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TREATMENT OF MANGANESE IN ACID AND NEUTRAL MINE DRAINAGE USING MODIFIED DOLOMITE

IULIANA LAURA CALUGARU[1], THOMAS GENTY[1,2] & CARMEN MIHAELA NECULITA[3]
[1]Technology Center for Industrial Waste (Centre Technologique des Résidus Industriels – CTRI), Canada
[2]Agnico Eagle Mines Limited, Canada
[3]Research Institute on Mines and Environment (RIME), University of Quebec in Abitibi-Temiscamingue, Canada

ABSTRACT

The treatment of manganese [Mn] in acid mine drainage (AMD) and neutral mine drainage (NMD) is prone to variation in performance, which depends on several factors, including pH, Mn and dissolved oxygen (DO) concentrations, catalysis by Mn-/iron [Fe]-solids, presence of ligands, and bacteria. Notwithstanding the recent technological and scientific advancements, Mn removal is notoriously difficult and still challenging because of its complex chemistry and high solubility. Precipitation of Mn(II), in AMD and NMD, occurs in the form of oxides, with prior oxidation to Mn(III) and Mn(IV), or as carbonates and sulphides. However, most treatment systems have limited efficiency in simultaneously treating Mn and other metals in AMD/NMD, necessitating secondary treatment for Mn removal. Modification of natural or residual materials was found efficient for the treatment of NMD. In this context, this study evaluated the performance of half-charred dolomite (1 h at 750°C) in batch testing (solid: liquid ratio of 3 g:400 mL) for Mn treatment in AMD and NMD. Results showed that modified dolomite treated more than 98% Mn in synthetic NMD (pH 6.1–6.3, up to 1 g/L Mn), at final pH of 9.7–10.6. Similar efficiency (98%) in Mn removal was also found for synthetic AMD (pH 3.6, up to 100 mg/L Mn and 1 g/L Fe, Mn:Fe molar ratio 1:10), while Fe was completely treated, at final pH of 9.7–9.8. In addition, Mn removal was 99.5% within the first 2 h (when pH increased to 8.0), while after 4 h, the efficiency was up to 99.9% (at final pH of 9.6). DO also decreased (from 8 to 2.2 mg/L), at initial Mn concentrations of 1 g/L, and dropped (from 8 to 0.7 mg/L), when Fe concentrations increased to 1 g/L (Mn:Fe molar ratio 1:10). Based on these findings, half-charred dolomite seems a promising option for the treatment of Mn in both AMD and NMD.

Keywords: acid mine drainage, Mn treatment, modified dolomite, neutral mine drainage.

1 INTRODUCTION

Mining operations can adversely affect the physicochemical and biological quality of the surrounding surface and ground waters in terms of pH (acidic/alkaline) and concentrations of toxic metals (e.g., aluminium [Al], cadmium [Cd], cobalt [Co], chromium [Cr], copper [Cu], Fe, mercury [Hg], Mn, molybdenum [Mo], nickel [Ni], lead [Pb], uranium [U], zinc [Zn]), metalloids (e.g., arsenic [As], antimony [Sb], selenium [Se]), as well as polyatomic anions [e.g., sulphate (SO_4^{2-}), cyanide (CN^-), thiocyanate (SCN^-), cyanate (OCN^-), nitrite (NO_2^-), nitrate (NO_3^-)] and cations [e.g., ammonium (NH_4^+)] [1–4].

Among the above-mentioned contaminants, Mn is notoriously difficult to remove from mine effluents prior to their discharge into the environment, mainly due to the high solubility of its minerals relative to other metals, inhibition of Mn precipitation at a molar ratio Fe/Mn > 4, reductive dissolution of Mn oxides by organic matter, sulphides and Fe(II), as well as the high pH (>8) required for its oxides formation and precipitation [5–8].

In acidic (pH < 6) and neutral (pH 6–8) mine drainage (AMD and NMD, respectively), the soluble Mn(II) form is present [9–11]. The oxidation of Mn to higher oxidation states (III and IV) to form slightly soluble oxides occurs at neutral pH in the presence of Mn-oxidizing bacteria, commonly present in nature [7, 8]. Thus, the oxidation requires a growth surface for the above-mentioned aerobic heterotrophic bacteria and sufficient DO, while the formation

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Table 1: Raw/modified materials utilized for Mn removal in various real/synthetic effluents.

