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The fraction analysis of chromium in manganese slag

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ABSTRACT

In present research, Tessier method was used to explore the fraction distributions of Cr (total) and Cr (III) in manganese slag. Nano-TiO_2 was used to concentrate and separate out Cr (III) from manganese slag. Meanwhile, the contents of various fraction compounds of chromium were determined by atomic absorption spectrophotometer. The experimental results showed that fraction distributions of Cr (total) and Cr (III) have the same trend, which was residual [Cr (total) 88.7%/Cr (III) 86.71%] > bound to Fe–Mn oxides [Cr (total) 5.16%/Cr (III) 6.47%] > exchangeable [Cr (total) 3.93%/Cr (III) 4.29%] > bound to organic matter [Cr (total) 1.88%/Cr (III) 2.20%] > bound to carbonates [Cr (total) 0.35%/Cr (III) 0.33%]. Because the main fraction of residual is stable and Cr (III) of low toxicity in each fraction is the main ingredient, the chromium release in the manganese slag stacking process has a low impact on environment.

1. Introduction

Manganese slag, which is generated by manganese produce, is considered as a kind of pollution substances and may cause environmental problem. The heavy metal chromium (Cr) from slag can transfer into soil and water, which will have an influence on the survival and development of human beings. Chromium can form various valence compounds which have different toxicity and bioavailability characteristics according to valence states. The most common valence states are Cr (III) and Cr (VI). Cr (III) can accumulate in body tissues and result in abnormal cellular metabolic rate, while the toxicity of Cr (VI) is 100 times stronger than Cr (III). Cr (VI) is easily absorbed by the human body and can invade the human body through the digestive system, respiratory system, skin and mucous membranes. The most serious harm is its potential carcinogenic risk. In the environment, chromium migration and transformation are related to the fraction distribution (Zhao et al., 2006; Jiang and Wang, 2004; Lin et al., 2013; Wang, 2013; Han et al., 2012), so the research of fraction distribution of chromium in manganese slag can benefit to understand the transformation and migration of chromium, predict its bioavailability, thereby indirectly evaluate the effects of Cr in manganese slag on environment.

Tessier method used in this experiment is a classical method of studying heavy metals in slag, and the content of heavy metals can be conveniently studied by atomic absorption spectroscopy. The analytical procedure involving sequential chemical extractions has been developed for the partitioning of heavy metals in soil or sediment into five fractions: exchangeable, bound to carbonates, bound to Fe–Mn oxides, bound to organic matter, and residual (Xu et al., 2002). The heavy metals existing in exchangeable and bound to organic matter fractions are environmentally sensitive (Chew et al., 2008), easy to transport and transform, and can be absorbed by plant. Heavy metal elements in these forms are most likely to have an important impact on environment. However, existence in bound to carbonates, bound to Fe–Mn oxides and residual are generally more stable (Dong et al., 2009), more difficult to release the heavy metal ion and have a less impact on environment. In the study of different forms of chromium, the ideal nano-TiO_2 is chosen to concentrate and separate out Cr (III) from manganese slag (Liang et al., 2010; Dunphy Guzman et al., 2006; French et al., 2009; Smith et al., 2008; Chen et al., 2007; Zhang et al., 2009; Xie et al., 2008). In the appropriate pH conditions, nano-TiO_2 can be sensitive to adsorb Cr (VI) and Cr (III). Some studies report that applied nano-TiO_2 is used to determine Cr (VI) and Cr (III) in natural water, the sensitivity can increase 100 times and the results have good reproducibility (Liang et al., 2000; Fan, 2003).

This paper takes the manganese slag as research object, and uses Tessier method and atomic absorption spectrometry to study the fraction distributions of chromium in the slag. Nano-TiO_2 had been used as the materials of concentration and separation to investigate various forms of Cr (VI) and Cr (III) compositions and estimate the environmental safety of manganese slag. These results can be used to guide storage and recycling of the manganese slag.

2. Experiment section

2.1. Experimental materials, reagents and equipment

Manganese slag (Tianyuan Manganese Industry), 100 nm TiO_2 powder, 25 nm TiO_2 powder, $K_2Cr_2O_7$, $CrCl_3 \cdot 6H_2O$, $MgCl_2$, NaAc·HAc, $NH_2OH \cdot HCl$, HNO_3, H_2O_2, HF, $HClO_4$, HCl, NH_3, (Shanghai Hushi

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Chemical Reagent Analysis Instrument Co., Ltd) atomic absorption spectrophotometer (AAS, TAS-990F), water bath, oscillator, centrifuge, and analytical balance.

2.2. Methods

2.2.1. Study on the content of total chromium and the chemical forms of chromium

2.2.1.1. Determination of Cr (total). The abandoned manganese slag waste from Tianyuan manganese industry was ground and screened with 200 mesh nylon. Then the manganese slag (0.5 g) was put in a crucible with the addition of 10 ml HF and 1 ml $HClO_4$, and heated in the furnace until the liquid evaporated. The product was followed by the addition of 5 ml HF, 1 ml $HClO_4$ and 5 ml 1 + 1 HNO_3 and heated the liquid to evaporate. Finally, the digested slag was added with distilled water in a constant volume. Cr contents were determined and the percent content of total chromium was calculated with 0.5 g manganese slag.

