

Research Article

Oxidative Precipitation of Manganese from Acid Mine Drainage by Potassium Permanganate

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Received 8 May 2013; Accepted 4 October 2013

Academic Editor: Eva Pocurull

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Although oxidative precipitation by potassium permanganate is a widely recognised process for manganese removal, research dealing with highly contaminated acid mine drainage (AMD) has yet to be performed. The present study investigated the efficiency of KMnO_4 in removing manganese from AMD effluents. Samples of AMD that originated from inactive uranium mine in Brazil were chemically characterised and treated by KMnO_4 at pH 3.0, 5.0, and 7.0. Analyses by Raman spectroscopy and geochemical modelling using PHREEQC code were employed to assess solid phases. Results indicated that the manganese was rapidly oxidised by KMnO_4 in a process enhanced at higher pH. The greatest removal, that is, 99%, occurred at pH 7.0, when treated waters presented manganese levels as low as 1.0 mg/L, the limit established by the Brazilian legislation. Birnessite (MnO_2), hausmannite (Mn_3O_4), and manganite (MnOOH) were detected by Raman spectroscopy. These phases were consistently identified by the geochemical model, which also predicted phases containing iron, uranium, manganese, and aluminium during the correction of the pH as well as bixbyite (Mn_2O_3), nsutite (MnO_2), pyrolusite (MnO_2), and fluorite (CaF_2) following the KMnO_4 addition.

1. Introduction

The oxidation of sulphide minerals exposed to oxygen and water produces acid effluents commonly referred to as acid mine drainage (AMD), described in detail elsewhere [1]. Although the generation of acid drainage is a natural phenomenon, mining activities can dramatically increase its production due to the large amounts of material usually exposed. In addition to its main characteristics (e.g., high acidity and sulphate levels), AMD features extensive chemical diversity, including metals such as iron, aluminium, and manganese in elevated concentrations [2]. These effluents are potentially hazardous to the environment. However, technologies available to deal with AMD are either unsuitable or costly [3]. Furthermore, practices are fairly exclusive and varying significantly from one site to another, which characterises several problems in terms of the implementation of available methodologies.

In Brazil, for instance, as a consequence of high contents of manganese in the soil, the concentration of this metal in

AMD can be up to 150 times the limit of 1.0 mg/L recognised by CONAMA Resolution 430 (Brazilian legislation) [4]. However, the majority of studies performed so far have addressed the removal of manganese from waters with low contamination such as drinking water (e.g., [5–8]). The management of AMD with exceptionally high concentration of manganese sets a totally new and challenging scenario within the remediation technologies and research on this topic is still necessary.

Overall, challenges in removing manganese from AMD arise from two main factors. First, the conditions of effluents, that is, pH and Eh, are unfavourable for manganese precipitation; second, AMD effluents are very complex in terms of chemical composition. Currently, the most widely employed treatment consists of active systems using chemical-neutralising agents such as sodium hydroxide and limestone to precipitate manganese [1, 9]. However, the need for high pH condition (i.e., $\text{pH} > 11$) raises expenses due to chemical consumption and yet leads to unsatisfactory treated waters considering the recommended pH range between

5 and 9 (CONAMA Resolution 430) [4]. Furthermore, this process also generates large amounts of bulky sludge, which requires further treatment and appropriate disposal [1, 10].

In this context, oxidative precipitation seems to be a more suitable alternative for removing manganese from AMD [11]. Manganese reacts with an oxidant agent generating a colloidal precipitate, which is then separated by filtration or sedimentation [12]. Several oxidant agents such as air [13], chlorine [14], ozone [15], sulphur dioxide, and oxygen [16] were evaluated in studies that focused mainly on slightly contaminated effluents. In general, potassium permanganate (KMnO_4) stands out with the advantage of removing other contaminants such as iron and organic compounds responsible for taste and odour [17]. Therefore, there is great interest in establishing optimised operating conditions that enable the use of KMnO_4 for remediating highly contaminated AMD.

The assessment of reaction rates as well as solid phases formed during remediation procedures provide valuable information in designing and optimising efficient treatment methods. Van Benschoten et al. [12] published an extensive work on the kinetics of manganese oxidation by KMnO_4 . According to these authors oxidation rates depend on concentrations of oxidant, hydroxyl ions, manganese oxides and free manganese. Other factors such as coprecipitation, adsorption [18], and the autocatalytic effect of precipitates [19] were also reported to affect the removal of manganese and other contaminants, which indicates the importance of investigating the solid phases produced.

