Morphology analysis of hexavalent chromium reduction to trivalent chromium with syrup under different pH conditions

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Abstract

Batch experiments were designed to ascertain the morphology and valence of chromium in the reduction of hexavalent chromium with syrup under different pH conditions. Results indicated that the syrup reduced hexavalent chromium to trivalent chromium, and the existing forms of Cr were mainly $\text{Cr}(\text{OH})_3$, CrOOH and CrOOH-Fe . The percentage of Fe–Mn oxide-bound state was 29.28%, 29.28%, 22.22% and 20.12%, respectively, and the percentage of organic binding state was 64.71%, 66.58%, 74.74% and 73.14%, respectively, in the reaction systems at different pH (2.0, 2.5, 3.0 5.6) conditions.

Keywords Morphological and valence analysis · Chromium reduction · Syrup

Introduction

Cr(VI) is a kind of typical heavy metal pollutant in groundwater. And it is extremely toxic and carcinogenic when present even at very low concentrations. It would cause serious contamination of surface water, groundwater and soil in local area (Saha et al. 2011; Yalçın Tepe 2014; Wise et al. 2019). Moreover, Cr(VI) is highly toxic and soluble in the environment and can be transported over long distances in the aquifers, which causes the pollution to expand (Chen et al. 2014; Gheju 2011). Most of the contaminated sites need to be remedied as soon as possible. The toxicity of Cr(III) is relatively small, and it is insoluble compared with Cr(VI) (Gao and Liu 2017; Kang et al. 2017; Malik et al. 2017; Wu et al. 2017). Hence, the reduction of hexavalent chromium to trivalent chromium is considered an important remediation strategy.

In situ remediation technology is a promising remediation technology for Cr(VI)-contaminated groundwater. Therefore, it is significant to search for economic, efficient and environmentally friendly in situ remediation reagent. Syrup,

also known as molasses, is a sticky, dark brown, semifluid by-product produced by sugar industry, which possesses the advantages of economic and no secondary pollution. Our previous work has demonstrated that syrup can reduce hexavalent chromium to trivalent chromium by chemical reduction under acid conditions without adding effective microorganisms, and Cr(VI) acts as an electrophile that readily accepts electrons from the hydroxyl and carbonyl groups of organic reducing substances, subsequently reducing to Cr(III) (Okello et al. 2012; Guan et al. 2014; Chen et al. 2015).

Meanwhile, syrup consists mostly of sucrose. As a used microbial carbon source, syrup have been successfully used for remediating Cr(VI) contamination in groundwater, such as in the Selma Superfund site and Department of Energy's site at Savannah River (US EPA 2003, 2011; Michailides et al. 2014). In the hexavalent chromium-contaminated groundwater site, bioremediation microorganisms can be divided into three classes: chromium-reducing bacteria, sulfate-reducing bacteria and iron-reducing bacteria (Somasundaram et al. 2009; Brodie et al. 2011; Pagnanelli et al. 2012; Sugiyama et al. 2012; Field et al. 2013; Ahemad 2014). We also discussed the effect of different factors on the chemical reduction of hexavalent chromium (Gu et al. 2014; Chen et al. 2016, 2017; Yan and Chen 2019). The mechanisms of in situ remediation Cr(VI)-contaminated aquifer with syrup has been preliminarily demonstrated to be the reaction process of combination of chemical reduction and biological reduction, in which functional microorganism divided into

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chromium-reducing bacteria and iron-reducing bacteria (Shashidhar et al. 2007; Chen et al. 2015; Bayuo et al. 2019).

However, little is known about the morphological analysis of trivalent chromium in the reduction of hexavalent chromium with syrup at present. In this work, the morphology of trivalent chromium is studied in the reduction of hexavalent chromium with syrup under different pH conditions by batch experiments. This is very meaningful for promoting the use of syrup in the remediation of Cr(VI)-contaminated soil and groundwater.

Materials and methods

Reagents

Syrup produced in accordance with the Chinese national standard (QB/T2684-2005) was purchased from Jinan Honghao Chemical Reagent Co., Ltd. Syrup contains abundant plant polyphenols such as flavonoid derivatives and phenolic compounds (38.4–48.8 mg/L). The specific parameters are shown in Table 1.

Potassium dichromate, sulfuric acid (98%), phosphorus acid (85%), sodium hydroxide, glacial acetic acid and anhydrous sodium carbonate were supplied by a Beijing chemical plant (Beijing, China). Folin–Ciocalteu was purchased from Beijing Dingguo Changsheng Biotechnology Co., Ltd. All the chemicals were of analytical pure grade and used as received without any further pretreatment. Reverse osmosis Milli-Q water (18 MΩ) was used to make all solutions and dilutions.

