Influence of ferric iron source on ferrate's performance and residual contamination during the treatment of gold mine effluents

Carolina Gonzalez-Merchan[a,d], Thomas Genty[a], Marc Paquin[b], Mélinda Gervais[a,b], Bruno Bussière[a], Robin Potvin[c,d], Carmen M. Neculita[a,*]

[a] Research Institute on Mines and Environment (RIME), University of Québec in Abitibi-Témiscamingue (UQAT), 445 Boul. de l'Université, Rouyn-Noranda, QC J9X5E4, Canada
[b] Research and Service Unit in Mineral Technology (Unité de Recherche et de Service en Technologie Minérale - URSTM), 445 Boul. de l'Université, Rouyn-Noranda, QC J9X5E4, Canada
[c] Technology Center for Industrial Waste (Centre Technologique des Résidus Industriels - CTRI), 425, Boul. du Collège, Rouyn-Noranda, QC J9X5E5, Canada
[d] College of Abitibi-Temiscamingue (CEGEP-AT), 425, Boul. du Collège, Rouyn-Noranda, QC J9X5E5, Canada

ABSTRACT

Ferrate [Fe(VI)] is increasingly used for the treatment of several contaminants in drinking water and municipal/industrial waste water. Recent findings also show that Fe(VI) is a promising alternative for the treatment of gold mine effluents contaminated by cyanides (CN^-), thiocyanates (SCN^-), and ammonia nitrogen (NH_3-N). However, the ferric [Fe(III)] salt used in Fe(VI) synthesis could affect this alternative's efficiency and costs, as well as residual contaminants in the treated effluent. The objective of this study was to evaluate the influence of three Fe(III) salts on the performance of Fe(VI) in the treatment of gold mine effluents and the residual contaminants produced in the process. To do so, the performance of wet Fe(VI) synthesized with ferric nitrate [$Fe(NO_3)_3$], ferric chloride ($FeCl_3$), or ferric sulfate [$Fe_2(SO_4)_3$] was evaluated for the treatment of a real gold mine effluent, with final adjustment of pH at ~7. The results showed that for the effluents treated with Fe(VI) synthesized in the presence of $Fe(NO_3)_3$, the final NO_3^- concentrations were 4 times higher relative to those in the treated effluents with Fe(VI) synthesized from either $FeCl_3$ or $Fe_2(SO_4)_3$. The use of $Fe_2(SO_4)_3$ in the wet Fe(VI) preparation did not entail a significant increase of the final SO_4^{2-} concentrations, which were very similar to initial ones (1220 vs. 1012 mg/L). At the same time, Fe(VI) synthesized from $Fe_2(SO_4)_3$ was the only one to remove the CN^- and NH_3-N almost totally (~99%). Finally, the production yield of Fe(VI) with $FeCl_3$ was lower than $Fe_2(SO_4)_3$ or $Fe(NO_3)_3$ (3400 vs. 5500 and 5635 mg/L, respectively). This low yield production of Fe(VI) from $FeCl_3$ entails more costly production costs. Thus, $Fe_2(SO_4)_3$ is potentially the most appropriate Fe(III) salt source for Fe(VI) synthesis for use in the treatment of contaminated mine effluents.

1. Introduction

Cyanide (CN^-) leaching has been used widely in the mining industry since 1889 because of the low cost of CN^- and its high efficiency in the extraction of gold and silver (Johnson, 2015). However, cyanidation generates complex effluents that are challenging to treat. Available CN^- treatment technologies are usually efficient, but they could generate ammonia nitrogen (NH_3-N) as a residual contaminant (Botz et al., 2005). Recent studies show that, among the advanced oxidation processes, the ferrate [Fe(VI)] is an advantageous option in the treatment of gold mine effluents because this strong oxidant limits the formation of toxic by-products (Sharma, 2011; Waite, 2015; Gonzalez-Merchan et al., 2016). Nevertheless, several challenges still

exist with respect to the practical implementation of Fe(VI) treatment technology, especially for highly contaminated effluents.

Fe(VI) is a strong oxidant-disinfectant and generates ferric iron [Fe(III)] (following Fe(VI) reduction), which reacts as a flocculent-coagulant, and efficiently treats both inorganic and organic contaminants (Jiang and Lloyd, 2002; Sharma, 2011; Goodwill et al., 2016). Additionally, oxidant Fe(VI) exhibits a high rate of reactivity and produces non-toxic by-products, such as Fe(III) and molecular oxygen (Ciampi and Daly, 2009; Eq. (1).

$$4FeO_4^{2-} + 10H_2O \rightarrow 4Fe^{3+} + 20OH^- + 3O_2 \qquad (1)$$

The Fe(VI) used for the treatment of contaminated effluents could be synthesized through electrochemical or chemical processes.