Geological models are particularly appropriate to assess solid phases in aqueous systems such as AMD. For instance, the software PHREEQC [20] has proved extremely useful in providing conceptual models focusing on water treatment and environmental remediation technologies [10, 21–23]. Based on ionic associations, the program, amongst other options, allows saturation-index calculations and chemical speciation. PHREEQC employs a solubility approach to identify thermodynamically possible solid phases, which may potentially support the conception and management of efficient treatment systems for AMD.

In this study the oxidative precipitation of manganese by KMnO_4 was investigated with the objective of achieving an effective treatment method for highly contaminated AMD. Experiments were divided into two parts: the first one was performed with MnSO_4 solutions prepared in the laboratory and the second with AMD samples collected in an inactive uranium mine at the Plateau of Poços de Caldas, southeast of Brazil. Processes were conducted at pH 3.0, 5.0, and 7.0. Precipitates were characterised by spectroscopy techniques and electron microprobe. In addition, a geochemical model using the PHREEQC software was developed to predict solid phases possibly formed at each stage of the remediation process.

2. Methodology

2.1. Liquid Samples. Laboratory solutions were prepared by diluting 0.31 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Vetec, Brazil) in 1.0 L of deionized water. Acid mine drainage samples, identified as A1

and A2, were collected in two different water dams located in one former and inactive uranium mine. Effluents were chemically characterised and results are shown in Table 1.

2.2. Bench Experiments. Experiments were carried out in glass beakers with 200 mL of liquid samples. Initially, under stirring and at room temperature ($25^\circ\text{C} \pm 0.5$), the pH was adjusted by adding sodium hydroxide or sulphuric acid. One aliquot was taken to determine the initial concentration of manganese which ranged from 90 to 105 mg/L. Afterwards, KMnO_4 4% (w/v) was added to the solutions based on pre-determined ratios: 1.63 mg KMnO_4 /mg Mn for experiments at pH 3.0 and 1.54 mg KMnO_4 /mg Mn for pH 5.0 and 7.0. Samples were collected at pre-established time and filtered in 0.45 μm membranes. Ratio and reaction time values were determined in a previous study based on statistic factorial design considering four parameters: concentration of the oxidant agent, reaction time, stoichiometry, and pH. Sulphuric acid solution and sodium bisulphite 5% (w/v) were added to the filtrate as quenching agents. Manganese, aluminium, calcium, iron, and zinc, were determined by atomic absorption spectrophotometry (VARIAN, model AA240FS). Uranium was assessed by X-ray fluorescence spectrophotometry (SHIMADZU model EDX-720).

2.3. Solid Samples. Solid samples at pH 7.0 were dried at room temperature and then analysed by Raman Spectroscopy (JOBIN-YVON, LABRAM model HR-800), Scanning Electron Microscope (JEOL JSM, model 840A), and Electron Probe Microanalysis coupled to EDS detector (JEOL JXA, model 8900 RT).

2.4. PHREEQC Modelling. The oxidative precipitation of manganese was modelled using the geochemical program PHREEQC-Version 2 [20]. The consistent thermodynamic database WATEQ4F [24] was used to construct forward models focusing on the assessment of saturation index (SI). The developed speciation-solubility model comprised defined amounts of the KMnO_4 4% (w/v) allowed to react reversibly with aqueous solutions simulating the compositions of MnSO_4 and AMD samples. Based on the conditions of the system, each phase precipitated when $\text{SI} > 0$ was reached or dissolved completely when $\text{SI} < 0$ to achieve the equilibrium, $\text{SI} = 0$. It is worth saying that the condition of equilibrium, $\text{SI} = 0$, does not guarantee that the solid physical state will prevail, but taking into consideration that AMD effluents are highly concentrated, the precipitation is relatively favourable. The simulation was conducted in three steps: (i) simulation of initial KMnO_4 , MnSO_4 and AMD solutions, (ii) addition of potassium permanganate, and (iii) equilibrium between solid phases and generating solution. In addition to the phases identified by Raman spectroscopy, all thermodynamically possible phases were also considered.

