Treatment of manganese-containing mine water: adsorption onto metal oxide decorated bentonite

AM. Muliwa, MS. Onyango, A. Maity and A. Ochieng

Abstract- Water pollution by toxic metals from mining industries is a serious threat to living organisms and the environment. Therefore, it is important to effectively remove metal contaminants from water using appropriate treatment technologies. In this study, bentonite manganese oxide (BMnO) composite was prepared, characterized and evaluated for Mn^{2+} ions adsorption from aqueous solutions. Batch experiments were conducted to explore the effect of different experimental conditions on adsorption efficiency. The adsorption of Mn was reasonably fast and the kinetic data fitted well with the pseudo-second-order model. Equilibrium results showed that increasing the solution pH and adsorbent dose, and temperature increased the adsorption efficiency while it was opposite with the initial concentration. Langmuir isotherm model described equilibrium data better compared to Freundlich isotherm model. The removal of Mn^{2+} ions proceeded by ion-exchange and adsorption. Metal oxide decorated bentonite can effectively reduce Mn^{2+} ions in polluted waters.

Keywords—Adsorption, bentonite, manganese, metal oxide

1. Introduction

Manganese is one of the toxic and non-degradable metallic species mainly discharged by industrial effluents from coal and oil burning, dry battery cells, ceramics and electrical coil manufacturing. It can exist in a range of oxidation states, +2, +3, +4, +6 and +7. Amongst these, the divalent form (Mn^{2+}) is the predominant species in most waters at pH 4-7, while highly oxidized forms occur at alkaline pH values (pH>7) or may result from microbial oxidation [1, 2]. Although small traces of manganese are essential nutrients for human body, exposure to high amounts can cause irreversible damages to the nervous system and other pathologies [3]. Concentrations in excess of drinking water standards can result in formation of oxide deposits in pipeline, discoloration of water and laundry, and impart an unpleasant metallic taste [4]. Therefore, reduction of manganese concentration in public and industrial water to acceptable levels is an important undertaking from human health and environmental point of view.

The chemistry of manganese in aqueous solution is quite complex, thus making it a difficult contaminant to remove. Many technologies, including precipitation, coagulation-flocculation , sedimentation, oxidation/reduction, solvent extraction, ion-exchange, evaporation and adsorption are available for control and minimization of water pollution by metals [5, 6]. However, most of these processes are characterized by shortcomings such as high operational and maintenance cost, low removal efficiency, and inapplicability to a wide range of toxic pollutants in low concentrations, and generation of toxic sludge [7]. Comparatively, adsorption process is considered a better alternative for decontamination of heavy metal ions polluted water because it requires low capital cost, it is flexible, simple in design, easy to operate, insensitive to toxic pollutants, and the availability of different adsorbents [8]. Moreover, it does not result in the formation of harmful substances. The performance of any adsorption system depends highly on the adsorbent's characteristics such as surface area and chemistry, and the selectivity [9].

Recently, there has been increased focus on application of natural materials such as clays as adsorbents for decontamination of metal polluted water. Clays are abundant, inexpensive, non-toxic, and modifiable [10]. Moreover, clays have layered structure, and they also exhibit high ion-exchange and swelling characteristics, as well as good cation exchange capacity, which make them potential candidates for metal ions removal [11]. However, clays are sticky when wet and they produce low capacity for metal ions. Thus, to enhance adsorption capacity, surface modifications using appropriate organic or inorganic components is required [12, 13]. Metal oxides (MO) nanoparticles are known to have high affinity for metal ions, but cannot be used alone in an adsorption system. This is because their small sizes creates high pressure drops in fixed-bed applications, and that they are not economically attractive [14]. Thus, if MO can be combined with inexpensive materials, like clays, can result to an adsorbent material with improved synergistic effects for metal ions removal.

In this study, bentonite clay was decorated by direct redox precipitations of manganese oxide (MnO) nanoparticles onto its surface, and was examined for adsorption of Mn^{2+} ions from aqueous solution. Equilibrium experiments were performed in batch mode to explore the influence of different process conditions on Mn^{2+} removal. The equilibrium data was fitted with the appropriate adsorption models to extract important adsorber design parameters.

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2. MATERIALS AND METHODS

2.1. Chemicals and adsorbent preparation

All chemicals were reagent grade and were purchased from Merck (Pty) Ltd-South Africa. Double distilled water was used for all rinsing and dilutions. A stock solution of 1000 mgMn^{2+}/L was prepared by dissolving an appropriate amount of Mn $(NO3)_2.4H_2O$ salt in 1000 mL distilled water.