Electrochemical Fe(VI) synthesis involves an electrolysis cell into which is placed a Fe anode that reacts in a strongly alkaline solution (NaOH/KOH) and is oxidized into Fe(VI) (Alsheyab et al., 2009). This process is advantageous because it does not require the addition of oxidizing agents, but it is very expensive and the final yields are influenced by the anode material composition, electrolyte concentration, solution temperature, and cell arrangement (Alsheyab et al., 2009; Goodwill et al., 2015). Fe(VI) synthesis by the electrochemical process is therefore recommended for large-scale production.

Chemical Fe(VI) synthesis includes two steps: (1) the production of Na_2FeO_4 [wet Fe(VI)], and (2) the separation of K_2FO_4 [dry Fe(VI)]. The K_2FO_4 is frequently used for its long-term stability, but its costly production requires multiple chemical reagents and a long synthesis time to obtain a high yield and purity. Consequently, the simple generation *in situ* of wet Fe(VI) at a low cost could be the most practical approach for the treatment of gold mine effluents (Waite, 2015). In fact, the preparation of Na_2FeO_4 involves the oxidation of a Fe(III) salt under alkaline conditions [sodium hydroxide (NaOH)] in the presence of an oxidant such as sodium hypochlorite (NaOCl). The following three Fe(III) salts can be used as alternatives in wet Fe(VI) synthesis: ferric nitrate [$Fe(NO_3)_3$], ferric chloride ($FeCl_3$), or ferric sulfate [$Fe_2(SO_4)_3$] (Thompson et al., 1951). These Fe(III) salts are also widely used in the mining industry as coagulants for the pre-treatment of total suspended solids (MEND, 2014). For example, previous results show that Fe(III) salts [$FeCl_3$ or $Fe_2(SO_4)_3$] allowed silica removal in a coal mine, where the efficiency by either Fe(III) salt was > 80% (Lin et al., 2017). However, the removal efficiency of contaminants by Fe(VI) synthesized with $Fe(NO_3)_3$, $FeCl_3$, or $Fe_2(SO_4)_3$ has not been compared. Therefore, the present study focuses on the Fe(III) salt for the pre-treatment of contaminants and/or the Fe(VI) synthesis, which could reduce the costs of effluents treatment in the mining industry. Nonetheless, the common Fe(III) salts – i.e., $Fe(NO_3)_3$, $FeCl_3$, or $Fe_2(SO_4)_3$ – could lead to different residual contaminants, including NO_3^-, Cl^-, or SO_4^{2-}, and high pH of treated effluents (Gonzalez-Merchan et al., 2016) that would require pH adjustment before being discharged into natural streams (MEND, 2014).

The present study is a continuation of a previous one where the removal efficiency of NH_3-N and CN^- with Fe(VI) was evaluated with synthetic and real effluents (Gonzalez-Merchan et al., 2016). The previous findings demonstrated that Fe(VI) was highly efficient in the treatment of gold mine effluents. However, little is known about the residual contamination generated during wet Fe(VI) synthesis and after a final pH adjustment of treated effluents. Thus, the objective of the present study was to evaluate the influence of Fe(III) salt sources on the Fe(VI) treatment efficiency for a gold mine effluent as well as the residual contaminants of the Fe(III) salt sources.

2. Materials and methods

2.1. Sampling and analysis of real effluent

The real effluents were sampled twice at an active gold mine site, at the inlet of CN^- treatment plant (Table 1). Treatability testing for CN^- and NH_3-N removal was previously performed (Gonzalez-Merchan et al., 2016), in which the initial Fe(VI) concentration synthesized with $Fe(NO_3)_3$ varied between 5 and 8 g/L. These previous findings showed that the wet Fe(VI) efficiently removed the CN^- and/or NH_3-N (> 99%).
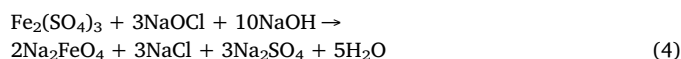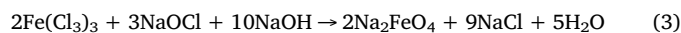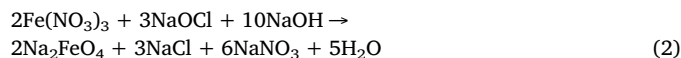
2.2. Ferrates synthesis from $Fe(NO_3)_3$, $FeCl_3$, or $Fe_2(SO_4)_3$

In a strong alkaline solution (pH 14), the oxidation of a Fe(III) salt by NaOCl produces wet Fe(VI) as Na_2FeO_4 (Thompson et al., 1951). Fe(III) salt sources used in the present study were $Fe(NO_3)_3 \cdot 9H_2O$, $FeCl_3$, and $Fe_2(SO_4)_3 \cdot 7H_2O$ (Eqs. (2)–(4)).