3. Results and Discussion

3.1. Oxidation Rates. Data for MnSO_4 solutions prepared in laboratory including different pH values are presented

TABLE 1: Chemical characterization of acid mine drainage solutions.

	A1	A2	Maximum limits for effluents discharge
Mn	102.6	92.3	1.0
Fe	2.8	0.8	15
Zn	3.2	2.8	5
Ni	0.1	0.2	2
Co	0.1	0.02	*
U	9.5	9.5	*
Ca	251.9	142.2	*
Al	194.8	176.2	*
Pb	0.1	<0.05	0.5
F ⁻	65.2	79.4	10
SO ₄ ²⁻	1818	1230	*
TOC	1.5	2.4	*
pH	3.1	3.6	5.0 to 9.0

Concentrations of all components are in mg/L. * CONAMA Resolution 430 has no limits for these components [4].

in Figure 1, where the region of low concentrations was highlighted. Laboratory solutions were firstly employed to evaluate oxidation rates of manganese without the interference of other contaminants. The equilibrium was reached within approximately 20 min of reaction, when manganese was almost completely removed. Comparatively, performances of experiments conducted at pH 5.0 and 7.0 were similar, with manganese contents being practically constant and below 0.1 mg/L after 10 min of reaction. On the other hand, at pH 3.0 the lowest manganese concentration was approximately 0.3 mg/L after 60 min of reaction. Nevertheless, all processes accomplished final concentrations of manganese lower than 1.0 mg/L [4], demonstrating that KMnO_4 doses and pH conditions chosen were appropriate.

As expected, owing to the reduced availability of reactants, oxidation rates initially high in all trials decreased over time. Overall, reactions at pH 5.0 and 7.0 were more efficient compared to pH 3.0. These results are consistent with those given by Van Benschoten et al. [12] reporting a trend of higher oxidation rates as the pH increases. These authors, however, have found significant differences between reactions at pH 5.5 and 7.0, which were not observed herein. Processes involving higher concentrations are more influenced by adsorption phenomenon due to the larger amount of precipitates. Indeed, those authors investigated initial concentrations approximately 100 times lower than those employed in the present study.

Overall, results demonstrated that in the absence of other contaminants there is directly proportional relation between the pH and the efficiency of processes in terms of manganese removal. Under conditions of high redox potential, Mn(IV) is thermodynamically favourable and predominant in aqueous systems containing manganese. As the Eh decreases slightly other compounds such as Mn_2O_3 and Mn_3O_4 can be also formed. However, all these phases might also develop even at lower Eh condition providing that the pH is raised as presented in the Figure 2. Therefore, the improved efficiency, that is, the greater precipitate development observed in higher pH,

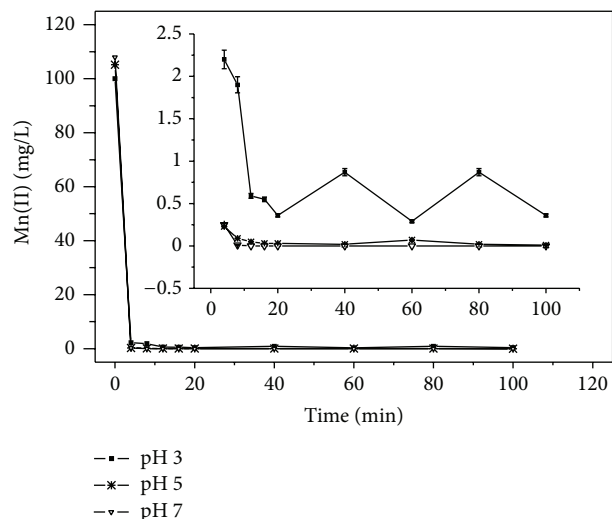


FIGURE 1: Effect of pH on manganese removal from laboratory solutions containing initial Mn(II) concentrations about 100 mg/L. Temperature, $25^\circ\text{C} \pm 0.5$.

levels was expected and consistent with results found in the literature [6–8, 12]. Further investigation, however, is needed to identify chemical mechanisms to explain the dependence of the rate of solid-phase formation on pH of the media.