Experimental methods

The diluted syrup solution was prepared by dissolving 1.00 mL of syrup into deionized water and then diluted to 1 L, that is, the concentration of syrup is 1.00 mL/L. The Cr(VI) solution was prepared by dissolving a certain amount of potassium dichromate into deionized water and then diluting to 1000 mL to obtain 20 mg/L Cr(VI) solutions.

Four groups of experiments were conducted to determine the effects of pH on the morphological of trivalent chromium in the Cr(VI) reduction with syrup. First, four copies of unsterilized sand were weighed, each with the weight of 600 g, respectively, and put into the brown reaction bottles under the

condition of constant room temperature $20\text{ }^{\circ}\text{C} \pm 1.0\text{ }^{\circ}\text{C}$. Then, reaction mixtures were obtained by taking 100 mL of 20 mg/L Cr(VI) solutions and adding 100 mL of diluted syrup solutions and adjusting the pH values of 2.0, 2.5, 3.0 and 5.8. The experiments were conducted in 250-mL brown reaction bottles. The initial pH of a solution was adjusted with the sulfur solution (0.5 M) and the sodium hydroxide solution (1.0 M). At regular time intervals, 10 mL of the mixed solution was withdrawn to determine the Cr(VI), total Cr concentration. After the reaction, morphological analysis was performed, and the determination method and procedure of chromium morphology are described in Sect. 2.3.

Analytical methods

Total Cr concentration, Cr(VI) concentration, pH and temperature were measured in all the experiments. The Cr(VI) concentration was determined by the diphenylcarbazide spectrophotometric method according to the “Standard Methods for the Examination of Water and Wastewater” at 540 nm using a UNIC 7200 visible spectrophotometer (Macy China Instruments Inc., Beijing, China). Total chromium was determined by flame atomic absorption spectrometry (Shimadzu International Trading Ltd, Shimane, Japan) according to the “Standard Methods for the Examination of Water and Wastewater” using a Shimadzu AA-7000F/AAC atomic absorption spectrophotometer (US EPA 2005). The valence state distribution of chromium on the surface of media was determined by X-ray photoelectron spectroscopy (XPS). The pH and temperature were determined by HI99141 Portable pH/Temperature Measuring Instrument.

The modified Tessier’s sequential extraction procedure was used to investigate the speciation of Cr in the reduction of hexavalent chromium with syrup. The media (sand) of different pH (2.0, 2.5, 3.0 and 5.8) reaction systems in the experiment were dried in the shade and then stored and set aside. The specific extraction procedure is as follows.

1. *Exchangeable chromium* Take 1.0 g sand and 8 mL of MgCl_2 solution with a concentration of 1 mol/L; place it in a 50-mL conical flask; oscillate for 1 h on a constant temperature cyclotron. And then centrifuge, separate and collect supernatant. After filtration, the concentration of heavy metal ions is determined by atomic absorption spectrometry. The remaining residue is cleaned with deionized water for further use.
2. *Bound to carbonates chromium* Take the residue from the upper step and place it in a 50-mL conical flask; add 8 mL sodium acetate solution with a concentration of 1 mol/L (pH 5.0 adjusted by acetic acid); oscillate for 2 h on a constant temperature cyclotron. And then centrifuge, separate and collect supernatant. The rest of the steps are the same as (1).

Table 1 Parameters of syrup

Brix (%)	Total sugar (%)	Water (%)	Sugar derivatives (%)	Other organics (%)	Minerals (%)
≥ 85	≥ 48	15–20	2–4	18–21	10–15

3. *Bound to iron and manganese oxides chromium* Take the upper residue, and put it in a 50-mL conical flask; add 20 mL of NH_4Cl with a concentration of 0.4 mol/L dissolved in 25% (v/v) acetic acid solution; place it in water bath of 96 ± 2 °C for 5 h; shake it once in half an hour, and then, cool to room temperature. And then centrifuge, separate and collect supernatant. The rest of the steps are the same as (1).
4. *Bound to organic matter chromium* Take the residue from the upper step, and place it in a 50-mL conical flask; add 3 mL HNO_3 with a concentration of 0.02 mol/L and 5 mL H_2O_2 with a mass fraction of 30%; place it in water bath of 85 ± 2 °C for 5 h; and shake it once in half an hour, add H_2O_2 with 3 mL mass fraction of 30%, adjust pH 2 with HNO_3 , place it in water bath of 85 ± 2 °C for 3 h, and shake it once in half an hour, and then, cool to room temperature. And then add 5 mL ammonium acetate solution with a concentration of 3.2 mol/L, which is dissolved in 20% HNO_3 , oscillate for 0.5 h on a constant temperature cyclotron. And then centrifuge, separate and collect supernatant. The rest of the steps are the same as (1).
5. *Residual chromium* Take the upper residue, and put it in a ptf digestion tank; add 3 mL concentrated hydrochloric acid, 3 mL hydrogen fluoride and 6 mL concentrated nitric acid; use a microwave digester for 2 h digestion. And then add 1 mL perchloric acid, and steam it on a hot plate until it becomes thick and remove fluorinion from the solution. Finally, dissolve it in 1 mL nitric acid with a volume ratio of 1:1 with a constant volume of 20 mL. And then centrifuge, separate and collect supernatant. The rest of the steps are the same as (1).

