

Effective Removal of Manganese from Mine Effluent Contaminated River Water Using Ca-Mg-(OH)₂ Nanocomposite

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Abstract

Contamination of various spheres of the receiving environments by manganese (Mn) emanating from mining activities has been an issue of prime environmental concern. Mn can result to notable aesthetic and health issues, and this notorious contaminant need to be removed prior contamination of ecological systems and for the benefit of the environment and living organisms. For this reason, Ca-Mg-(OH)₂ nanocomposite was synthesized and duly assessed for the removal of Mn from contaminated river water. Optimum conditions were observed at 15 min of mixing, 0.5 g dosage and 200 rpm mixing speed. Mn removal was achieved at 92%, 72% and 83%, whereas turbidity was removed to 57%, 95% and 87% by MgO, CaO and Ca-Mg-(OH)₂. The pH was also increased significantly. Mn containing aqueous solution was interacted with CaO, MgO, and Ca-Mg-(OH)₂ nanocomposite. PHREEQC geochemical model was used to confirm the species and mineral phases of Mn. Ca-Mg-(OH)₂ was found to be superior in removing Mn from contaminated river water.

Keywords: Contaminated River Water, Ca-Mg-(OH)₂, CaO, MgO, PHREEQC Geochemical Model, Water Treatment

Introduction

Rapid population growth proportionally resulted to rapid industrial development which in turn causes pollution to the environment as a whole (Lee *et al.* 2017). Mn being one of the elements exposed to the environment by industrial effluents occurs naturally and it is discovered in different geological spheres (Rudi *et al.* 2020). High concentrations of Mn can negatively affect living organisms on exposure, and thus, requires to be removed from drinking water prior consumption. Its removal in drinking water is mostly as a result of eco-toxicological effects that it poses to the environment. Based on toxicity assays, the maximum allowable limit for drinking water has been set at 400 µg/L as stipulated in World Health Organization (WHO 2004) and 300 µg/L as stated by the United States Environmental Protection Agency which also set 50 µg/L as an aesthetic limit for drinking

water guideline (US EPA 2019). A wide array of technologies including precipitation, oxidation, adsorption, bio-phyto-remediation, ion exchange, and crystallization have been employed for Mn removal from aqueous environments (Nkele *et al.* 2022). However, owing to the drawbacks of other technologies, chemical precipitation is still the best technology for the removal of Mn from the aquasphere, specifically when Mn need to be recovered. Different precipitating agents have been used and they comprise hydrated lime, lime, limestone, magnesite, periclase, brucite, soda ash, caustic soda, and dolomite, amongst others (Masindi *et al.* 2022). However, the use of calcined dolomite has never been explored. This study was therefore conceptualised with the principal aim of evaluating the performance of mechanochemically synthesized Ca-Mg-(OH)₂ nanocomposite for the removal of Mn from aqueous environments. This will be the

first study in design and execution to assess the use of mechanochemically synthesized Ca-Mg-(OH)₂ nanocomposite for Mn removal from aqueous solution. The reaction chemistry and fate of Mn will be determined using state-of-the-art analytical techniques along with PH REDox EQUilibrium (in C language) (PHREEQC) geochemical modelling.

Materials and methods

Samples for aqueous solution have been collected from Wilge River. Hydrated lime (Ca(OH)₂) and periclase (MgO) were procured from Protea Chemicals Pty (Ltd), South Africa. The nanocomposite was prepared by mechanochemical synthesis, using vibratory ball milling and calcination, where Ca(OH)₂ and MgO (both powdered) were homogenised at 1:1wt% mass ratio for 30 minutes using the vibratory ball-mill at 1600 rpm. To fulfil the objectives of this research, one factor at a time (OFAAT) modality has been utilized, specifically, the effect of dosage (g), mixing speed (rpm), and contact time (min) were evaluated. Aqueous samples characterization was done by using multimeter (Hach 40d 13994 pH401) and spectrophotometers (DR 3900 Hach and TL2350 Hach) for Mn, pH, turbidity and electrical conductivity (EC) de-

termination. Characterization of solid samples was done using Fourier Transform Infrared Spectrometer (FTIR) (PerkinElmer's Spectrum 100 FTIR instrument containing a PerkinElmer Precisely Universal Attenuated Total Reflectance (ATR) sampling accessory with a diamond crystal). Experiments were performed in triplicate and results were reported as mean values. The PHREEQC geochemical model was employed to complement experimental results.