3.2. Characterization of Acids Effluents. Table 1 presents the chemical composition of both mine waters identified as A1 and A2 as well as the limits for discharge of effluents set by the Brazilian legislation CONAMA Resolution 430 [4]. Manganese, fluoride, and pH were outside the established limits [4]. In addition, although the Brazilian legislation does not indicate any restriction, the levels of calcium, aluminium, and sulphate were particularly high compared to concentrations usually found in natural waters. The elevated concentration of these contaminants might result from the typical oxisol present in the mining region, which is extremely weathered and contains high aluminium, calcium, and fluoride levels. These elements are leached from piles of waste rock and tailings, where the generation of AMD takes place. High sulphate is a typical characteristic of AMD, product of the multistep reaction between the pyrite and the oxygen in aqueous media.

3.3. Oxidative Precipitation with KMnO_4 . Figure 3 shows the variation of manganese contents in the effluents A1 and A2 throughout the oxidative precipitation by KMnO_4 in bench scale. Similarly to the results obtained for the MnSO_4 solutions, not only the reaction rates were higher but also the efficiency improved when the pH increased, offering a thermodynamically more favourable condition for the development of precipitates as previously described (Item 3.1). For instance, at pH 7.0, in the first 4 min of reaction, 99.7% and 98.3% of manganese were removed, respectively, from the effluents A1 and A2. While at pH 3.0, removals were

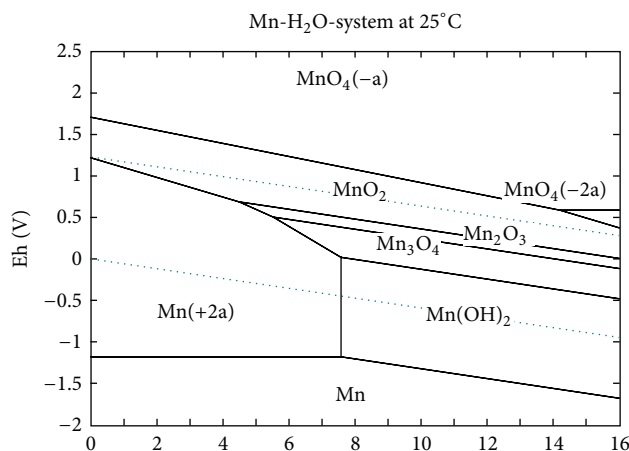


FIGURE 2: Eh-pH diagram showing the predominant manganese forms Mn-H₂O systems. Temperature, 25°C ± 0.5.

85.4% and 96.1%. Based on the established discharge limit of 1.0 mg/L [4], only processes at pH 7.0 were efficient.

Results also evidenced impacts of the presence of other contaminants in AMD on the overall efficiency of the process. In contrast with experiments conducted with MnSO₄ solutions, (Item 3.1), the process was not as much effective when applied for AMD samples. Unexpectedly, removals obtained at pH 5.0 were lower than those obtained at pH 3.0 and 7.0, and significant differences were observed between trials carried out at pH 5.0 and 7.0. Mechanisms by which other elements interfere in the oxidative precipitation by KMnO₄ require further investigation. Higher KMnO₄ consumption is possibly not the major source of the observed differences. Most of the elements were already in oxidised form, with the exception of the iron, originally found in divalent form, Fe²⁺ at very low concentration in the AMD samples studied.

On the other hand, adsorption and coprecipitation were reported on the available literature as essential elements on aqueous systems containing manganese [12, 25, 26]. Therefore, these factors may be also important in the scope of this research. It seems reasonable to suggest that the number of available sites for manganese adsorption decreases in the presence of other elements, since this process is neither preferential, nor particularly selective, towards manganese ions [25].

Adsorption also supports manganese removal in KMnO₄ ratios lower than the stoichiometric ones, considering the MnO₂ formation summarised in (1), that is, 1.92 mg de KMnO₄/mg de Mn II [12, 27]. The amount of KMnO₄ used in the present study represents only 85% of the stoichiometry ratio. Hence, it is inferred that 15% of soluble Mn was removed by adsorption on manganese oxides surface instead of oxidative precipitation [25]. In fact, the adsorption of unoxidised manganese (II) also depends on the pH condition as pointed out by Murray et al. [28].

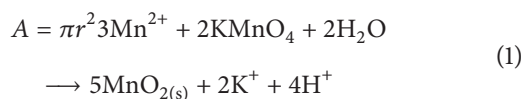


Table 2 presents the concentration of other contaminants aluminium, calcium, fluorine, iron, manganese, zinc, and uranium in the effluents A1 and A2 at each step of the treatment procedure, that is, correction of the pH and oxidative precipitation by KMnO₄. In fact, the oxidation at pH 7.0 had the advantage of being less subjected to the action of other components such as iron, zinc, and uranium, largely removed during the correction of the pH.

