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TECHNICAL COMMUNICATION

Preliminary Studies on Precipitating Manganese Using Caro's Acid and Hydrogen Peroxide

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Abstract We report preliminary studies on the precipitation of manganese compounds by oxidation with Caro's Acid (peroxomonosulphuric acid, H_2SO_5) or hydrogen peroxide (H_2O_2), from solutions with [Mn] = 1.2 g/L to achieve residual [Mn] <1 mg/L at a pH range of 5–9. It was found that with the addition of sodium carbonate and either Caro's acid or hydrogen peroxide, it was possible to reduce manganese from 1.2 g/L to less than 1 mg/L in 60 min (batch reaction) at 25°C (at pH $\geq$ 5 using H_2SO_5, and pH = 9 using H_2O_2). By comparison, simple hydroxide precipitation under the same conditions at pH = 9 would only lower [Mn] to 165 mg/L.

Keywords Caro's acid · Effluent treatment · Hydrogen peroxide · Manganese precipitation

Introduction

Aqueous effluents, in particular those from mineral and metallurgical industries, may contain dissolved metals as well as other contaminants. The operations required for treating effluents for reuse as process or cooling water, or for discharge to the environment, have to ensure the removal of contaminants to the levels permitted, at a pH usually within the range 5–9, at the lowest possible cost. Some dissolved contaminants, such as sulphide, cyanide, and various organic compounds, may be converted by oxidation into species of much lower toxicity such as sulphate, cyanate, and carbonate. However, this will not usually work with dissolved metals. Instead, precipitation is the preferred operation. Various metals, such as iron, zinc, and copper, may be removed by hydroxide precipitation at a pH range of 5–9. This does not work efficiently for manganese though, as the solubility of $Mn(OH)_2$ in that pH range exceeds Brazil's discharge limit of 1 mg/L (CONAMA 2008), because of the formation of soluble MnO (aq) species. Removal of manganese usually requires increasing the pH above 10 to precipitate manganese hydroxide, separating the precipitate, and finally lowering the filtered effluent to a pH below 9 for either reuse or discharge to the environment.

Manganese has been cited in toxicological reviews (Cranor 2008) as possibly contributing to adverse subclinical neurotoxic developmental effects and endocrine disruption (Hester and Harrison 1999; Phillips and Harrison 1999). The World Health Organization's recommended drinking water standard for manganese is 0.4 mg/L (WHO 2009); in some countries, like Brazil, drinking water standards are as low as 0.1 mg/L. Local discharge permits for effluents are then set so that the concentration of manganese (like all other listed substances) in a receiving water body used for drinking water will not exceed permissible limits.

Manganese can be removed from effluents by precipitation as $MnCO_3$ (Aziz and Smith 1996; Stoica et al. 1998)

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or as $Mn(OH)_2$. However, decreasing [Mn] to <1 mg/L cannot be attained in the desired pH range of 5–9 because Mn(II) hydroxide is not sufficiently insoluble, as shown in the Eh–pH diagram of the Mn–H_2O system calculated in the present work (Fig. 1). At [Mn] $\leq$1.0 mg/L, the aqueous neutral complex MnO (aq) and not the solid $Mn(OH)_2$ is the predominant species. However, manganese may be removed from aqueous solutions by oxidation to valence states III and IV (MnO·OH and MnO_2).

Earlier studies (e.g. Aziz and Smith 1996) have reported that manganese removal requires the use of strong oxidizing agents such as permanganate, chlorine, hypochlorite, chlorine dioxide, or ozone, and that the oxidation of Mn(II) to Mn(IV) by aeration alone is slow unless the pH is alkaline. Eckenfelder (1989) also refers to the possibility of improving manganese precipitation from effluents by oxidation with oxygen, but only at pH > 9.4. For a lower pH range, the possibility of achieving high precipitation efficiency employing more costly oxidants: ozone, permanganate, or chlorine dioxide, was reported. Sincero and Sincero (2002) also indicated the need for oxidation of manganese in solution in order to be able to attain efficient precipitation at lower pH ranges, which otherwise would only be possible at pH > 11.5. Pavlovic et al. (2007) studied the precipitation of manganese as hydroxide together with a group of heavy metals from a synthetic effluent, and found the concentration of manganese reached a minimum at pH value of 11.0. Johnson and Younger (2005) observed that the removal of manganese from mine waters in an aerated reactor required 8 h to precipitate 95% of the metal from an influent with initial [Mn] = 120 mg/L.