Effluent characteristics	Material characteristics	Test characteristics	Performance	Ref.
Synthetic effluent, 19.39 mg/L Mn	Raw dolomite	Solid to liquid ratio 10 g:1 L ml,15 days	<19.3% removal, >15.6 mg/L residual conc., pH 7.2–7.3	[20]
	Charred dolomite (1 h at 600°C)		>95% removal, <0.97 mg/L residual conc., pH 9.3–9.7	
	Modified dolomite [charred/aq. Mn(II)]		>89% removal, <1.99 mg/L residual conc., pH 7.7–8.1	
	Modified dolomite [charred/aq. Mn(II) & $KMnO_4$]		>95% removal, <0.84 mg/L residual conc., pH 8.5–8.7	
Real AMD, pH=3.5, 6.2 mg/L Mn and 53.5 mg/L Fe	Wood ash	Solid to liquid ratio 0.5 g:1 L, 20 min	100% Fe removal, >56% Mn removal, 2.68 mg/L residual Mn conc., pH 8.3	[19]
	$Ca(OH)_2$	Solid to liquid ratio 0.2 g:1 L, 20 min	100% Fe removal, <30% Mn removal, 4.35 mg/L residual Mn conc., pH 8.26	
Synthetic effluent, pH = 5.2, 50 mg/L Mn or 50 mg/L Fe	Deciduous sawdust	Solid to liquid ratio 20 g:1 L, 10 min	30% Mn removal, 10% Fe removal	[21]
Real NMD, pH = 6.2, 20.5 mg/L Mn and 104 mg/L Fe	Zeolite (obtained by hydrothermal treatment) from AMD sludge, originated from coal fly ash	Solid to liquid ratio 10 g:1 L, 1 h	>99% Fe removal, 64% Mn removal, pH 8.3	[18]
Synthetic effluent, 10 mg/L Mn	Coal fly ash	Solid to liquid ratio 100 g:1 L, 5 min	>99.7% removal, <0.02 mg/L residual conc.	[14]
	Coal fly ash zeolite (from hydrothermal treatment)		>99.6% removal, <0.04 mg/L residual conc.	
Synthetic effluent, 100 mg/L Mn	Coal fly ash	Solid to liquid ratio 10 g:1 L, 2 h	3.4% removal, 96.6 mg/L residual conc.	[16]

	Coal fly ash zeolite (from hydrothermal treatment)		85.6% removal, 14.4 mg/L residual conc.	
Synthetic effluent, pH = 2 and 6, 10 mg/L Mn	Natural zeolite, clinoptilolite rich	Solid to liquid ratio 10 g:1 L	37.1% removal, for initial pH=2, 8 h, 97.3% removal, for initial pH=6, 1 h	[10]
Synthetic effluent, pH 6, 10 mg/L Mn and 10 mg/L Fe			38.8% Fe removal, 1 h, 12.9% Mn removal, 8 h	
Synthetic AMD, pH = 3.5, 20 mg/L Mn and 400 mg/L Fe	Natural zeolite, clinoptilolite	Solid to liquid ratio 37 g:1 L, 6 h	18.9% Mn removal, 59.9% Fe removal	[17]
Synthetic effluent, 20 mg/L Mn		Solid to liquid ratio 37 g:1 L, 6 h	95.2% Mn removal, 0.96 mg/L residual conc.	
Synthetic effluent, pH = 3, 10 mg/L Mn	Raw crab shell	Solid to liquid ratio 5 g:1 L	≥95% Mn removal, 72 h, pH 9.2–10.2	[5]
	Deproteinized crab shell		≥95% Mn removal, 48 h, pH 9.2–10.2	
	$CaCO_3$	Solid to liquid ratio 125 g:1 L	≤85% Mn removal, 72 h, pH 7.8–8.3	

and precipitation of Mn oxides are autocatalytic. Nevertheless, the major hurdle for an efficient Mn removal is represented by the dissolved Fe(II), which is adsorbed on the surface of Mn oxides and reduces them to Mn(II) soluble [7, 8]. Besides oxides, Mn(II) can be removed from mine effluents as sulphides and carbonates, under reducing and alkaline conditions [5, 12]. In general, the effective removal of Mn from mine drainage requires additional polishing steps in the design of the treatment systems, to priorly reduce Fe and Al concentrations [8, 13].