3.4. Characterisation of Solid Samples. As experiments conducted at pH 7.0 effectively removed manganese from AMD and MnSO₄ solutions, precipitates produced in these trials were appropriately characterised. Solids were found poorly crystalline and Raman spectroscopy was selected to identify the phases. Figure 4 shows Raman spectra for precipitates (Figures 4(b), 4(c), and 4(d)) and also for a standard synthetic birnessite (Figure 4(a)). Although several points of surfaces were selected, no distinct absorption outlines were detected, indicating homogeneity of samples. By comparing the vibrational modes [29], presented in Figures 4(a) and 4(b) it is reasonable to assume that processes performed with MnSO₄ solution (Figure 4(b)) results mainly in Birnessite (MnO₂). Lovett [27] reported that the transitions of aqueous systems containing manganese to more oxidising conditions, that is, higher pH and Eh, facilitate formation of oxides. Among several possibilities (e.g., hausmannite, manganite, and pyrolusite) birnessite and feitknechtite forms are more likely to be formed. Birnessite was also found during the biological treatment of AMD by Tan et al. [21].

In contrast, significant alterations of intensity and possible overlays were verified for precipitates arising from the treatment of A1 and A2 effluents (Figures 4(c) and 4(d)). In Figure 4(c) lower intensity in 574.0 cm⁻¹ and higher in 654.2 cm⁻¹ possibly indicate hausmannite (Mn₃O₄) [29], while higher intensity around 616.5 cm⁻¹ in Figure 4(d) suggests manganite (MnOOH) [29]. Lower definition and overlays (Figures 4(c) and 4(d)) evidence the impact of the presence of other elements on manganese oxides grid. Distinct structures were also revealed by scanning electron microscopy analysis. Solids formed from effluents (Figures 5(b) and 5(c)) are less porous when compared with precipitates from solution MnSO₄ (Figure 5(a)). The presence of other elements filling the structure of manganese oxides was confirmed in microanalysis by electron microprobe associated with EDS detector. Analyses identified other metals, such as aluminium, calcium, zinc, iron, uranium, and rare earths as well as fluoride and oxygen in solids generated during the treatment of the effluents A1 and A2.

3.5. Modeling with PHREEQC. PHREEQC software and the WATEQ4F database were employed to provide an enhanced understanding of the process, given the extensive chemical complexity of AMD effluents. The geochemical model developed included all thermodynamically possible phases and successfully simulated the treatment process. Evaluations focused exclusively on saturation index (SI) and phases were assumed to be formed when SI ≥ 0 [20].