2.2.1.2. Study on the chemical forms of chromium in manganese slag. Using Tessier sequential extraction method, heavy metal Cr existing in manganese slag was divided into exchangeable, bound to carbonates, bound to Fe–Mn oxides, and bound to organic matter and residual. The sample of 2.0000 ± 0.0005 g was taken and the extraction conditions of Tessier method were given in Table 1.

Each extraction fraction was centrifuged at 10,000 r/min for 10 min and was added into the tube for measuring. The residue was used in the fraction analysis of heavy metal. The fraction analysis of the samples was determined by atomic absorption spectrophotometry. Cr contents of each fraction had been calculated and the experimental results were listed in Table 2.

2.2.2. Leaching of nano-TiO_2 on Cr (III)

2.2.2.1. Determination of adsorption rate. Cr (III) and Cr (VI) solution (1 g/l) were prepared with $CrCl_3 \cdot 6H_2O$ and $K_2Cr_2O_7$ respectively. 8 ml solutions were put into centrifuges with the four tubes with Cr (VI), the other four tubes with Cr (III). The two kinds of chromium solutions were adjusted pH to 2, 4, 6 and 8 respectively with $NH_3 \cdot H_2O$ and HCl. After adding 250 mg TiO_2 powder (100 nm) to these tubes, the solutions were vibrating for 30 min, standing for 30 min and centrifuging. The supernatants were separated then used to determine Cr (III) and Cr (VI) contents by atomic absorption spectrometry. The residues were washed twice with distilled water, the washing liquids were similarly measured by atomic spectrophotometer to determine Cr content. The curves of pH value and adsorption rate were obtained (Fig. 1). Adsorption rate was calculated by the following equation:

$$R\% = \frac{c_0 - c - c_1}{c_0} \times 100\%$$

where c_0 represents the initial concentration of Cr, c represents the Cr concentration of the supernatant after adsorption, and c_1 represents the Cr concentration in the washing distilled water.

Table 2
The Cr contents and distributions of each fraction.

Fractions	Tessier method	
	Cr (μg)	Fractions distribution (%)
Exchangeable	1255.90	3.93
Bound to carbonates	111.19	0.35
Bound to Fe–Mn oxides	1649.62	5.16
Bound to organic matter	600.00	1.88
Residual	28327.30	88.70

2.2.2.2. Determination of desorption rate. The sediment after absorption was washed twice with distilled water and the supernatant was measured by atomic spectrophotometer to determine Cr content. Eight slag samples were added 2 mol/l HCl to each sample. After vibrating for 30 min, standing for 30 min and centrifuging, the supernatants were measured by atomic spectrophotometer to determine Cr content. The residues were washed twice with distilled water, the washing liquids were similarly measured by atomic spectrophotometer to determine Cr content and desorption rate was calculated. Desorption rate was calculated by the following equation:

$$w\% = \frac{c_2 + c_3}{c_m} \times 100\%$$

where $c_m = c_0 - c - c_1$, c_2 is the concentration of Cr in the supernatant after adding the hydrochloric acid, and c_3 is the concentration of Cr in the washing liquid.

The same experiments were repeated with 25 nm TiO_2. The results of 25 nm TiO_2 of chromium adsorption rate at different pH values were shown in Fig. 2. Also in the same conditions, the desorption rate was presented in Table 3.

2.2.3. The fraction analysis of Cr (III) in manganese slag

The manganese slag (2 g) was added in the centrifuge tube (four parallel experiments) with 8 ml 5% HCl in tube. After vibrating for 120 min, standing for 30 min, and centrifuging for 10 min with 10,000 r/min speed, all the supernatants were moved to other centrifugal tube with $NH_3 \cdot H_2O$ adjusting pH to 8.0. Then 200 mg TiO_2 powder (100 nm) was added to the solution. The supernatant was separated from the slag after concussion and centrifugation. The supernatant was measured and the slag was used for Cr (III) fraction study. The experimental conditions and test process were the same as those of the various forms of separation of total chromium. The contents of various Cr (III) fractions were presented in Table 4.

3. Results and discussion

3.1. Total content of chromium and each fraction content in manganese slag

Through calculation, the total chromium content is 41,430 μg in 2 g manganese slag and provides 2.07% of the total mass of manganese slag. The sum of each fraction was 31,943.99 μg that means the difference rate between the total chromium content and the sum of each

Table 1
Extraction conditions of Tessier method.

Fractions	Extract agents and condition				
	Agents	Concentration (mol/l)	Volume (Ml)	Time (min)	T (°C)
Exchangeable	$MgCl_2$	1.0, pH = 7	8.0	90	RT
Bound to carbonates	NaAc·HAc	1.0, pH = 5	8.0	330	RT
Bound to Fe–Mn oxides	$NH_2OH \cdot HCl$	1.0, pH = 2	8.0	330	85
Bound to organic matter	HNO_3, H_2O_2	0.02, pH = 2	3.0, 5.0	120	85
Residual	HNO_3/HF/$HClO_4$/HCl	–	8/2/2/2	90	85