Removal of Heavy Metals by the Ferrite Process

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Abstract: The purpose of this study is to investigate the treatment of Cr (VI) and Ni (II) wastewater by the ferrite process.In this paper, the ferrite process of Cr (VI) and Ni (II) synthetic solution by hydrothermal reaction and its technological parameters was studied. The most optimum reaction conditions were explored: pH=9.0, temperature=70℃, stirring time=40min, stirring speed=120 rpm. Leaching toxicity of heavy metals from Ni–Cr ferrite prepared in the experiment was much lower than the regulated limit of Toxicity Characteristic Leaching Procedure (TCLP), indicating that Ni–Cr ferrite had a better chemical stability.

Keywords: chromium; nickel; ferrite; wastewater

1 Introduction

With the wide use of heavy metals in industrial manufacturing operations, the treatment of wastewater contaminated by heavy metals becomes a serious environmental issue. Among heavy metals, nickel is one of the most utilized by western society in the manufacturing process of stainless steel, super alloys, metallic alloys, coins, batteries etc. Direct exposition to nickel causes dermatitis. Some nickel compounds, as carbonyl, are carcinogenic and easily absorbed by skin. The exposure to this compound at an atmospheric concentration of 30ppm for half an hour is lethal [1].The hexavalent chromium is carcinogenic and mutagenic as a priority list of pollutants, which irritates plant and animal tissues even in small quantities. some of hexavalent chromium compound are viewed as strong oxidants and irritant poisons to mucosal tissues. Poisoning effects of these compounds may include metabolic acidosis, acute tubular necrosis, kidney failure and death [2].

The existing literature reports many studies on removal of heavy metals from water and effluents, including chemical precipitation, physical treatment such as ion exchange, solvents extraction and adsorption. However, heavy metals cannot be degraded or destroyed, even though they can be efficiently removed from water, heavy metal sludge generated still will release harmful heavy metals to soil and groundwater, which could generate secondary waste residual that has been considered undesirable due to poor meeting standards of US EPA [3].

The proposal of "ferrite process" carves out a new way for the treatment of wastewater contaminated by heavy metals. In the ferrite process, the heavy metal ions are incorporated into the lattice points of ferrites during the formation of spinel structure by the oxidation of the Fe(II) ions [4] and these doped ferrites could still be used as environment-friendly magnetic materials or ferrite pigments with no harm. Many investigations have been developed on the formation of ferrites containing Al, Cr, Cu, Mg, Mn, Ni, Zn, etc., and physical and chemical properties of these ferrite composites have been studied as well [5,6,7,8]. Application of ferrite process have been employed in wastewater treatment [8], acid mine drainage treatment [9], municipal solid waste incineration ash treatment [10], etc.

However, there is no much research about Cr(VI) and Ni (II) in the literature at the same time and, in practice, pollution with Cr (VI) and Ni (II) waste water is frequently encountered together [3,11]. In this paper, the ferrite process of Cr (VI) and Ni (II) synthetic solution by hydrothermal reaction was investigated to explore the technological parameters.

2 Materials and Methods

2.1 Chemicals and Analysis

The chemical reagents used including $Ni(NO_3)_2 \cdot 6H_2O$, $K_2Cr_2O_7$, $FeSO_4 \cdot 7H_2O$, NaOH, HNO_3, HCl , etc. were of analytical grade and purchased from Lanzhou Huabo Co., China. The final chromium concentrations were determined using UV–visible spectrophotometer and the nickel ions were analyzed by the Atomic Absorption Spectrophotometer (AAS, US). The pH of the solutions was measured in pH-meters. Magnetic performance of ferrite was checkout by ferromagnet.

2.2 Experiment Procedures

The experiment was operated in a litre beaker with mechanical stirring device. 500ml (100mg/L) Ni^{2+} solution and 500ml (176mg/L) Cr^{6+} solution were put into the beaker (the concentration is 50mg/L and 88mg/L respectively after mixed), and the initial pH was adjusted to 3.0. A certain $FeSO_4 \cdot 7H_2O$ (2.12 g) was added and pH was adjusted to 9.0 in ten minutes with stirring in the temperature of 70℃. After reaction, the solution was analyzed and the deposition was washed with deionized water for five times and acetone for three

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times. The sample acquired was dried under 60℃ and sealed in bottles for characterization.

2.3 Leaching Test

The US Environmental Protection Agency (USEPA) Toxicity Characteristic Leaching Procedure (TCLP) method is commonly used to determine if a waste is hazardous or otherwise. In this study, TCLP was mainly used to determine the chemical stability of the synthesized ferrite. The TCLP tests carried out in this study were in accordance with the standard procedures by USEPA. According to the standard, the solution having pH of 4.93±0.05 was chosen as the extraction fluid in this study. The ratio of solid to liquid was 1:20. The samples were rotated at the rate of 30±2 rpm for 18 h, and then were filtrated after undisturbed placement for half an hour. The filtrate was kept in the plastic bottle for the toxicity analysis of heavy metal.

3 Results and Discussions

3.1 Effect of pH

Effect of different pH adjusted by NaOH on concentrations of heavy metals in supernatant liquor is shown in Fig. 1. It is evident that the decomposition rates of Ni^{2+} and Cr^{6+} rise quickly before 7.5 (pH). From the magnetic performance of sediments, the results indicate that the sediments were mainly composed by hydroxides before 7.5 (pH) and the sediments were mainly composed by ferrites after 7.5 (pH). When the numerical value of pH was greater than 9.5, the decomposition rates of Ni^{2+} and Cr^{6+} dropped instead, and the phenomenon shows that the overtop pH is not in favor of the form of ferrites. High pH value caused heavy metals in solution not to enter the ferrite crystal lattice, thus, pH was chosen as 8-9.5.