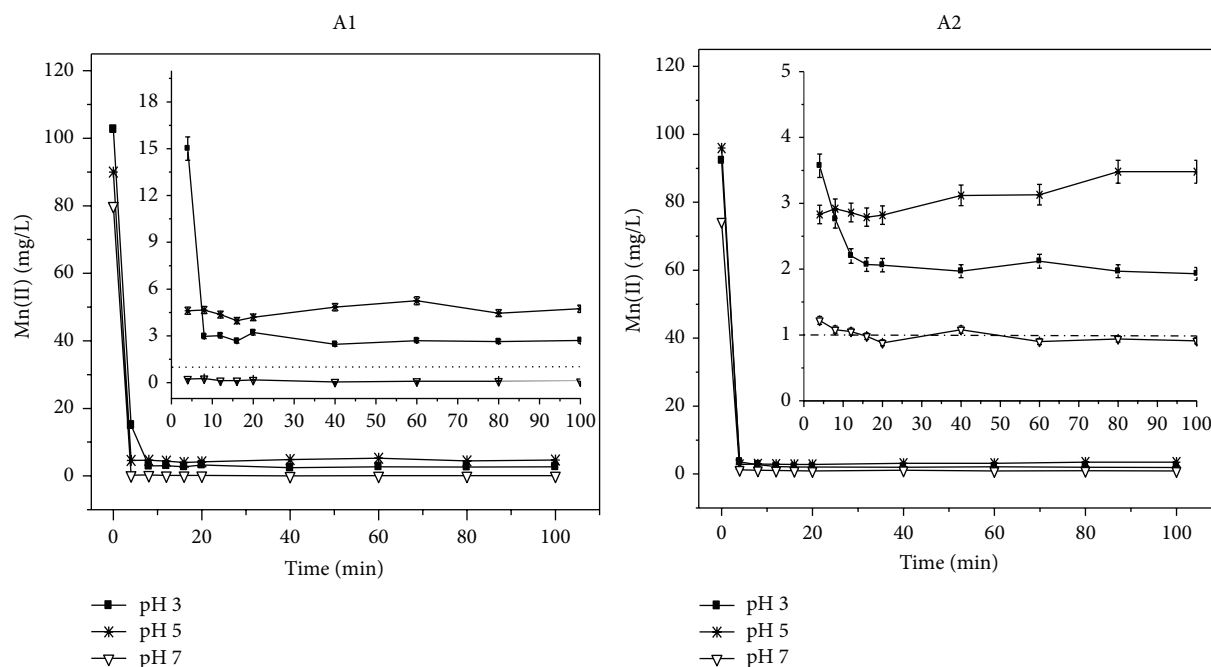


FIGURE 3: Effect of pH on the manganese removal with KMnO_4 from AMD effluents, A1 and A2. Temperature, $25^\circ\text{C} \pm 0.5$. The dotted line represents the limit for manganese discharge (i.e., 1.0 mg/L) set by CONANA Resolution 430 [4].

TABLE 2: Removal percentages of chief components from AMD effluents A1 and A2 over pH adjustment and oxidative precipitation with KMnO_4 .

Stage Effluent	Removals (%) at pH adjustment step*						Removals (%) at oxidative precipitation step*					
	pH	3.0	5.0	7.0	3.0	5.0	3.0	5.0	7.0	3.0	5.0	7.0
Al		1.6	16.8	83.2	6.1	41.9	97.5	10.4	52	83.2	2.3	26.2
Ca		2.4	2.4	9.8	0.9	3.1	19.5	0	12.5	14.4	20.6	17.2
F		65.6	15.3	68.6	61.7	36.4	62.0	0	56.4	8.7	25.7	0
Fe		24.1	24.1	85.5	0	100	100	75.9	55.3	14.5	100	0
Mn		0	12.3	22.3	0	0	19.5	97.4	83.1	77.6	97.9	96.2
Zn		29.3	29.4	29.5	7.1	11.2	69.6	19.8	21.8	70.5	22.4	18.3
U		29.5	24.2	29.5	26.3	21.1	21.1	17.9	23.2	17.9	0	0

* Removals percentages are related to initial concentrations presented in Table 1.

Based on simulations during the correction of the pH possible solid phases formed include $\text{Fe}(\text{OH})_3$, $\text{Fe}_3(\text{OH})_8$, goethite (FeOOH), hematite and maghemite (Fe_2O_3), magnetite (Fe_3O_4), gibbsite ($\text{Al}(\text{OH})_3$), basaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4$), boehmite and diaspore (AlOOH), jurbanite (AlOHSO_4), $\text{UO}_2(\text{OH})_2$ and schoepite ($\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$), hausmannite, manganite, and pyrolusite. Therefore, only iron, uranium, manganese and aluminium would be removed at this stage. Experimentally, however, removal of calcium and zinc was verified, Table 2, whereas removal of both elements was not thermodynamically feasible, and this may be another evidence of adsorption processes.

Addition of KMnO_4 was characterised by large removals of calcium and manganese as birnessite, pyrolusite and nsutite (MnO_2), hausmannite (Mn_3O_4), bixbyite (Mn_2O_3), manganite (MnOOH), and fluorite (CaF_2). The final step

simulated the prolonged contact between formed phases and resultant solution. Subsequent to the equilibrium, manganese was found mainly in oxidation state IV as birnessite, pyrolusite, and nsutite (MnO_2). This result was coherent with those presented by Hem and Lind [30] who studied models to predict the formation of manganese oxides in aqueous systems. According to these authors, in extended contact, the degree of oxidation of manganese increases by the disproportionation of phases, such as manganite and hausmannite.

