

## Evaluation of metabisulfite and a commercial steel wool for removing chromium(VI) from wastewater

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**Abstract** Efficiency of metabisulfite and a commercial steel wool as reducing agents in the removal of Cr(VI) from wastewaters was evaluated. Chromium(VI) was converted to Cr(III), precipitated with NaOH, and removed by filtration. A reduction of more than  $1.0 \times 10^5$  and  $4.0 \times 10^5$  fold in total Cr and the Cr(VI) concentrations, respectively, was observed by employing steel wool masses as low as 0.4420 g to 30-mL solutions of wastewater. Chromium(III) hydroxide obtained after the treatment was recycled and used as marker in cattle nutrition studies. The liquid residue obtained after the treatment was reused as precipitation agent replacing NaOH.

**Keywords** Total Cr · Cr(VI) · Wastewater treatment · Metabisulfite · Steel wool

### Introduction

The most common chromium oxidation states are Cr(III) and Cr(VI). However, each of these species presents distinct characteristics. Chromium(III) is considered an essential nutrient and it is involved in the metabolism of glucose, lipids, and proteins. The deficiency of this mineral in the diet is related to high concentrations of glucose in the blood, high levels of cholesterol and triglycerides, and the reduction of HDL (high density lipoproteins) (Anderson 1998). On other hand, Cr(VI) is toxic to human beings, animals, and plants even at low concentrations, and it is related to several clinical problems such as nasal irritation and ulceration, skin hyper-sensitivity reactions, dermatitis, and even lung cancer. The toxic properties of Cr(VI) result from the free diffusion of this species through the cellular membrane (Shrivatava et al. 2002).

Chromium compounds present different applications. They are mainly used as anti-corrosive, in the constitution of pigments, and in the industry of refractories. Sulphochromic solution, for instance, is still used in standard methods to determine organic matter in soils, chemical oxygen demand (COD) in water quality studies, and laboratory glassware (Guillemont et al. 2006; Shervedani and Babadi 2006). These diversified and important applications make chromium compounds important sources of Cr(VI) contamination to the environment.

According to the Environmental Protection Agency (EPA) and the European Environment Agency (EEA), the maximum chromium concentrations allowed for wastewater for hexavalent [Cr(VI)] and trivalent chromium [Cr(III)] are 0.1 and 0.5 mg L<sup>-1</sup>, respectively (US EPA 2003; I.C. Consultants 2001). The limits allowed for some

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This article is in memory of E. F. A. Neves.

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inorganic elements are include in the Resolution number 357 of Conselho Nacional do Meio Ambiente, the official Brazilian governmental agency responsible for environmental and water resources protection (Conselho Nacional do Meio Ambiente 2005). For instance, for total Cr, it is establish a maximum concentration of  $0.5 \text{ mg L}^{-1}$  in discarded effluents.

Determination of organic carbon in soil according to method ISO 14235—Soil quality—determination of organic carbon by sulphochromic oxidation, is based on the oxidation of organic matter by a mixture of potassium dichromate solution (in excess) and sulphuric acid at a temperature of  $135^\circ\text{C}$  (International Organization for Standardization 1998). Potassium dichromate is a strong oxidizing agent under acidic conditions, which is usually achieved by the addition of sulphuric acid. The reaction of dichromate with organic matter is given by:

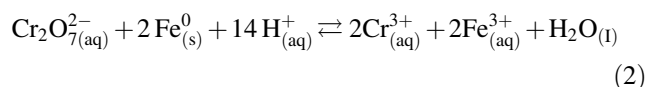


The Cr(VI) species in the dichromate ions are reduced to Cr(III) and the initial orange-red solution is converted to green. It is assumed that the oxidation of one carbon atom from the organic matter produces four electrons and that there is a direct relationship between the Cr(III) formed and the amount of organic carbon. The calibration of the method is carried out using soils with different organic carbon amount, previously determined by using the Walkley–Black titration (Nelson and Sommers 1996). The excess of dichromate used in this reaction generates Cr(VI) residues that require suitable treatment before being discarded in the environment.

The conventional chromium treatments include ion-exchange, membrane separation, chemical reduction/precipitation and adsorption. Since these methods are expensive because demand high energy input and large quantities of chemical reagents, alternative methods have been suggested (Gupta and Ali 2004). The biosorption can be cited as an ecofriendly, low cost and efficient option to chromium treatment.

In general, the treatment used for the sulphochromic effluent resulting from the total carbon analysis is the reduction of the dichromate ions to Cr(III), followed by alkaline precipitation. The use of sodium metabisulfite as reducing agent and precipitation of Cr(III) as  $\text{Cr}(\text{OH})_3$  with NaOH is a common method in routine laboratories (Lunn and Sansone 1989).

Metabisulfite can be replaced by alternative reducing agents such as ferrous ions. Commercial steel wool, composed of approximately 95% iron, could represent an inexpensive, easily obtained source of Fe ions that could be used to treat Cr(VI) residues produced in chemical laboratories.