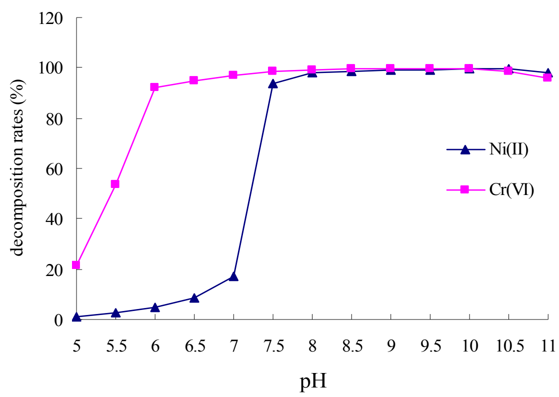

Figure 1. Effect of pH on the ferrite process

3.2 Effect of Reaction Temperature

The rise of temperature can cause gelatinous hydroxides hydrolyze and is adapt to form ferrites. However, the overtop temperature can make excessive Fe^{2+} transform into Fe^{3+} result in the shortage of Fe2+, and go against the form of ferrites. Effect of reaction temperature (from 30℃ to 90℃) on ferrite process is given in Fig. 2. The results and magnetic performance of sediments indicate that, the sediments were mainly composed by hydroxides including heavy metal hydroxides, ferrous hydroxide and ferric hydroxide when temperature below 40 ℃ , hydroxides and ferrites coexist together when temperature within 40℃-65℃, the sediments were mainly composed by ferrites when temperature within 65℃-85℃, hydroxides and ferrites coexist again when temperature overtop 85℃, the decomposition rates of Ni^{2+} and Cr^{6+} is maximum and the magnetic performance is best when temperature within 70℃-75℃. The heavy metals can be removed effectively at 70℃, in order to avoid wasting energy, 70 ℃ was enough for the hydrothermal ferrite process.

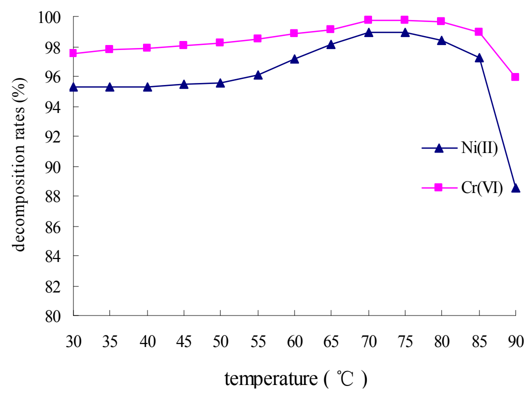

Figure 2. Effect of temperature on the ferrite process

3.3 Effect of Stirring

Stirring is indispensable in ferrite process, its aim is to mix the reagents, oxide Fe^{2+} to Fe^{3+} fractionally and provide ferric that ferrite crystal lattice need. However, the stirring time shouldn't be too long, if not, the ferrous will be oxide to ferric mostly lead to the shortage of ferrous, affect the form and quality of ferrite. Mostly, the stirring time is 40 min from the feeding of ferrous to reaction end. The relationship of decomposition rates of Ni^{2+} and Cr^{6+} with stirring speed is given in Fig. 3. As shown by Fig. 3, the initial heavy metal ions decomposition rate increased with increasing stirring speed but fell while stirring speed preponderated over 120 rpm. The reason is that over quick stirring speed can cause the replace reaction of heavy metals weaken and the oxidation of ferrous too many which affect the balance of ferrous and ferric. In this experiment, the optimum stirring speed is 120 rpm and the decomposition rates of Ni^{2+} and Cr^{6+} can achieve peak value.

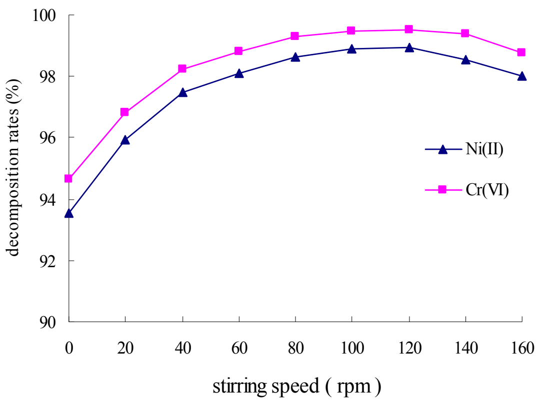

Figure 3. Effect of stirring speed on the ferrite process

3.4 The Chemical Stability of Synthesized Ferrite

To find out the chemical stability of synthesized ferrite by the hydrothermal treatment, the USEPA TCLP methods were adopted to evaluate the leaching toxicity of ferrite. The synthesized ferrite analyzed was formed in the optimum environment (pH=9.0, temperature=70℃, stirring time=40min, stirring speed=120 rpm). The leaching concentrations of heavy metals were much lower, such as that of Cr was 0.42 mg/L and Ni was 0.79 mg/L. It was clear that the heavy metals could be combined in steady and compact crystal lattice of ferrite, and were difficult to be dissolved in the leaching condition of pH 4.93±0.05. The results of the chemical stability of synthesized ferrite by the hydrothermal treatment were satisfactory.

4 Conclusions

Ferrite process of wastewater by hydrothermal reaction was investigated and the following results were achieved:

(1) Under the hydrothermal treatment, ,Ni and Cr can be transformed into high value-added Ni–Cr ferrite by adding iron source ($FeSO_4 \cdot 7H_2O$) with the precipitator (NaOH).

(2) The most suitable reaction conditions were explored: pH=9.0, temperature=70℃, stirring time=40min, stirring speed=120 rpm.

(3) Leaching toxicity of ferrites was far below the regulated limit of TCLP.

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