Table 1
Physicochemical composition of mine effluent in mg/L, except for pH (n° = 2).

Parameter	Values[a]
pH	7.7–7.9
Eh (mV)	423 ± 34
CN^-	1.8 ± 0.3
SO_4^{2-}	1012 ± 54
NH_3-N	20 ± 3
NO_2^-	8.0 ± 1.5
NO_3^-	39 ± 10
Cl^-	36

[a] Mean ± standard deviation.

$$2Fe(NO_3)_3 + 3NaOCl + 10NaOH \rightarrow$$
$$2Na_2FeO_4 + 3NaCl + 6NaNO_3 + 5H_2O \qquad (2)$$

$$2Fe(Cl_3)_3 + 3NaOCl + 10NaOH \rightarrow 2Na_2FeO_4 + 9NaCl + 5H_2O \qquad (3)$$

$$Fe_2(SO_4)_3 + 3NaOCl + 10NaOH \rightarrow$$
$$2Na_2FeO_4 + 3NaCl + 3Na_2SO_4 + 5H_2O \qquad (4)$$

The quantities/volumes of NaOH, NaOCl, and Fe(III) salts to be used in the Fe(VI) synthesis were estimated by stoichiometry according to Eqs. (2)–(4). Then, for each wet Fe(VI) prepared, the salt sources were $Fe(NO_3)_3 \cdot 9H_2O$, $Fe_2(SO_4)_3 \cdot 7H_2O$, and anhydrous $FeCl_3$, in which the masses added were 5.0, 6.5, and 2.0 g, respectively. These Fe(III) salt sources were added in four steps at a constant temperature of 35 °C for one hour (Jiang and Lloyd, 2002; Thompson et al., 1951; Sun et al., 2013). All solutions were prepared with ACS grade chemicals. The solutions were then filtered with a glass filter at 0.45 μm, and Fe(VI) concentrations in the filtrate were determined by UV–VIS spectroscopy (Lee et al., 2005; Gonzalez-Merchan et al., 2016).

2.3. Treatability testing

The treatability tests were carried out in nine 1 L beakers, which were filled with 500 mL of effluent. For each test, eight beakers contained the Fe(VI) doses, at 20, 25, 30, 35, 40, 45, 50, and 55 mg/L, and the ninth beaker was the control. The Fe(VI) doses were selected based on the results from preliminary tests (Gonzalez-Merchan et al., 2016). The reaction time was set to one hour, while the stirring speed was 200 RPM. Finally, the pH of treated effluents was adjusted to 6.2–8.8 by the addition of H_2SO_4. This pH value falls within an acceptable range (6–9.5) according to Canadian regulatory criteria (MMER, 2017). The effluents were left to rest for 30 min, and the supernatants were filtered (0.45 μm) before and after pH adjustment.

2.4. Physicochemical characterization of contaminated and treated effluents

The main physicochemical parameters of the effluents were analyzed before and after the treatability tests, as well as after the pH adjustment. They included pH, oxidation-reduction potential (Eh), and concentrations of CN^-, NH_3-N, nitrites (NO_2^-), NO_3^-, SO_4^{2-}, Cl^-, and total Fe. The pH and Eh were measured using Hach electrodes (pH PHC 101 and ORP/REDOX MTC 101, respectively), and were recorded as ± 0.01 pH and 1 mV, respectively. The NH_3-N was determined with a selective electrode (Orion 9512HPBNWP), according to the standard method [APHA, 2012; detection limit (DL) was 0.02 mg/L]. The CN^- was measured using a colorimetric method (USEPA, 1996; DL was 0.02 mg/L). The anions (Cl^-, SO_4^{2-}, NO_2^-, and NO_3^-) in the treated effluents were analyzed before pH adjustment by Ion Chromatography (IC; CEAEQ, 2014a; DL was 0.7 mg/L). Total Fe was analyzed through inductively coupled plasma atomic emission spectroscopy (ICP-AES; CEAEQ, 2014b; DL was 6 μg/L).