Result and discussion

Experimental results for the effects of contact time, dosage, and mixing speed on turbidity, Mn, pH, and EC are presented in this section.

Effect of contact time

An illustration of the outcomes for the effect of contact time is shown in **Figure 1(a-b)**. An examination of six (6) different contact times, i.e., in minutes, (5, 10, 15, 20, 25 and 30) was done and the results are summarised in **Figure 1**.

Effective % removal for Mn was achieved by all precipitating agents with an increase in contact time (Figure 1a). The removal of Mn was variable for each agent. Specifically, MgO had higher % removal whereas CaO

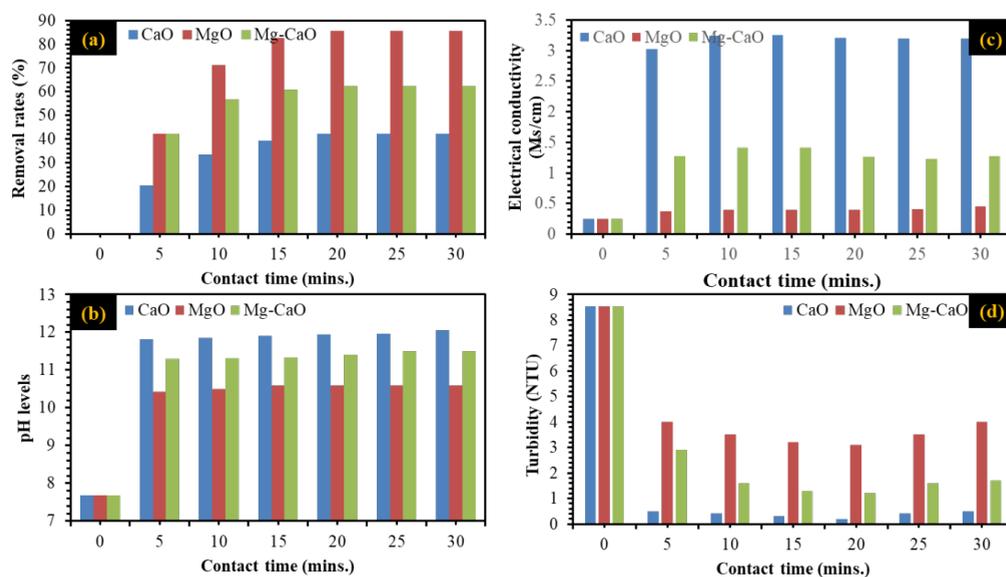


Figure 1 Variation in % removal of Mn (a), pH value (b), EC (c), and turbidity (d) as a function of contact time (Conditions: 0.5 g difference of each precipitant, 368 µg/L Mn²⁺, 15 min contact time, 250 rpm and 10 min of settling time).

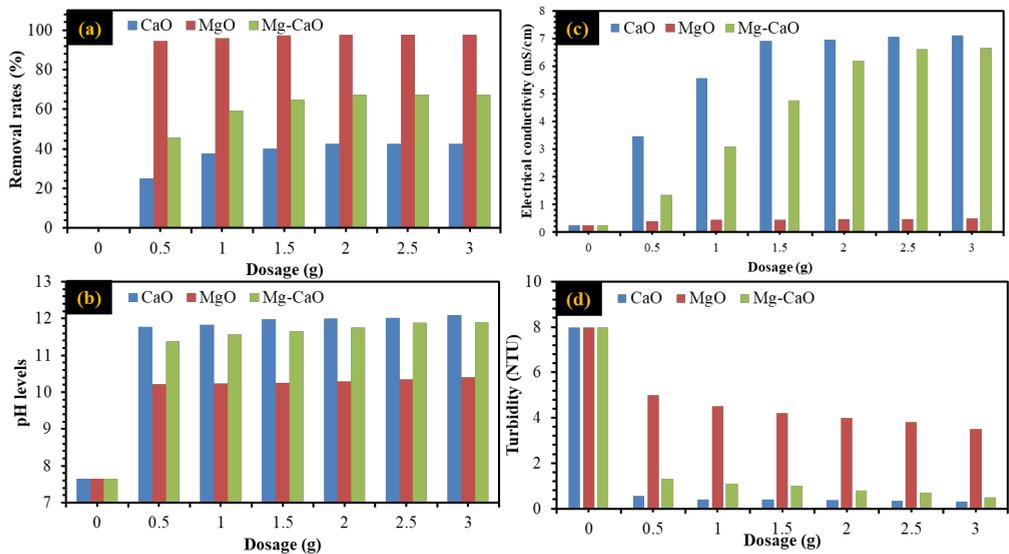


Figure 2 Variation in % removal of Mn (a), pH value (b), EC (c) and turbidity (d) as a function of dosage (Conditions: 0.5 g difference of each precipitant, 368 $\mu\text{g/L}$ Mn^{2+} , 15 min contact time, 250 rpm and 10 min of settling time).

