Kinetics and mechanism of hexavalent chromium removal by basic oxygen furnace slag

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ABSTRACT

Basic oxygen furnace slag (BOFS) has the potential to remove hexavalent chromium (Cr(VI)) from wastewater by a redox process due to the presence of minerals containing Fe^{2+}. The effects of the solution pH, initial Cr(VI) concentration, BOFS dosage, BOFS particle size, and temperature on the removal of Cr(VI) was investigated in detail through batch tests. The chemical and mineral compositions of fresh and reacted BOFS were characterized using scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) system and X-ray diffractometer (XRD). The results show that Cr(VI) in wastewater can be efficiently removed by Fe^{2+} released from BOFS under appropriate acidic conditions. The removal of Cr(VI) by BOFS significantly depended on the parameters mentioned above. The reaction of Cr(VI) with BOFS followed the pseudo-second-order kinetic model. Fe^{2+} responsible for Cr(VI) removal was primarily derived from the dissolution of FeO and Fe_3O_4 in BOFS. When H_2SO_4 was used to adjust the solution acidity, gypsum ($CaSO_4 \cdot 2H_2O$) could be formed and become an armoring precipitate layer on the BOFS surface, hindering the release of Fe^{2+} and the removal of Cr(VI). Finally, the main mechanism of Cr(VI) removal by BOFS was described using several consecutive reaction steps.
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Introduction

Wastewater containing hexavalent chromium (Cr(VI)) mainly originates from various industry processes such as electroplating, metal polishing, paint making, and leather tanning (Sun et al., 2014; Yang et al., 2014b). In the last decades, Cr(VI) has attracted comprehensive attention due to its high toxicity. Cr(VI) commonly exists in the form of soluble and mobile oxyanions that can cause carcinogenic and teratogenic effects (Cieslak-Golonka, 1995; Kotaś and Stasicka, 2000; Yang et al., 2014a). In contrast, trivalent chromium (Cr(III)) is generally present as hydroxides or complexes with organic ligands and thus exhibits less solubility, mobility and toxicity for living organisms (Yang et al., 2014a). Therefore, the conversion of Cr(VI) into Cr(III), which can be removed by precipitation or adsorption processes, has usually been chosen as an effective method to reduce the environmental effects of Cr(VI).

The conversion of Cr(VI) to Cr(III) in conventional methods was achieved using chemical reductants that consisted of ferrous salt, sulfite, and thiosulfate (Kurniawan et al., 2006; Pan et al., 2014; Qin et al., 2005). Recently, various new materials containing Fe^{2+} or zero-valent iron have been prepared and used to reduce Cr(VI) to Cr(III), such as C/FeS/Fe composites (Yang et al., 2014a), Mg–Al layered double hydroxide doped with Fe^{2+} (Kameda et al., 2014), and nanoscale zero-valent iron supported on mesoporous silica (Petala et al., 2013). Additionally, it has been demonstrated that the removal of Cr(VI) can also be achieved based on photocatalytic reduction or adsorption through artificial synthetic photocatalysts or adsorbents (Liu et al., 2014; Wang et al., 2014; Srivastava et al., 2015).

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Nevertheless, more inexpensive and available materials are still highly desired to decrease the operational cost.

In particular, industrial wastes or various natural minerals have been widely used to reduce toxic Cr(VI) to less toxic Cr(III). Gheju and Balcu (2011) indicated that Cr(VI)-contaminated wastewater can be successfully treated by reduction with scrap iron originating from metal processing. Park et al. (2008) demonstrated that the removal of Cr(VI) by waste slag generated from the iron making industry could be ascribed to its reduction to Cr(III) by Fe^{2+} released from the slag under acidic conditions. It was reported that redox mechanisms were responsible for the removal of Cr(VI) by a reclaimed limestone residue containing iron (Ochola and Moo-Young, 2004). The reduction of Cr(VI) to Cr(III) and subsequent precipitation of Cr(III) have been accomplished using ferrochromium slag during the treatment of wastewater from a ferrochromium plant (Erdem et al., 2005). Kıyak et al. (1999) and Özer et al. (1997) suggested that copper smelter slag and steel wool can effectively reduce Cr(VI) from synthetic wastewater due to the reducing action of Fe^{2+} or $Fe(0)$ within these two materials. Additionally, natural siderite ($FeCO_3$) and clino-pyrrhotite ($Fe_{0.88}S$) can be also used as the reductants to remove Cr(VI) from aqueous solution (Erdem et al., 2004; Lu et al., 2006).