To limit the cost of Mn treatment, several natural and residual materials were evaluated, including the following: hydrated lime [$Ca(OH)_2$], limestone ($CaCO_3$), montmorillonite, bentonite, hydrotalcite, natural zeolite, coal fly ash and its hydrothermal synthetic zeolite, sludge originated zeolite, dolomite [$CaMg(CO_3)_2$] and activated dolomite, raw and deproteinized crab shells, Fe(III)-impregnated activated carbon, sawdust and wood ash [5, 8, 10, 11, 14–21]. However, some of these materials (Table 1), such as dolomite and activated dolomite, deciduous sawdust, coal fly ash and coal fly ash zeolite, natural zeolite, limestone, and raw and deproteinized crab shells, were evaluated for Mn removal in synthetic effluents, in the absence of Fe. In addition, except for the raw dolomite and deciduous sawdust, the referred to materials were found effective for Mn removal at concentrations less than 20 mg/L. Nonetheless, the fastest kinetics (5 min) were observed for the coal fly ash and its synthetic zeolite [14], whereas the slowest kinetics (15 days) were observed for the activated dolomite [20]. Conversely, whenever the Fe is present, in either real or synthetic effluents, Mn removal is adversely affected, as in the case of wood ash and hydrated limestone [19], sludge originated zeolite [18] or natural zeolite [10].

Among the materials evaluated for Mn removal, dolomite (a sedimentary carbonate mineral, worldwide spread and available at low cost) was found efficient for the treatment of several metals and metalloids (including in mine drainage), such as Pb, Cd, Cu, Ag, Co, and As [22–27]. Moreover, thermal activation considerably enhanced its efficiency for the removal of As, Co, Cr, Mn, Ni and Zn [20, 28–31]. Thermally activated dolomite was also found effective for the treatment of several metals (Ag, As, B, Ba, Co, Cr, Hg, Mn, Ni, Pb, Sn, Sr, Ti and V) in a shipyard wastewater [32].

In this context, the objective of this study was to comparatively evaluate the performance of raw and half-charred dolomite, for Mn treatment in NMD or in AMD, in the presence of Fe (Mn:Fe molar ratio of 1:10).

2 MATERIALS AND METHODS

2.1 Raw and activated dolomite

The dolomite rock used in this study was provided by Temiska Silice (Saint-Bruno-de-Guigues, Quebec, Canada). Its thermal activation was performed by charring in an oven (Thermolyne Furnace) for 1 h, at 750°C. These activation conditions were found optimal in a previous study where Ni and Zn were successfully treated in NMD [31].

Both raw and charred dolomite samples were first grinded. Then, the following physicochemical parameters were determined: particle size distribution, specific surface, pH, pH_{PZC}, elemental composition and mineralogy [31].

Thermal decomposition of dolomite produces [20, 28–30] either a mixture of $CaCO_3$ (calcite) and MgO (periclase, resulting from the dissociation of $MgCO_3$) (eqn (1)) or MgO and CaO, by further decomposition of $CaCO_3$ (eqn (2)). If the process is stopped at ≈800°C, a

Table 2: Conditions used in treatability testing.