had lower % removal efficacy. As with the work performed by Selina *et al.* (2006), the researchers have discovered that dolomite (32%) and magnesite (28%) showed the highest % removal for Mn as a function of contact time. Figure 1b shows an increase in pH after the addition of the agents in aqueous solution and it is almost constant as time increases. This could be attributed to quick reaction rates that swiftly reach the state of equilibrium. EC (mS/cm) was at its highest with CaO and at its lowest with MgO including their composite. This indicates dissolution during the interaction of the precipitating agent with aqueous solution (Figure 1c) and lastly, Figure 1d shows the decrease of turbidity (NTU) after the addition of precipitants. MgO shows a decrease from time 0 – 15 min, after 15 min, turbidity starts to increase while lime showed reduction at 5 minutes upwards. Interestingly, CaO is more effective in removing turbidity as compared to MgO and its Ca-nanocomposite.

Effect of precipitant dosage

An illustration of the outcomes of the effect of feedstock dosage (g) is shown in Figure 2(a-b). An examination of six (6) different dosages

(i.e. 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0) was done and the results are summarised in Figure 2.

The outcomes of the variations in Mn, pH value, EC (mS/cm), and turbidity (NTU) as a function of dosage are shown in Figure 1(a-c). As summarised, it was observed that MgO was more effective in decreasing Mn levels (Figure 1a). Ca-Mg-(OH)_2 and CaO shows a slight change in % removal rate with changing dosages. The levels of pH increased drastically when 0.5 g of precipitants were added and then slowly increased with an increase in the dosage (Figure 2a). Charerntanyarak (1999) performed a study where Mn was removed using chemical coagulation as well as precipitation and it was discovered that the optimum pH obtained by lime treatment was greater than 10.5. In Figure 2c, CaO and Ca-Mg-(OH)_2 increased EC to above SANS 241 drinking water limit hence requiring a coupling technology unless if smaller dosage is used. In general, MgO demonstrated poor performance in turbidity reduction.

Effect of mixing speed

An illustration of the outcomes of the effect of mixing speed (rpm) is shown in Figure 3(a-b). An examination of six (6) different mixing

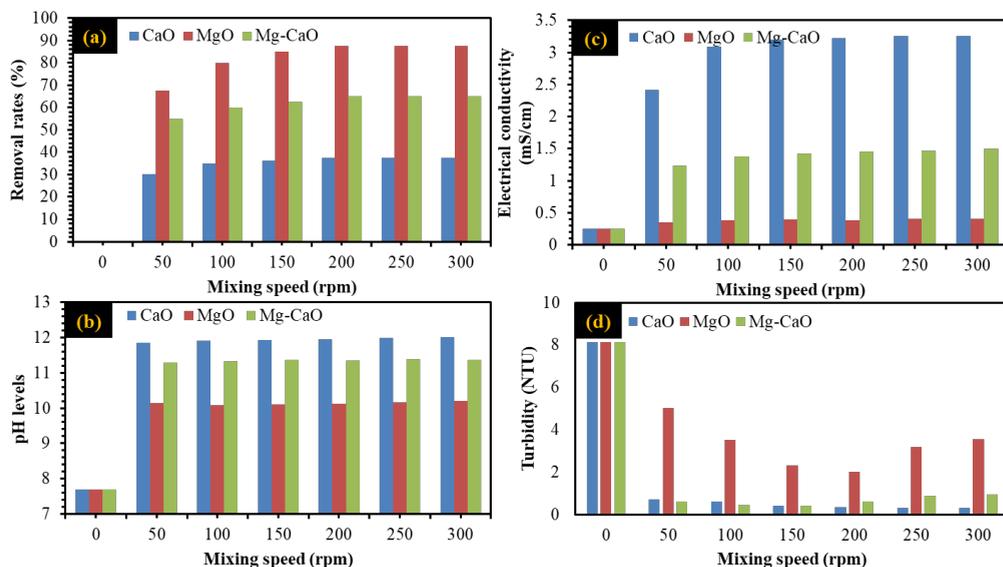


Figure 3 Variation in % removal of Mn (a), pH value (b), EC (c) and turbidity (d) as a function of mixing speed (Conditions: 0.5 g difference of each precipitant, 368 $\mu\text{g/L}$ Mn^{2+} , 15 min contact time, 250 rpm and 10 min of settling time).