Özer et al. (1997) presented a study based on the reduction of Cr(VI) species present in aqueous solutions employing steel wool. In this work, the Cr(III) species generated by the oxi-reduction reaction were precipitated with solid  $\text{CaCO}_3$  and a solution of NaOH. The process was investigated in continuous and batch systems.

The present work investigates the efficiency of metabisulfite as reducing agent in the treatment of Cr(VI) effluents and compares it with an inexpensive commercial steel wool. The steel wool method was optimized for treatment of a high Cr(VI) concentration residue from a ISO 14235 soil analysis. Chromium(III) hydroxide obtained after wastewater treatment was recycled and used as marker in cattle nutrition studies.

## Experimental

All solutions were prepared with analytical grade reagents (Merck, USA) and high-purity water (Milli-Q Water System, Millipore, Bedford, MA, USA). The following analytical grade reagents were used: NaOH,  $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $(\text{CH}_3)_2\text{CO}$ , and  $\text{HNO}_3$ . All experiments were carried out in triplicate.

The reducing agents used to convert Cr(VI) to Cr(III) in the wastewater were Fe and  $\text{Na}_2\text{S}_2\text{O}_5$  (Synth, São Paulo, Brazil). The Fe source was a fine fibrous steel wool (Bombril<sup>®</sup>, Brazil) which is widely used for surface cleaning purposes both reducing agents were evaluated for the treatment of wastewater containing Cr(VI) generated in organic matter determinations in soil analysis.

The 1,5-diphenylcarbazide spectrophotometric method (APHA 1975) was used to determine the Cr(VI) concentrations in the samples (limit of detection,  $\text{LOD} = 10 \mu\text{g l}^{-1}$ ) before and after the treatments. A Femto spectrophotometer model 432 (FEMTO, S. Paulo, Brazil) was used and the measurements were performed at 545 nm.

A Varian SpectrAA-800 flame atomic absorption spectrometer (Varian, Mulgrave, Australia) equipped with a deuterium lamp background corrector was used for total chromium determination. The instrumental parameters were set according to the manufacturer recommendations. In all experiments an air–acetylene flame, flowing at  $13.5$  and  $2.9 \text{ L min}^{-1}$ , respectively, was used. A Cr hollow cathode lamp (Varian) was used and the measurements were performed at  $357.9 \text{ nm}$ .

A study to determine the optimum reducing agent mass to be used in the wastewater treatment was carried out after

the determination of both total Cr and Cr(VI) concentrations in the original sample. Different reducing agents masses were evaluated to treat 30 ml of wastewater sample: the stoichiometric mass and 30% in excess. Reducing agents studied and the respective masses are summarized in Table 1.

The wastewater sample aliquot and the reducing agent were mixed in a glass flask and left 3 h to rest. Afterwards, 1.96 g of NaOH was added in order to increase the pH and, consequently, promote the precipitation of Cr(OH)<sub>3</sub>. The mixture was filtered through a 25 μm filter and the solid residue was burnt to ashes in a muffle furnace during 6 h. Table 2 presents the heating program used in this procedure. Both total Cr and Cr(VI) concentrations were determined in the filtered solution, after treatment, in all experiments.

### Results and discussion

A concentration of 12,200 ± 100 mg L<sup>-1</sup> of total chromium was determined in a typical wastewater sample collected after a soil organic matter determination (International Organization for Standardization 1998). The Cr(VI) average concentration and the standard deviation determined from three consecutive readings were 9,440 ± 30 mg L<sup>-1</sup>. These results confirm the potential environmental contamination with carcinogenic Cr(VI) (Cieslak-Golonda 1986) if no treatment were applied to the sulphochromic effluents. Taking into account that a low organic carbon content in a soil analyzed may imply a higher Cr(VI) concentration in the effluent, worse scenarios could be contemplated. Thus, a procedure able not only to

**Table 1** Study of different reducing agents and their respective masses used for Cr(VI) reduction in a 30 mL aliquot of sulphochromic wastewater

Experiment	Reagent	Mass (g)
A	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	0.8232
B	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	1.0700
C	Steel wool	0.3400
D	Steel wool	0.4420

**Table 2** Heating program for Cr(OH)<sub>3</sub> burn to ashes

Step	Time (h)	Temperature (°C)
A	2	120
B	1	200
C	1	300
D	1	400
E	1	500

considerably reduce Cr(VI) concentrations but also to increase the solution pH before discarding these wastewater in the environment is needed.

Based on Cr concentrations determined, stoichiometric masses of either Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> or Fe (as steel wool) were used to reduce 30 mL of the sulphochromic wastewater. After 3 h of reaction, the solution pH was increased by adding NaOH, and the Cr(OH)<sub>3</sub> precipitated was separated from the solution by filtration. To evaluate the efficiency of each reducing agent, both the total Cr and the Cr(VI) concentrations were determined in the filtered solution by FAAS and 1,5-diphenylcarbazide spectrophotometric method (APHA 1975), respectively.

During the Cr(VI) reduction by the steel wool, a small gas evolution was observed, probably due to the production of hydrogen from the reaction between sulphuric acid in the sample and iron in the steel wool. Table 3 presents the sample pH after 3 h of redox reaction with each reducing agent evaluated.