Basic oxygen furnace slag (BOFS), which is a by-product of the steel industry, originates from the further refining of iron in a basic oxygen furnace (Barca et al., 2013). BOFS is a heterogeneous oxide material which primarily consists of Fe, Si, and Ca, as a result of the use of fluxing agents (lime) during the steelmaking process (Xue et al., 2009). BOFS has been used to treat practical wastewater and confirmed to be an efficient substrate to remove phosphorus by the precipitation reaction of PO_4^{3-} with Ca^{2+} from the dissolution of slag (Barca et al., 2012; Bowden et al., 2009; Cha et al., 2006). In fact, some minerals containing Fe in BOFS may also have the potential to reduce Cr(VI) to Cr(III) in wastewater. To our knowledge, however, little was known about the viability of utilizing BOFS to remove Cr(VI) from the aqueous phase.

In this work, the removal of Cr(VI) from synthetic wastewater by BOFS was investigated through batch tests. The effects of pH, initial Cr(VI) concentration, BOFS dosage, BOFS particle size, and temperature on the removal efficiency of Cr(VI) were examined in detail. The kinetics of Cr(VI) removal by BOFS under above conditions was also investigated to describe the time-dependent concentration of Cr(VI). Finally, fresh and aged BFOS was characterized to explore the mechanism of Cr(VI) removal using an X-ray diffractometer (XRD) and scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) system.

1. Experimental

1.1. Materials

BOFS was from Anshan Iron and Steel Group Corporation in Liaoning province of China. BOFS was ground into fine powder and sieved to obtain samples with different size ranges (0–0.038 mm; 0.045–0.058 mm; 0.058–0.106 mm; 0.106–0.180 mm). The chemical composition (the most stable oxides of elements) of BOFS was analyzed through X-ray fluorescence (ZSX100e,

Rigaku Corporation, Japan), and the results showed that the slag consisted of CaO (47.08%), Fe_2O_3 (36.12%), SiO_2 (8.04%), MgO (4.94%), MnO (1.99%), Al_2O_3 (0.78%), TiO_2 (0.56%), P_2O_5 (0.30%), Cr_2O_3 (0.15%), SrO (0.03%), and Nb_2O_5 (0.02%).

1.2. Batch tests

Synthetic wastewater containing Cr(VI) (75–150 mg/L) was prepared through dissolving reagent grade $K_2Cr_2O_7$ in tap water. Tap water was selected for the synthetic wastewater because other authors have demonstrated that it contains a range of ions that are present in natural waters and thus acts to simulate natural environmental conditions (Bowden et al., 2009; Drizo et al., 2002). The total average concentration of Fe^{2+} and Fe^{3+} in tap water is only 0.2 mg/L, suggesting that Fe^{2+} in tap water has little effect on Cr(VI) removal by BOFS. The solution pH was adjusted to desirable values through adding appropriate quantities of H_2SO_4 (9.2 mol/L) or NaOH (0.25 mol/L) solution. The pH was measured using a pH meter (PHS-3C Model, Shanghai Precision& Scientific Instrument Co. Ltd., China).

The dissolution behaviors of Fe^{2+} and Fe^{3+} from BOFS were examined first. BOFS (2.0 g) of 0–0.038 mm particle size was added into 200 mL tap water that contained 3.0 mL H_2SO_4 solution (9.2 mol/L) but did not have Cr(VI). The suspension was continuously stirred at 25°C and intermittently sampled. After centrifugation, changes of Fe^{2+} and Fe^{3+} concentrations with time were measured. In addition, the temporal changes of Fe^{2+}, Fe^{3+} and Cr(VI) concentrations were analyzed when the initial Cr(VI) concentration in tap water was 100 mg/L.

A series of batch tests were performed to investigate the feasibility of Cr(VI) removal by BOFS. All tests were carried out in beakers containing 200 mL wastewater at atmospheric pressure. Generally, a weighed amount of BOFS with a particular particle size was introduced into the wastewater. The mixture was continuously stirred using a stirring apparatus with a temperature control system, which met the demands of the study on temperature effects. The solution was intermittently sampled and centrifuged at 3000 r/min for 5.0 min. Then, the supernatant was used to measure changes of Cr(VI) concentration. At the end of the tests, the aged BOFS was collected and dried at 105°C for subsequent characterization analysis.

1.3. Analysis methods

Total Cr was measured using the atomic absorption spectrometric method (AAS, TAS-990). A colorimetric method was used to measure the changes of Cr(VI), Fe^{2+}, and Fe^{3+} concentrations using a UV–visible spectrophotometer (UV-2550, SHIMADZU, Japan). Interaction of Cr(VI) with 1,5-diphenylcarbazide in acidic solution resulted in the formation of a pink compound, which was able to be analyzed at 540 nm by the spectrophotometer. The amount of Cr(III) can be obtained by deducting Cr(VI) from total Cr. The red-orange compound formed by the reaction between Fe^{2+} and 1,10-phenanthroline in acidic solution can be measured at 510 nm. Additionally, Fe^{3+} can be completely reduced to Fe^{2+} using sufficient hydroxylamine hydrochloride. Thus, the Fe^{3+} concentration can be obtained from the difference in absorption with or without the addition of hydroxylamine hydrochloride into the solution. SEM-EDS (SSX-550,