In the present work, the effect of chemical oxidation leading to precipitation of manganese oxides was carried out as a preliminary study. The effect of combining oxidation and manganese carbonate formation was also investigated. Hydrogen peroxide and Caro's acid were considered as oxidants, as these are powerful non-contaminating oxidants that are being employed in effluent treatment in various industries; Caro's acid, in particular, is being used to treat cyanide-containing effluents in gold extraction plants.

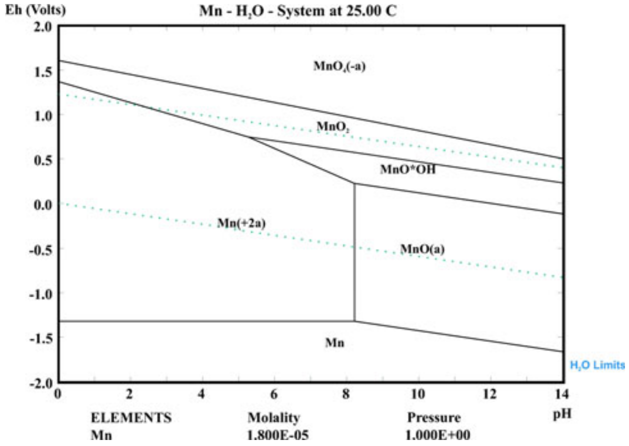

Fig. 1 Eh–pH diagram of the Mn–H_2O system at [Mn] = 1.8 × 10^{-5} mol/L = 1.0 mg/L, generated by HSC program version 5.1

Santos (2004) reported that the addition of hydrogen peroxide to an initial manganese solution of [Mn] = 1 g/L promoted fast (15 min) and efficient precipitation at pH 9 by the formation of manganese dioxide (reaction 1).

$$Mn^{2+} + H_2O_2 + 2OH^- \rightarrow MnO_2(s) + 2H_2O \qquad (1)$$

Hydrogen peroxide (H_2O_2) can be dosed into process solutions and effluents directly in concentrated or diluted forms. It can be used to generate highly oxidizing OH free radicals by photo-activation with UV radiation, by reaction with Fe^{2+}/Fe^{3+} ions (Fenton process), or by reaction with O_3. Also, it can be converted into Caro's Acid, by mixing concentrated H_2SO_4 (minimum 95%) and H_2O_2 (50–70%), according to reaction (2).

$$H_2SO_4 + H_2O_2 = H_2SO_5 + H_2O \qquad (2)$$

Caro's Acid can be continuously generated at the point of usage in a compact static mixer (Castrantas et al. 1995). Reaction 1 is virtually instantaneous and highly exothermic. The output of the generator is a hot solution (110–120°C) that must be immediately dosed into the process/treatment tank. Compared with other oxidants (including H_2O_2), Caro's Acid delivers higher oxidation speed, does not require addition of catalysts, and quickly and efficiently produces clear effluent solutions and slurries (Teixeira et al. 2005). Burkin and Chouzadjian (1983), in a study of manganese removal from zinc process solutions, showed that using Caro's acid allows efficient precipitation of manganese dioxide at a lower pH range (reaction 3).

$$Mn^{2+} + H_2SO_5 + 2OH^- \rightarrow MnO_2(s) + H_2SO_4 + H_2O \qquad (3)$$

Materials and Methods

In the present work, the effect of using Caro's acid and hydrogen peroxide (combined with the addition of carbonate) to precipitate manganese was studied using a synthetic effluent with 1.2 g/L of initial [Mn], over the pH range of 3–10. The experiments were conducted in batch mode in beakers containing 1 L of solution with mechanical stirring at 25°C. A concentration of 1.2 g/L Mn was selected because it is the Mn concentration currently being dealt with at a copper extraction plant in Peru, although most effluents from mining, concentration, and extraction plants have much lower concentrations. The manganese