Since a portion of the acid present in the solution had been consumed in the reaction with the steel wool, the solution acidity decreased. On the other hand, the efficiency of the Cr(VI) reduction might have been affected by the iron consumption. Thus, a mass of steel wool containing 30% more Fe than the stoichiometric value required to reduce the Cr(VI) present in the effluent was evaluated. For comparison, the same study was carried out with Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>. Table 4 presents both the total Cr and Cr(VI) concentrations in the effluent determined after treatment with either stoichiometric or 30% in excess masses of both

**Table 3** Effluent pH measured after 3 h of reaction with either Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> or steel wool (mean ± standard deviation, n = 3)

Reducing agent	pH solution
Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	0.69 ± 0.03
Steel wool	1.27 ± 0.02

**Table 4** Remaining total Cr and Cr(VI) concentrations in 30 mL of effluent after treatment with either Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> or steel wool and subsequent metal precipitation (mean ± standard deviation, n = 3)

Reducing agent	Reducing agent mass (g)	Total Cr concentration <sup>a</sup> (μg L <sup>-1</sup> )	Cr(VI) concentration <sup>b</sup> (μg L <sup>-1</sup> )
Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	0.8232	371 ± 25	114 ± 8
	1.0700	325 ± 20	97.5 ± 5.1
Steel wool	0.3400	141 ± 11	51.9 ± 4.2
	0.4420	118 ± 10	23.5 ± 12.4

<sup>a</sup> Determined by FAAS at 357.9 nm

<sup>b</sup> Determined by the 1,5-diphenylcarbazide spectrophotometric method

steel wool and  $\text{Na}_2\text{S}_2\text{O}_5$  reducing agents and subsequent metal precipitation.

It can be seen that both reagents were able to reduce total Cr concentrations below the  $0.5 \text{ mg L}^{-1}$  recommended for wastewaters by the Brazilian legislation (Conselho Nacional do Meio Ambiente 2005). It may also be observed that, as expected, larger reducing agent masses led to better efficiency of Cr(VI) removal. This may be explained by fundamental kinetic and equilibrium aspects and the role of the reagents concentrations in a chemical reaction.

The steel wool method presented even better results than metabisulfite. By using such small masses as 0.4420 g and considering the initial concentrations [ $12,200 \text{ mg L}^{-1}$  for total Cr and  $9,440 \text{ mg L}^{-1}$  for Cr(VI)] it was possible to reduce both total Cr and the Cr(VI) concentrations more than  $1.0 \times 10^5$  and  $4.0 \times 10^5$  fold, respectively. Considering Cr(VI) concentrations, the steel wool method with a reducing agent mass 30% higher than the stoichiometric value presented results more than four and twofold lower than those recommended by the U.S. Environment Protection Agency (EPA) and the European Environment Agency (EEA), respectively (EPA =  $100 \text{ } \mu\text{g L}^{-1}$ ; EEA =  $50 \text{ } \mu\text{g L}^{-1}$ ) (I.C. Consultants 2001).

In addition to the better results observed for the steel wool method, some aspects such as low cost (less than US\$ 0.20 per liter of effluent), availability and low toxicity must be considered. Another advantage is the possibility of using iron powder—usually a waste product in metallurgy industries—as reducing agent. Additionally to a further reduction in costs, this strategy would contribute to decrease soil and water contamination by high Fe concentrations in areas near those factories.

The solid residue obtained after sample treatment was burnt to ashes in order to convert metal hydroxides into oxides. The residue composed mainly of  $\text{Cr}_2\text{O}_3$  was used as marker in cattle nutrition studies in the experimental farm unit of the Embrapa Pecuaria Sudeste (Sao Carlos, SP, Brazil), a Brazilian governmental agency dedicated to agrotechnology.

The remaining liquid residue presented pH close to 12.0, which most likely eliminates the possibility of high concentrations of other harmful metals in solution. On other hand, the residue can not be discarded in the environment due to its elevated pH. To make the method even more economic and environment friendly, this residue can be recycled and used to replace NaOH as precipitation agent.

## Conclusion

Considering all the methods that still use Cr species and the high amount of Cr(VI)-contaminated effluents produced

every day, wastewater treatment has become an important environmental issue. Some legislations established maximum concentration limits (MCL) only for total Cr, but due to the increasing concern about the role of Cr(VI) in some types of cancer, most recent legislations on water quality have also established MCLs for this chemical specie.

Both methods evaluated were efficient in both total Cr and Cr(VI) removal from wastewater. Even better results could be found if higher reducing agents masses were used. Thus, both methods can be used to support most recent legislative requirements on wastewater disposal. The steel wool method presented the better results and factors such as low cost, simplicity, low toxicity and availability of the reducing agent allow us to recommend it as the best choice. Cr(VI) removal from wastewater by this method has the advantage of being economic and environment friendly. The solid residue obtained after sample treatment was burnt to ashes in order to convert metal hydroxides into oxides ( $\text{Cr}_2\text{O}_3$ ) which can be used as marker in cattle nutrition studies and the liquid residue (pH 12) can be reused as precipitation agent in the last part of the procedure.

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