Results and discussion

Reaction results under different pH conditions

The results of Cr(VI) reduction reaction under different pH conditions are shown in Fig. 1. As seen in Fig. 1, hexavalent chromium is eventually removed completely under different pH conditions. We have done a lot of research on hexavalent chromium reduction reaction with syrup in the early stage, discussed the effect of pH on the reduction of hexavalent chromium and preliminarily proposed the reaction mechanism that is the process of combination of chemical reduction and biological reduction (Chen et al. 2015, 2016, 2017). The experimental results were consistent with previous results in the paper; therefore, we will not repeat the discussion. In this paper, we would further analyze the chromium valence and morphology instead of discussing the reaction process.

Fig. 1 Effect of pH on Cr(VI) reduction by syrup

Analysis results of chromium valence state

After hexavalent chromium reduction with syrup, the valence state distribution of chromium on the surface of media was determined by X-ray photoelectron spectroscopy (XPS). Spectra of XPS for $\text{Cr}(2p_{3/2})$ and $\text{Cr}(2p_{1/2})$ on medium surface are shown in Fig. 2. The result of data processing shows that the peak shape was relatively obvious when the binding energy of chromium is 577.017 eV. The existing forms of Cr are mainly $\text{Cr}(\text{OH})_3$, CrOOH and CrOOH-Fe on this peak. The test results are similar to the results of Wise et al. (2019). This result further demonstrated the reduction of hexavalent chromium to trivalent chromium with syrup under different pH conditions.

Morphological analysis results

The morphological analysis results of chromium in the reaction system at different pH conditions are shown in Fig. 3 and Table 2. Data show chromium mainly exists in Fe–Mn oxide-bound state and organic-bound state on the media surface of hexavalent chromium reduction reaction system. The percentage of Fe–Mn oxide-bound state was 29.28%, 29.28%, 22.22% and 20.12%, respectively, and the percentage of organic binding state was 64.71%, 66.58%, 74.74% and 73.14%, respectively, in different pH (2.0, 2.5, 3.0 5.6) reaction systems. As the pH value of the reaction system increases, the percentage of trivalent chromium existing in the aquifer as Fe–Mn oxide binding state gradually increases, while the percentage of chromium in the organic binding state decreases. The reason may be that the reaction mechanism is different under different pH conditions. When the pH of reaction system is low, chemical reduction is the main mechanism of Cr(VI) reduction with syrup, and at this time, the organic binding state of chromium formed by the combination of trivalent chromium

Fig. 2 Spectra of XPS for Cr($2p_{3/2}$) and Cr($2p_{1/2}$) on medium surface

Fig. 3 Speciation analysis of chromium at different pH conditions

Table 2 Content of different forms of chromium

Initial pH (final pH)	Exchange chromium	Bound to carbonates chromium	Bound to Fe–Mn oxides chromium	Bound to organic matter chromium	Residual chromium
5.6(7.12)	0.1412	0.1809	1.1132	2.6231	–
3.0(7.02)	0.1303	0.1415	1.0564	2.8632	–
2.5(3.68)	0.1023	0.1093	0.8327	3.1101	–
2.0(3.10)	0.1023	0.1068	0.7919	3.2176	–

and organic compounds is deposited and adsorbed on the surface of the medium. When the pH of the reaction system is high, biological reduction is the main mechanism of Cr(VI) reduction with syrup. A considerable part of the resulting chromium trivalent may co-precipitate with iron and manganese ions in the reaction system and precipitate on the surface of the aquifer medium.

Conclusion

Syrup could reduce hexavalent chromium to trivalent chromium under different pH conditions. The existing forms of Cr were mainly Cr(OH)₃, CrOOH and CrOOH–Fe. Chromium mainly exists in Fe–Mn oxide-bound state and organic-bound state on the media surface of hexavalent

chromium reduction reaction system. Exchangeable chromium and bound to carbonates chromium was is very low on the media surface of hexavalent chromium reduction reaction system. The results further support that the reaction mechanism is the reaction process of combination chemical reduction and biological reduction.

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