Effluent/ dolomite type	Parameter	Metal	pH	Sampling (h)	Doses (mg/L)
NMD/raw	Uptake function of concentration	Mn	6.2–6.3	48	50, 100, 153, 202
NMD/charred			6.1–6.3		50, 100, 153, 202, 426, 1353, 1815, 2693
AMD/charred		Mn/Fe	3.6		58/443, 99/934 145/1470, 188/1860
NMD/raw NMD/charred	Uptake function of time	Mn	6.7	1, 2, 4, 8, 24, 48	77.5

solid rigid mixture of calcite and periclase is obtained. This new material has a porous structure, with over 50 times the specific surface area of the raw dolomite [29, 31–33]:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \tag{1}$$

$$CaCO_3 \rightarrow CaO + CO_2 \tag{2}$$

2.2 Synthetic effluents (solutions)

The performance of raw and half-charred dolomite was assessed using synthetic effluents (NMD and AMD) prepared with ACS grade of sulphate salts ($MnSO_4{\cdot}H_2O$ and $FeSO_4{\cdot}7H_2O$) and deionized water (Table 2). The pH of the AMD was adjusted with concentrated (98%) H_2SO_4. The ionic strength for both NMD and AMD types of effluents was adjusted with solid NaCl.

2.3 Batch testing conditions, sampling, analysis and data processing

The experiments were conducted in 50 mL propylene tubes containing a volume of 40 mL synthetic effluent, at a temperature of 25°C and at 300 rpm agitation speed. The solid to liquid ratio (3 g:400 mL) was selected according to the literature [24, 31]. The maximum Mn concentration in the synthetic NMD (pH 6.1–6.3) was 202 mg/L (for the raw dolomite) and 2,693 mg/L (for the half-charred dolomite) (Table 2). In the synthetic AMD (pH 3.6), the maximum Mn and Fe concentrations were 188 and 1,860 mg/L, respectively. Solely the half-charred dolomite was evaluated for the treatment of the synthetic AMD (Table 2). Nitrogen was purged for 2 min, within each propylene tube. At the end of the 48 h batch experiments, the supernatant was filtered, the pH and DO were measured, while the concentrations of Mn and Fe were analysed with an AA spectrometer. Additional batch testing was performed in order to evaluate the uptake of Mn in synthetic NMD (pH 6.7) as a function of time. The synthetic NMD contained 77.5 mg/L Mn, and the sampling was carried out at 1, 2, 4, 8, 24 and 48 h (Table 2). The pH, and the DO and Mn concentrations were measured for each filtered sample.

Metal removal (%) was calculated with eqn (3):

$$\% \text{ Removal} = [C_o - C_f].100/\, C_o \tag{3}$$

where C_0 and C_f, represent, respectively, the initial and final concentrations of metal in solution (mg/L).

3 RESULTS AND DISCUSSION

3.1 Materials characterization

The dolomite samples used in this study had high purity (87.1%). After 1 h of charring at 750°C, 7.2% of the solid consisted of dolomite, while two new mineral phases appeared, i.e. calcite (53.7%) and periclase (19.9%). The resulting charred dolomite (pH 11.6) showed strongly basic relative to the raw dolomite (pH 7.9), while the pH_{PZC} of raw dolomite increased from 9.6 to 11.1 after the charring. A sevenfold increase in specific surface (0.6–4.2 m^2/g) was also observed for the charred dolomite [31].

3.2 Batch testing results

Charred dolomite showed very effective for Mn removal in the synthetic NMD, as more than 89% of Mn was removed from solutions initially contaminated up to 1,353 mg/L (Table 3).

Minor residual concentrations (up to 3.3 mg/L) of Mn in the treated NMD were found only up to maximum initial concentration of 892 mg/L (Table 3). Effectiveness of the charred dolomite then decreased, when Mn concentration increased above 892 mg/L in the synthetic NMD, whereas raw dolomite seemed sparsely effective even at low (49.6 mg/L) Mn

Table 3: Performance of raw and charred dolomite for Mn removal in synthetic NMD as a function of the initial concentration, in batch testing.

C_0 (mg/L)	C_f (mg/L)	Removal (%)	pH	DO (mg/L)
		Dolomite		
49.6	43.7	11.9	7	8.7
99.9	91.5	8.4	6.8	8.6
153.3	148.4	3.2	6.7	8.3
202.3	196.1	3.1	6.6	8.2
		Charred dolomite		
49.6	1.4	97.2	10.6	7.9
99.9	1.5	98.5	10.5	7.7
153.3	3.1	98.0	10.4	6.9
202.3	3.3	98.4	10.3	6.3
426	0.02	99.9	10.2	4.1
892	0.04	99.9	9.7	2.3
1353	147	89.1	8.4	1.4
1815	592	67.4	7.8	1.4
2693	1350	49.9	7.5	1.7

Table 4: Performance of charred dolomite for Mn removal in the presence of Fe (1:10) in synthetic AMD, as a function of the initial concentration, in batch testing.