Bentonite powder was obtained from ECCA (Pty) Ltd, South Africa. It was washed repeatedly with water to remove impurities, then it was dried at 100^oC for 24h. A given mass of the dried bentonite was added into a $KMnO_4$ solution, and the mixture was stirred magnetically for 30min. To this mixture, HCl was added, and thereafter, heated and maintained at 90^oC for 1h. The brown mixture was then allowed to cool to room temperature after which it was vacuum filtered and rinsed with water until the filtrate pH was neutral. Finally the solids were vacuum-dried overnight and stored waiting further use. The morphology was observed using scanning electron microscope (SEM, JEOL JSM-6610-LV), operated at an accelerating voltage 15 kV and beam current 20 mA.

2.2. Adsorption equilibrium experiments

In all batch equilibrium experiments, 50mL solutions in 100mL plastic sample bottles, and a thermostatic bath shaker, operated at 160 rpm were used, unless otherwise stated. The effect pH (2-10), adsorbent mass (0.025-0.225 g), temperature (298-318K), and concentration (50-200 mg/L) on Mn removal were explored. For each experiment, one parameter was varied while others were kept constant. Samples were agitated for 24h, filtered and analyzed for residual Mn^{2+} ions using ICP-AES. The removal efficiency and uptake were determined by mass balance expressions as follows:

$$R\% = \left(\frac{C_O - C_e}{C_O} \right) \times 100 \tag{1}$$

$$Q_e = \left(\frac{C_O - C_e}{m} \right) \times V \tag{2}$$

where C_o and C_e are initial and equilibrium concentration (mg/L), Q_e is the uptake (mg/g), m is the mass of adsorbent (g) and V is the solution volume (L).

The effect of contact times was explored by adding a given amount of adsorbent into 1 L Mn^{2+} ions solution, under stirring at 160 rpm. Samples were taken periodically for 3h, and were analyzed and Mn^{2+} ions uptake at any time t.

Adsorption experiments were also carried out using real neutral mine water to determine the suitability of CBMnO adsorbent in real wastewater applications. The water samples were obtained from a Gold mining company in Gauteng Province, and the analysis showed that concentration of manganese was 50 mg/L, among other co-ions, and had a pH 6.8; attributable to limestone pretreatment.

3. RESULTS AND DISCUSSION

3.1. Material characterization

Figure 1 shows SEM images of bentonite (a) and BMnO (b). As can be seen, the surface of bentonite was observed to contain discrete spherical particles while the surface of BMnO composite was appeared more dense indicating possible deposition of MnO particles on the surface. Further, the surface of BMnO had a rough morphology which is an important characteristic for adsorption. The presence of MnO onto the bentonite was confirmed by Mn and O peaks in the EDX spectra (not presented).
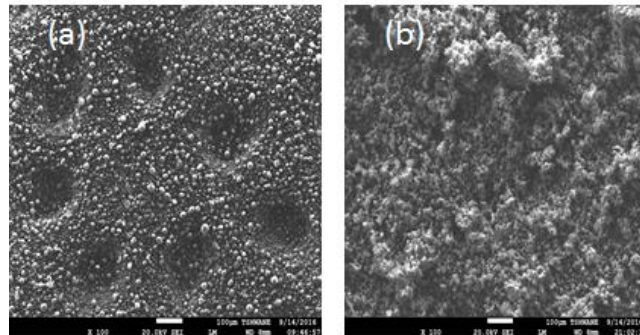

Fig. 1 SEM images of BMnO (a) before and (b) after Mn^{2+} ions adsorption

3.2. The effect of solution pH and removal mechanism

Preliminary experiments showed that the removal efficiency increased with increase in pH. Obviously, this was due to the BMnO surface becoming increasingly negatively charged (deprotonation effects). Literature reports indicate that the charge at the metal (Me) oxide-solution interface occurs as follows:

$$-Me-OH^O + H_2O = -Me-O^- + H_3O^+ \tag{3}$$

$$-Me-OH^O + H_3O = -Me-OH^+ + H_2O \tag{4}$$
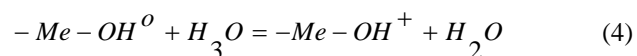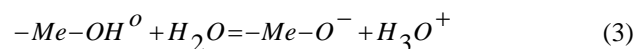
For the purposes of mimicking the characteristics of real neutral mine water, all experiments were conducted at pH 6. At this pH, also, Mn does not precipitate, hence quantification was exclusively based on adsorptions. Further, the removal mechanism of divalent metal ions by MO surface have been reported to take place *via* ion-exchange and adsorption processes. To validate this, final solutions pHs were measured after each experiment. It was found that all final solutions pHs decreased indicating that protons were released into the solutions.