Table 1 [Mn] in filtered samples (mg/L) after manganese precipitation in batch experiments at different precipitation conditions from initial [Mn] = 1.2 g/L, at 25°C and pH = 9

Time (h)	No oxidant added	H_2O_2 (200% excess)	H_2O_2 200% excess + Na_2CO_3 200% excess
0.5	400	30	0.59
1.0	175	0.56	0.35
2.0	184	0.35	0.38

stock solution was prepared from analytical grade $MnSO_4$. Oxidation and precipitation reagents employed were: H_2SO_5 (10% w/w); H_2O_2 (5% w/w prepared from H_2O_2 50% w/w technical grade), and Na_2CO_3 (50% w/w analytical grade). Caro's acid was prepared following Solvay's published procedure (Solvay 1982), by controlled mixing of concentrated grades of H_2O_2 (50% technical grade) and H_2SO_4 (98% analytical grade), starting from a molar ratio of H_2SO_4 to H_2O_2 of 3:1, which yielded a solution with 26% w/w H_2SO_5. That was further diluted with water to a 10% w/w working concentration. Oxidation and precipitation reagents were added at the start of each experiment, and the pH immediately adjusted (within 15 s) to the desired value using NaOH (50% w/w analytical grade). The contents were left stirring for 1 h and then filtered through 1 µm filter paper for the determination of dissolved Mn by atomic absorption spectroscopy. A previous set of runs (reported in Table 1) indicated that 1 h was sufficient time for precipitation to attain equilibrium. In these experiments, the excess figures refer to amounts of H_2O_2 and/or Na_2CO_3, above that required by stoichiometry.

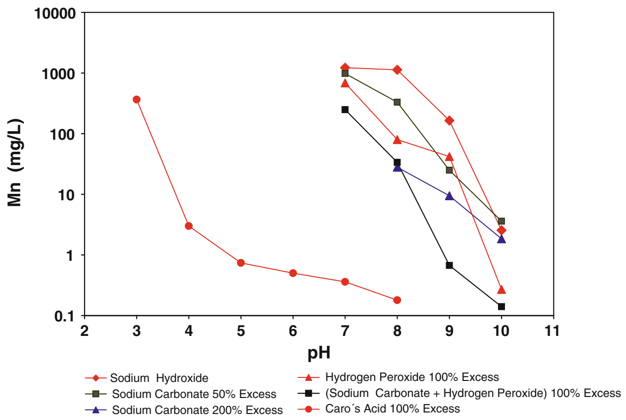

Fig. 2 Results of precipitation batch experiments, initial [Mn] = 1.2 g/L, *T* = 25°C, *t* = 1 h

Results and Discussion

Figure 2 shows the experimental results as a diagram of log [Mn] versus pH for the various precipitation conditions reported in Table 2. Excess figures in the table refer to excess amounts of H_2SO_5, H_2O_2, and/or Na_2CO_3 above that required by stoichiometry. The plots show a decreasing dependence of log [Mn] versus pH, as it would be expected for solubility reaction equilibria of metal oxides and hydroxides with their cations (and eventual hydroxo- and oxo-complexes) in water. It was found that by a suitable combination of oxidation and carbonate addition, it was possible to remove manganese to levels below 1 mg/L at pH 9 or below.

Caro's acid promotes very efficient precipitation ([Mn] <1 mg/L) at a range of pH > 5. Hydrogen peroxide promoted efficient precipitation at pH 9, but required a 200% excess (Table 1). At pH 9, neither oxidation by hydrogen peroxide (up to 100% excess) nor carbonate precipitation (up to 200% excess) by themselves were able to yield the desired precipitation efficiency. However, a combination of peroxide and carbonate (both at 100% excess level) had a synergistic effect, promoting precipitation to the desired target of [Mn] <1 mg/L.