Table 1 The effect of optimized operational parameters on the removal of contaminants from aqueous solution (Optimum conditions: 15 min, 0.5 g, and 200 rpm for the precipitating agents).

Parameter	SANS 241 Limit	Raw water	Alkalinity generating agents		
			MgO	CaO	Ca-Mg-(OH) ₂
Mn ($\mu\text{g/L}$)	≤ 400	1000	82	276	170
pH	≤ 9.7	7.68	10.17	11.87	11.35
Turbidity (NTU)	≤ 1.00	8.21	3.50	0.409	1.05
% Mn removal	-	0	92	72	83
% Turbidity removal	-	0	57	95	87

speed (i.e., 50, 100, 150, 200, 250 and 300) was done and the results are summarised in Figure 3.

Mixing speed plays a big role in influencing the removal of contaminants. As observed in Figure 3a, Mn was effectively reduced with an increase in mixing speed. MgO had higher % removal for Mn whereas hydrated lime, expressed as CaO, had the lowest removal rate. pH was highly increased and precipitation has taken place in the achieved pH levels (Figure 3b). The acceptable limit for EC by SANS 241 is 1.7 mS/cm and looking at Figure 3c, CaO increased EC above the acceptable limit whereas MgO barely increased the parameter. Figure 3c shows turbidity removal

with increase in mixing speed and CaO achieved the best removal efficiency.

Treatment of real river water at optimum conditions

The effect of optimized operational parameters on the removal of contaminants from aqueous solution was investigated and the outcomes are shown in Table 1.

Table 1 compares the SANS 241 limits with the water treated with different precipitating agents and the % removal. The removal of Mn was effective for every alkaline agents. MgO reduced Mn greater as compared to the other agents while CaO performed better in turbidity. Specifically, the % removal of

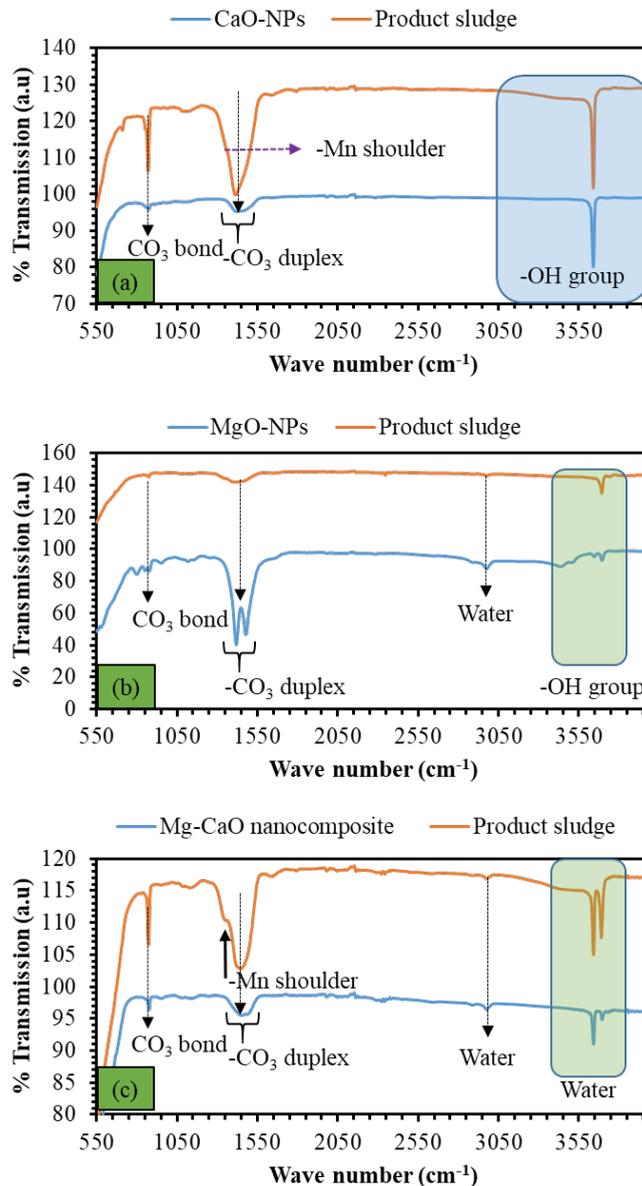


Figure 4(a-c) Illustration of FTIR and functional groups together with their wavenumbers for reacted and produced CaO-NPs, MgO-NPs as well as Mg-CaO nanocomposite (Ca-Mg-(OH)₂ nanocomposite)