Overall, it is worth mentioning that speciation-solubility models do not offer temporal and special information; that is, kinetics and distribution parameters were not considered. Therefore, although solid phases were thermodynamically possible, kinetically the development of determined phase might not be favourable. In fact, whether solid phases, for

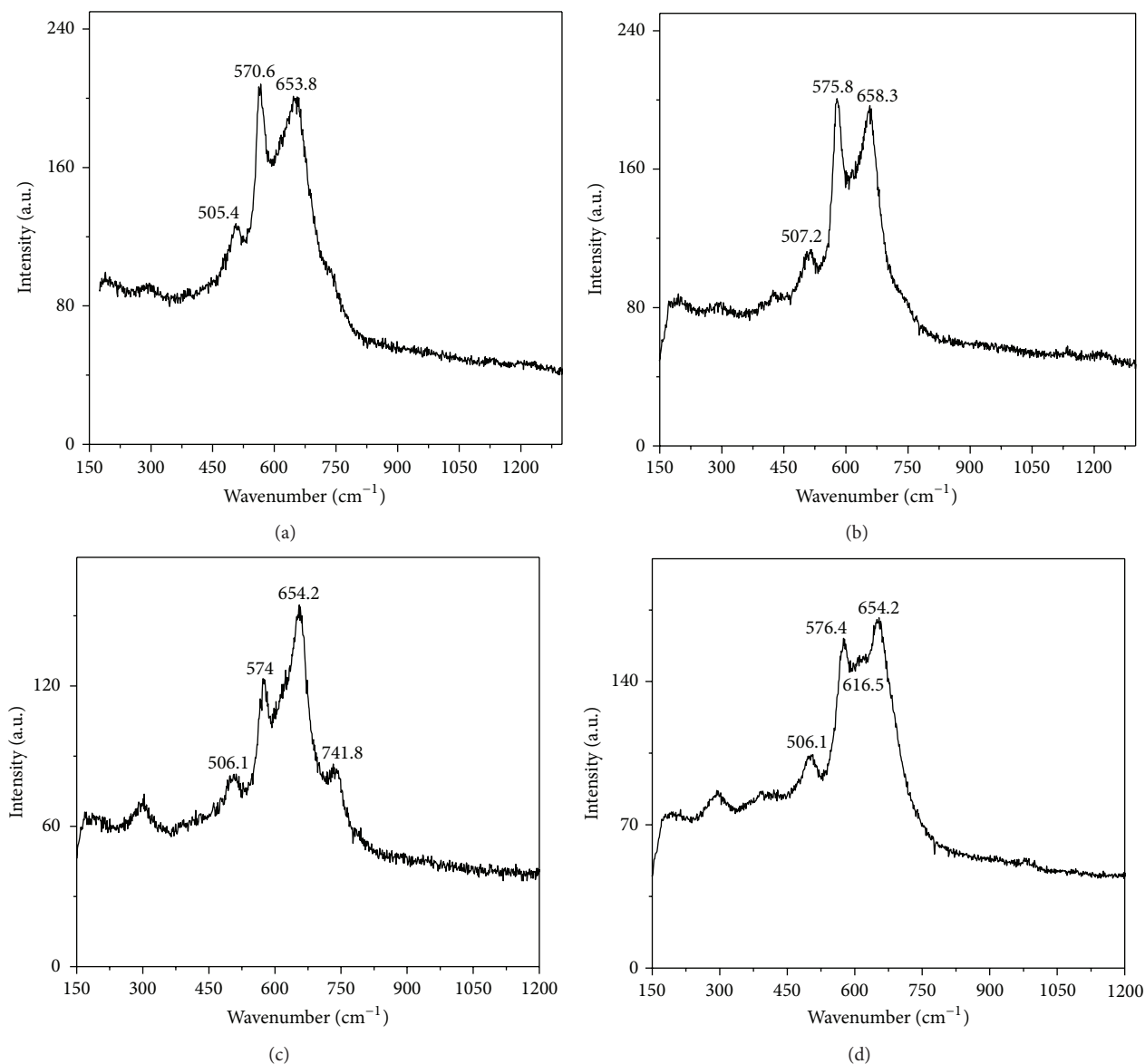


FIGURE 4: Raman spectra (a) standard synthetic birnessite (MnO_2); (b) precipitate from MnSO_4 solution; (c) precipitate from effluent A1; (d) precipitate from effluent A2. Trials at pH 7.0, $25^\circ\text{C} \pm 0.5$, and 1 atm.

instance, goethite, $\text{UO}_2(\text{OH})_2$ and manganite, were actually formed or whether most of metals are incorporated into the manganese oxides phase is difficult to predict.