Mn			Fe			Mn:Fe Final ratio	pH	DO (mg/L)
C_0 (mg/L)	C_f (mg/L)	Removal (%)	C_0 (mg/L)	C_f (mg/L)	Removal (%)			
57.6	0.005	99.9	443	BDL	99.9	N/A	9.8	3.33
99	1.5	98.5	934	BDL	99.9	N/A	9.7	0.72
145	107	26.2	1470	145	90.1	1:1.3	6.9	0.24
188	162	13.8	1860	714	61.6	1:4.3	6.8	0.13

BDL: below detection limit; N/A: not applicable.

concentrations (Table 3). The initial pH of the uptake experiments was 6.1–6.3, whereas the final pH was 7–6.6 (for the raw dolomite) and 10.6–7.5 (for the charred dolomite).

Solely charred dolomite was evaluated for the treatment of Mn in the presence of Fe (1:10), in synthetic AMD (pH 3.6), and it was found effective up to 99 mg/L Mn and 934 mg/L Fe (Table 4).

It was observed that further increase of Fe concentration significantly decreased Mn removal, consistently with previously reported findings [10, 18, 19]. Fe removal was satisfactory (90%) up to 1,470 mg/L as initial concentration, but residual Fe was usually high (145 mg/L) in treated AMD (Table 4).

The pH varied from basic to neutral while DO concentration was significantly reduced. Oxidation of Fe(II) to Fe(III) followed by Fe(III) hydrolysis could explain the decrease of both DO and pH.

The results of batch testing on the uptake of Mn in synthetic NMD as a function of time (Table 5) were consistent with the previous results of this study. Hence, dolomite showed limited efficiency, whereas charred dolomite allowed significant reduction of Mn concentration within only 2 h of contact with the synthetic NMD. Noteworthy, 80% of Mn was removed within 1 h; however, residual Mn concentration was still high (15.6 mg/L). The initial Mn and DO concentrations were 77.5 and 8.1 mg/L, respectively, at a pH of 6.7. The DO recorded little variation for both raw and charred dolomite. The neutralizing effect of dolomite seemed slow compared to charred dolomite (that settled to 10.4 after 24 h). Consequently, to explain Mn removal, chemical sorption seems more probable than oxidation and precipitation, as Mn concentrations dropped from 77.5 to 0.37 mg/L within 2 h, whereas pH raised from 6.7 to 8 within the same interval of time.

3.3 Comparative performance of half-charred dolomite and some recently evaluated raw and modified materials for Mn treatment

The performance of some materials such as raw and activated dolomite, hydrated lime, limestone, wood ash and sawdust, natural zeolite, coal fly ash and coal fly ash zeolite, synthetic zeolite prepared from sludge resulting from the AMD treatment with coal fly ash, raw and deproteinized crab shell, recently evaluated for the treatment of Mn in different aqueous solutions, is presented in Table 1.

Table 5: Performance of charred dolomite for Mn removal in synthetic NMD as a function of time, in batch testing.

Time (h)	C_f (mg/L)	Removal (%)	pH	DO (mg/L)
		Dolomite		
0	77.5	0.0	6.7	8.1
1	72.5	6.5	6.8	8.0
4	70	9.7	6.8	7.0
24	70.5	9.0	6.9	8.0
48	69	11.0	8.2	8.0
		Charred dolomite		
0	77.5	0.0	6.7	8.1
1	15.6	79.9	7.2	7.5
2	0.37	99.5	8.0	6.8
4	0.01	99.9	9.6	7.22
8	0	100	9.8	7.49
24	0.1	99.9	10.4	7.0
48	0.01	99.9	10.4	7.2

Among natural materials, raw dolomite seems the least effective [20], natural zeolite the most effective [10, 17], whereas an important solid to liquid ratio is necessary to improve the effectiveness of the limestone [5] for Mn removal.

