron (III) sulphate as a coprecipitation agent was found to be effective for solutions containing low As(III) concentrations ($\leq 10 \text{ mg/L}^{-1}$) [11]. Jia et al. [12] proposed a two-step co-precipitation by using Fe(III) and Al(III) for arsenic removal and immobilization. De Klerk [13] proved that a continuous process was more efficient than combination of these single steps. A new three-stage treatment with ferrous iron and lime could be effective in disposal of DAW [14]. Compared with the traditional sulfide feeding method (surface feeding), immersed distributor feeding was found more efficient

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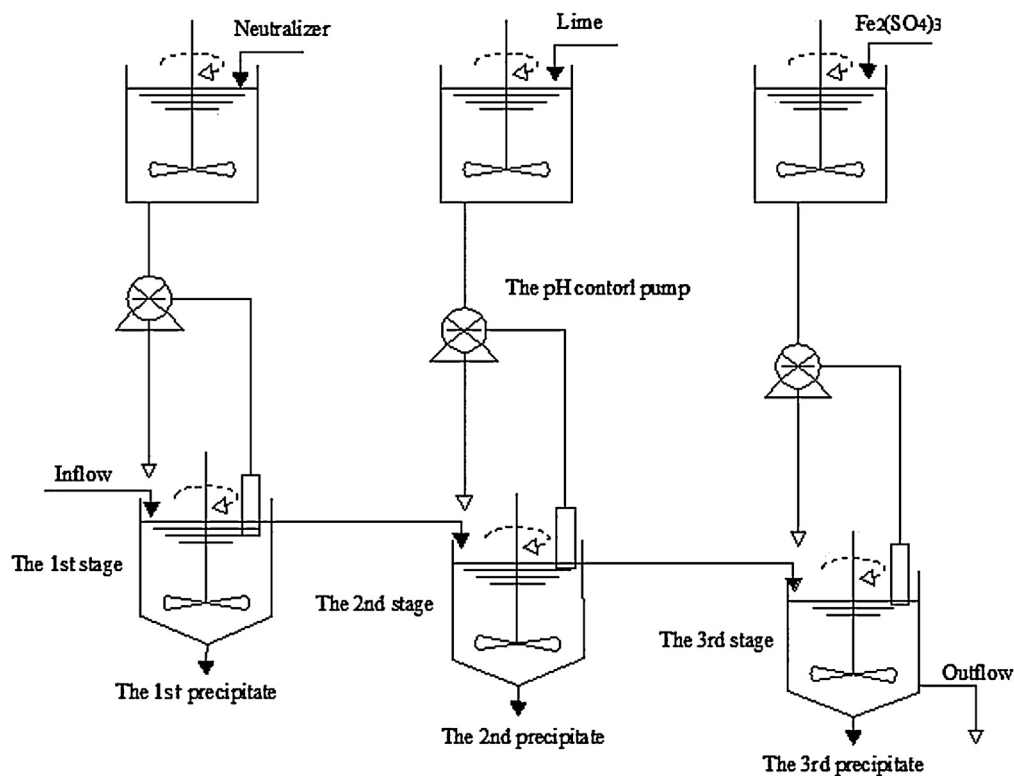


Fig. 1. The designed three-stage treatment process in this experiment.

and economical [15]. However, there were still some difficulties in industrial application. For example, it was difficult to control the pH value in the 1st stage by lime, and arsenic content in obtained gypsum was higher than 0.1 wt.%.

To solve these problems, a novel three-stage treatment was proposed to improve the arsenic content in slag and increase the recycling of gypsum to a large extent. The 1st stage was performed to neutralize sulfuric acid and control the arsenic content of sediment by using CaCO_3 as a neutralizer. The 2nd stage focused on producing sediment with high arsenic content and reducing its total quantity with lime as a neutralizer. At the same time, the effect of CO_3^{2-} on the stability of precipitation was studied. The 3rd stage aims to further remove the residual arsenic to keep its content below 0.2 mg L^{-1} by addition of ferric sulfate.

2. Materials and methods

2.1. Materials

Four chemical materials were used in the study: calcium carbonate (CaCO_3 , 5 wt. %), lime (Ca(OH)_2 , 5 and 10 wt.%), calcium oxide (CaO , 5 wt.%), and ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$, 10 wt.%). Note that three neutralizers (CaCO_3 , Ca(OH)_2 and CaO with 5 wt.%) were used to remove sulfuric acid, while 10 wt.% lime was used to remove arsenic in the 2nd stage.

Samples of DAW in this study were collected from a sulfuric acid production plant located in Hubei, China. They were settled for 2 days, and then filtrated with a filter paper (80 mm aperture) to remove suspended solids. The compositions of the wastewater in two batches at different time were shown in Table 1. It can be seen that the concentration of arsenic in the wastewater was $5.2\text{--}8.6 \text{ g L}^{-1}$. The pH of wastewater was about 0.5.

Table 1

Compositions of dirty acid wastewater samples (unit: mg L^{-1}).

Constituent	Cu^{2+}	Zn^{2+}	Cd^{2+}	Total As	SO_4^{2-}	Pb^{2+}
Case I	40.5	65.2	50.8	5,240	6,000	9.6
Case II	32.1	57.3	44.1	8,633	9,600	20.4

2.2. Methods

For the laboratory simulation of a novel three-stage treatment, three tank reactors (with the reactor volume of 2 L and flow rate of 35 mL min^{-1}) were configured in series, as shown in Fig. 1. The aims of each of the three stages were (1) neutralizing sulfuric acid, (2) producing high arsenic content sediment and (3) removing the residual arsenic. The typical pH values in each reactor range from 1 to 3 (1st stage), 8 to 12.5 (2nd stage), and 12 to 7 (3rd stage) accordingly. Pumps were used to control the solution pH by addition of base into each reactor. The time setting for each stage was 1 h, 3 h and 0.5 h, so as to guarantee a steady state of the reaction. At the end of each stage, the supernatant liquid would flow to the next reactor, and the solids were centrifuged and dried for subsequent analysis.

All precipitate samples were dried at 50°C for 8 h. To determine the content of heavy metal, all precipitate samples were digested in acidic solution (20-ml sulfuric acid and 10-ml nitric acid were added to the 2 g-sample) and filtrated with membrane (pore size $0.45 \mu\text{m}$). The stability experiment was conducted in HDPE (high density polyethylene) bottles, in which the ratio of precipitate and DI water was 20:1 and the stirring rate was 30rpm (revolutions per minute).

2.3. Analyses

The crystalline structure was analyzed by X-ray powder diffraction (XRD, BRUKER, D 8 ADVANCE). Scanning electron microscope

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