Mn achieved $\geq 72\%$, $\geq 92\%$ and $\geq 83\%$ for CaO, MgO and Ca-Mg-(OH)₂, respectively, whilst the reduction in turbidity achieved $\geq 95\%$, $\geq 57\%$ and $\geq 87\%$, respectively. The pH exceeded the SANS 241 limit for CaO and its Mg-nanocomposite hence requiring the reduction in dosage.

Characterization of solid samples

Functional groups

The FTIR spectra and functional groups for reacted and produced CaO-NPs, MgO-NPs, and Mg-CaO nanocomposite (Ca-Mg-(OH)₂ nanocomposite) are illustrated in Figure 4(a-c).

Table 2 Predicted phases of Mn post precipitation

Mineral name	SI	Chemical name	Mineral name	SI	Chemical name
Birnessite	7.18	MnO ₂	Hausmannite	19.70	Mn ₃ O ₄
Bixbyite	15.35	Mn ₂ O ₃	Manganite	7.54	MnOOH
Nsutite	8.22	MnO ₂	Pyrolusite	9.40	MnO ₂
Rhodochrosite	2.72	MnCO ₃	Rhodochrosite(d)	1.98	MnCO ₃
Dolomite	0.19	CaMg(CO ₃) ₂	Calcite	0.00	CaCO ₃

The infrared spectrum of reacted and produced CaO-NPs, MgO-NPs, and Mg-CaO nanocomposite (Ca-Mg-(OH)₂ nanocomposite) are shown in Figure 4(a-c). As illustrated in Figure 4a, the peaks are observed at 850, 1450 and 3650 cm⁻¹. In particular, the carbonate bond stretch was observed at 850 cm⁻¹ and a broad bend was observed at 1450 cm⁻¹ for both spectrums but the peaks were much higher in the produced sludge. For both spectrums, a strong absorbance peak was observed at 3650 cm⁻¹. Galván-Ruiz *et al.* (2009) corroborate these results. Figure 4b indicates different spectrums for reacted MgO-NPs and produced sludge. The produced sludge had a weak bend on 1450 cm⁻¹ wavenumber whereas the reacted MgO-NPs had strong symmetric and asymmetric stretches at the same wavenumber. At 2950 cm⁻¹, water was present for both spectrums and at 3750 cm⁻¹, there were weak peaks and OH groups present for both spectrums. Nga *et al.* (2020) supports the findings. In Figure 4c, for both spectrums, carbonate bonds are present at wavenumber 850 cm⁻¹. A strong broad bend is seen on the produced sludge which had a shoulder and a weak bend is depicted by the Mg-CaO nanocomposite at wavenumber 1450 cm⁻¹. Presence of water is denoted at 2950 and 3650 cm⁻¹ wavenumbers. In general, the metals-functional groups denoted lack of change in the chemical properties of the product sludge.

Geochemical modelling

The illustration of the feasibilities of Mn precipitation and its mineral phase is shown in Table 2.

In Table 2, the precipitation of various mineral phases have been predicted. The precipitation of this chemical in aqueous solution was predicted to be viable. This was not identified in FTIR since their concentration could be very low due to low concentration in feed water.

Conclusions and recommendations

This novel study successfully demonstrated the feasibility of mechanochemically synthesizing Ca-Mg-(OH)₂ nanocomposite and evaluate its use for the removal of Mn from aqueous solution. Optimum conditions were observed to be 15 min of mixing, 0.5 g of dosage, and 200 rpm of mixing speed. A notable increase in pH were observed for all the reagents. Furthermore, findings denote MgO to have the highest % removal for Mn whilst CaO had the highest capacity towards turbidity removal. Ca-Mg-(OH)₂ nanocomposite showed traits of both CaO and MgO which led to the conclusion that it was more effective in performance as compared to individual materials. As expected, the solids indicated the presence of water, hydroxyl and carbonate bonds, i.e., before and after the interaction. As such, the developed nanocomposite will go a long way in curtailing the impacts of Mn in drinking water and further afield.

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