Although limited in extent, the results obtained in this preliminary investigation show that both oxidants, Caro's acid and hydrogen peroxide, can significantly simplify manganese removal operations in such way that a liquid

Table 2 Residual [Mn] after precipitation and filtration (mg/L) with different precipitation systems from initial [Mn] = 1.2 g/L at 25°C, 1 h batch runs at constant pH

pH	No oxidant added	Na_2CO_3 with 50% excess	Na_2CO_3 with 200% excess	H_2O_2 with 100% excess	H_2O_2 with 100% excess + Na_2CO_3 with 100% excess	Caro's acid with 100% excess
3						366
4						3.0
5						0.74
6						0.50
7	1,221	983		688	249	0.36
8	1,131	330	28	80	34	0.18
9	165	25	9.5	42	0.67	
10	2.6	3.6	1.9	0.27	0.14	

effluent may be treated for direct manganese precipitation without having to take pH to more than 10.

Conclusion

It is possible to remove manganese from liquid effluents without raising the pH to more than 10 by employing suitable oxidizing conditions with either Caro's acid (pH 5–9), or hydrogen peroxide in combination with carbonate (at pH 9). In either of these conditions, it was possible to lower the [Mn] from 1.2 g/L to less than 1 mg/L in 1 h batch reaction at 25°C. These results were significantly better than manganese hydroxide precipitation at pH 9 which, under the same conditions but without oxidation, left a residual [Mn] = 165 mg/L.

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References

Aziz HA, Smith PG (1996) Removal of manganese from water using crushed dolomite filtration technique. Water Res 30(2):489–492

Burkin AR, Chouzadjian KA (1983) Precipitation of manganese dioxide from zinc electrolyte solutions using peroxomonosulphuric acid. In: Proceedings of the 3rd International Symposium on Hydrometallurgy, Atlanta, GA, USA, AIME, pp 603–615

Castrantas HM, Manganaro JL, Rautiola W (1995) Treatment of cyanides in effluents with Caro's acid. US Patent 5,397,482

CONAMA (Conselho Nacional do Meio Ambiente, Ministério do Meio Ambiente, Brasil) (2008) Discharge standards for effluents in surface waters. Resolução 397. http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=563

Cranor C (2008) The legal failure to prevent subclinical developmental toxicity. Basic Clin Pharmacol Toxicol 102:267–273

Eckenfelder WW Jr (1989) Industrial water pollution control. McGraw-Hill, New York City, 106 pp

Hester RE, Harrison RM (1999) Endocrine disrupting chemicals. Issues in Environmental Science and Technology #12, The Royal Society of Chemistry, London, UK, 51 p

Johnson KL, Younger PL (2005) Rapid manganese removal from mine waters using an aerated packed-bed bioreactor. J Environ Qual 34:987–993

Pavlovic J, Stopic S, Friedrich B, Kamberovic Z (2007) Selective removal of heavy metals from metal-bearing wastewater in a cascade line reactor. Environ Sci Pollut Res 14(7):518–522

Phillips B, Harrison P (1999) Overview of the endocrine disrupters issue. Issues in Environmental Science and Technology # 12, The Royal Society of Chemistry, London, UK, 15 p

Santos JS (2004) Remoção de Manganês de Águas e Efluentes Industriais com Utilização do Peróxido de Hidrogênio, Rio de Janeiro, Diss de Mestrado, Dept de Ciência dos Materiais e Metalurgia, Pontifícia Univ Católica do Rio de Janeiro, pp 62–65

Sincero AP, Sincero GA (eds) (2002) Physical-chemical treatment of water and wastewater. CRC Press/IWA Publ, Boca Raton, pp 604–605

Solvay (1982) Caro's acid laboratory procedure for hydrometallurgy. Solvay Interox, Technical Bull AO5.5, Brussels, Belgium

Stoica L, Dinculescu M, Plapcianu C (1998) Mn(II) recovery from aqueous systems by flotation. Water Res 32(10):3021–3030

Teixeira LAC, Andia JP, Yokoyama L (2005) Oxidation of cyanide solutions using Caro's acid. In: 2nd Mercosur Congr on Chemical Engineering, Rio de Janeiro, ENPROMER. http://www.enpromer2005.eq.ufrj.br/nukleo/pdfs/0229_enpromer2005.pdf

WHO (World Health Organization) (2009) Guidelines for drinking water quality, 3rd edn, vol 1, Ch 8, Chemical aspects. http://www.who.int/water_sanitation_health/dwq/GDW8rev1and2.pdf, p 49