3.3. Effect of sorbent mass

The amount of an adsorbent used in any given adsorption system is an important factor to consider from the economic point of view and the discharge standards compliance. Figure 2 shows the effect of BMnO mass on the removal efficiency of Mn^{2+} ions. The adsorption efficiency was found to increase from 47.35% to 100% when the mass was increased from 0.025 to 0.225 g. The increment corresponded with a decrease

in adsorption capacity from 73.4 to 22.2 mg/g. The increase in removal with the increase in mass was attributed to increased adsorption sites while the decrease in capacity could be explained by the presence of unsaturated adsorption sites.
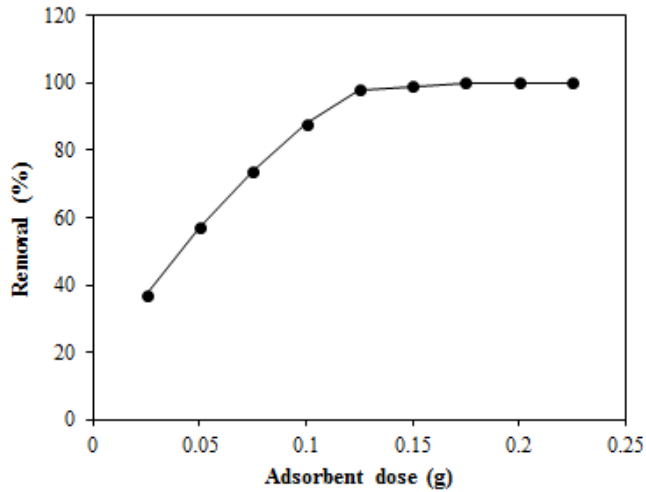

Fig. 2. Effect of adsorbent dose on Mn^{2+} ions removal (pH=6, Vol=50 mL, Temp=298K)

In another set of experiment, results revealed that the removal efficiency decreased with the increase in initial concentration of Mn^{2+} ions. The decline in adsorption efficiency was due to the fact that at lower concentration, there are sufficient adsorption sites available, but at higher concentration, Mn^{2+} ions are greater than the adsorption sites [15].

3.4. Adsorption isotherms and thermodynamic studies

Adsorption isotherms are important in the determination of capacity and selection of a suitable adsorbent. Isotherm models are based on the homogeneity or heterogeneity of the adsorbent's surface. Information on adsorption isotherms is well documented in literature [16]. The experimental data was fitted to Langmuir, Freundlich and Tempkin models. The linear Langmuir isotherm equation is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{k_L Q_m} + \frac{C_e}{Q_m} \tag{5}$$

where k_L and Q_m are the Langmuir constant (L/g) and monolayer capacity (mg/g), respectively.
The Freundlich isotherm model equation is mathematically expressed as:

$$Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

where K_F and n are the Freundlich parameters representing capacity ($L^n mg^{1/n}/g$) and intensity, respectively.
The linearized Tempkin isotherm model is expressed as:

$$Q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \tag{7}$$

where b_T (kJ/mol) is the Tempkin constant related to heat of adsorption, A_T (L/g) is Tempkin isotherm constant, R (8.314 J/mol.K) is the ideal gas constant, and T (K) is the absolute temperature.

Table 1 presents a summary of isotherm parameters, obtained from the respective linear plots, as per Eqs. (5), (6), and (7). Results showed that Langmuir model gave the highest values of linear regression coefficient, ($R^2>0.999$) than Freundlich and Tempkin models. Further, the monolayer capacity, Q_m increased and k_L decreased with increase in temperature. Moreover, the higher values of R^2 suggest that adsorption of Mn^{2+} ions onto BMnO composite is best described by Langmuir model, and occurs by monolayer process.