Concerning the waste materials, the least effective seems the sawdust of deciduous trees, and the most effective the coal fly ash and the raw crab shell. In the same time, Mn removal is faster by fly ash (>99.7% removal within 5 min) than by raw crab shell (≥95% Mn removal within 72 h).

Modification of natural and waste materials improves their performance in Mn withdrawal. For instance, modified dolomite [20] becomes very effective in terms of % removal (>95%) and residual Mn concentration (<0.84 mg/L) while maintaining a neutral pH of treated effluent (8.5–8.7). However, the initial concentration of Mn was lower (about 20 mg/L) compared to this study (892 mg/L), whereas the duration of batch testing was longer (15 vs 2 days). It is to observe that half-charred dolomite evaluated in this study decreased the Mn concentration from 77.5 to 0.37 mg/L within 2 h, while the pH of the treated effluent was 8.0. The solid to liquid ratio in this study was 7.5 g for 1 L, which is comparable to 10 g for 1 L, employed by Mamchenko et al. [20].

Coal fly ash seems effective for Mn removal at low initial concentrations [14] (10 mg/L, >99.7% removal), but less effective at higher initial concentrations (100 mg/L, 3.4% removal) [16]. Yet, its conversion into zeolite improves the performance for Mn removal (100 mg/L, 85.6%) [16].

Although very effective for Mn removal, natural zeolite seems to significantly lose its efficiency wherever Fe is present [10, 17]. However, synthetic zeolite prepared by hydrothermal treatment of sludge originated from AMD treatment with coal fly ash, removed 99% Fe and 64% Mn from a real NMD (pH 6.2, 20.5 mg/L Mn, and 104 mg/L Fe) while maintaining the pH of the final effluent at 8.3 [18].

Better performance was obtained by half-charred dolomite, within this study, as Mn and Fe were removed up to 98.5% (1.5 mg/L residual concentration) and 99.9% (BDL) respectively, from a synthetic AMD (pH 3.6, 99 mg/L Mn, and 934 mg/L Fe).

4 CONCLUSIONS

In this study, both raw and half-charred dolomite (1 h, at 750°C) were evaluated through batch testing for their performance in Mn removal from synthetic AMD and NMD. The results showed that charred dolomite treated more than 98% Mn in synthetic NMD (pH 6.1–6.3) when the initial Mn concentration was up to 892 mg/L. Moreover, Mn removal was very efficient (89%) when the initial Mn concentration was 1,353 mg/L. Nonetheless, the residual concentration was 147 mg/L Mn. The uptake kinetic was relatively fast, as Mn concentration dropped from 77.5 to 0.37 mg/L within 2 h. However, 79.9% Mn was removed within the first 1 h. Meanwhile, raw dolomite showed poor performance in the same testing conditions.

In synthetic AMD (pH 3.6, Mn:Fe molar ratio 1:10), better performance in Mn and Fe removal was achieved at maximum initial concentrations of 99 and 934 mg/L, respectively. Above 1,470 mg/L, Fe removal was still satisfactory (90.1%), despite the fact that residual Fe was high (145 mg/L), whereas Mn removal was poor (29.2% for 145 mg/L initial concentration).

Half-charring of dolomite strongly enhanced its alkaline character and neutralizing capacity. However, the pH increase seems rather slow to cause an eventual major removal of Mn by precipitation, as 99.5% of Mn was removed from 77.5 mg/L initial Mn concentration at a final pH of 8.0.

The most severe drop in DO was found during AMD treatment. As simultaneously decrease of pH was also observed, Fe(II) was probably partially oxidized to Fe(III), which then hydrolysed and precipitated. An important decrease of DO was also observed at higher concentrations of Mn in NMD (above 426 mg/L). In this last case, Mn(II) probably precipitated as oxidized Mn(III) or Mn(IV).

Based on these findings, half-charred dolomite could be considered as a promising option for the treatment of Mn in both AMD and NMD. Further research is warranted to evaluate the mechanisms of Mn removal.

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