TABLE I
ISOTHERM PARAMETERS

Isotherm	Parameter	298K	308K	318K
Langmuir	Q_m	60.98	53.76	49.02
	k_L	0.781	0.565	0.358
	R^2	0.998	0.997	0.995
Freundlich	k_F	31.65	27.79	23.81
	n	5.552	6.086	5.949
	R_2	0.961	0.985	0.975
Tempkin	b_T	0.363	0.450	0.482
	A_T	0.144	0.169	0.079
	R^2	0.992	0.997	0.990

3.5. Effect of contact time and dynamic modelling

The effect of contact time on Mn^{2+} ions uptake by BMnO composite is shown in Fig. 3. The uptake was rapid initially, and decreased gradually with time. Notably, higher uptakes were observed with high initial concentration, and the equilibrium time for 50, 100 and 150 mg/L were 30, 40 and 80 min, respectively. The rapid Mn^{2+} ions uptake at the commencement of adsorption was attributed to plenty of vacant sites, and as the system approached equilibrium, the vacant sites diminished due to saturation [17].
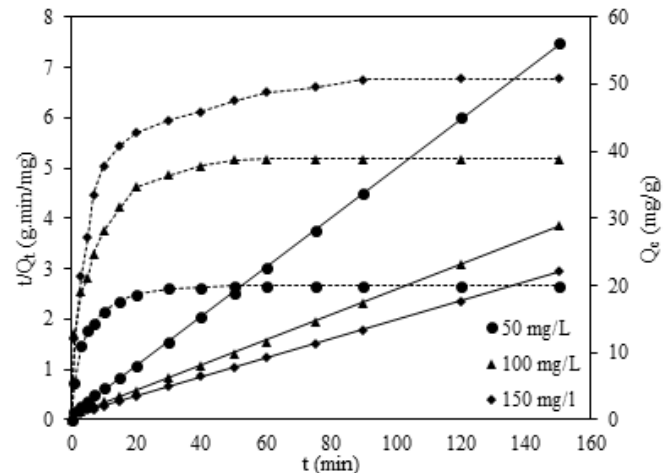

Fig. 3. Effect of contact time and linear kinetic models fits

The experimental data was analyzed using two most

commonly used dynamic models; the pseudo-first order and pseudo-second order models, expressed empirically, by Eqs. (8) and (9), respectively, as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t \qquad (8)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (9)$$

where Q_t (mg/g), k_1 (min^{-1}) and k_2 (g mg^{-1}min^{-1}) are the time depended Mn^{2+} ions uptake, pseudo-first order and pseudo-second order rate constants, respectively. Figure 3 shows a combined plots of kinetic profiles and the linear pseudo-second order kinetic, while Table 2 illustrates all the kinetic parameters of the two models at different Mn^{2+} ions concentration. From Table 2, it was observed that the values of R^2 for pseudo second-order model are close to unity than those of pseudo-first order model. Moreover, the theoretic capacity values for pseudo-second order model are in good agreement with those obtained experimentally. The values of k_2 decreased with increase in Mn^{2+} ions concentration. These results suggest that pseudo-second order model is more applicable and the adsorption of Mn^{2+} ions onto BMnO composite is inclined towards chemisorption [18].

TABLE 2
KINETIC PARAMETERS

Model	Parameter	Concentration (mg/L)		
		50	100	150
Pseudo-first order	Q_e	10.98	30.47	35.31
	k_1	0.093	0.0.103	0.056
	R^2	0.986	0.983	0.957
Pseudo-second order	Q_e	20.40	40.00	52.63
	k_2	0.023	0.008	0.004
	R^2	0.999	0.998	0.999

Experiments with real mine water samples showed that CBMnO was selective towards Mn^{2+} ions, and complete removal could be achieved with 0.5 g of the adsorbent. However, co-ions were partially removed. This implied that an extra treatment unit, for instance, reverse was required to achieve complete removal.

4. CONCLUSIONS

In this study, BMnO composite was prepared, characterized and examined for Mn^{2+} ions adsorption from aqueous solution. SEM characterization showed morphological changes after by MnO particles were precipitated onto bentonite surface. The results obtained from kinetic experiments showed that Mn^{2+} uptake was fast and kinetics followed the pseudo-second order model. The equilibrium capacity depended on process conditions such as mass of adsorbent and initial concentration. The Langmuir isotherm model described the equilibrium data well, and Mn^{2+} ions removal is an endothermic process. The findings of this study suggest that BMnO is an efficient adsorbent of Mn^{2+} ions, and can be applied in the polishing of pre-treated mine water.

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