4. Conclusions

Manganese present in highly contaminated AMD was rapidly and effectively oxidised by KMnO_4 in a process enhanced at higher pH. At pH 7.0, the process removed 99% of manganese initially present, meeting the limit established by Brazilian legislation of 1.0 mg/L, within 20 min of reaction. Results evidenced that adsorption and coprecipitation are important factors in the removal of manganese and other contaminants such calcium and zinc. Consistent with instrumental analyses, the developed geochemical model using PHREEQC code successfully predicted the formation of birnessite (MnO_2),

hausmannite (Mn_3O_4), and manganite (MnOOH) as well as phases containing aluminium, calcium, iron, and uranium in the precipitates. Overall, although experiments were performed in a bench scale, results obtained support the oxidative precipitation by KMnO_4 as a potential treatment for heavily contaminated AMD. However, further investigation remains necessary to clarify chemical mechanisms involved in the control of the oxidation rates of manganese present in highly concentrated solutions as well as the influence of the pH in this process.

Acknowledgments

The authors are grateful to the Brazilian agencies CAPES, Fapemig and CNPq for the financial support.

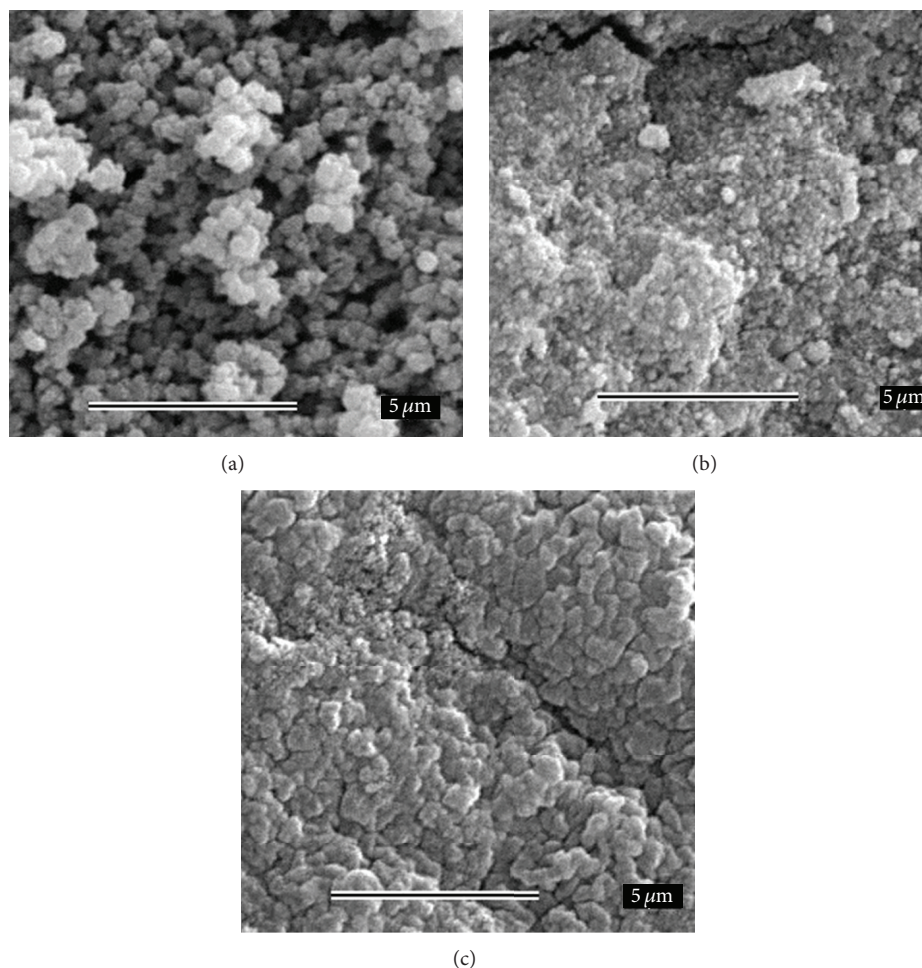


FIGURE 5: Micrographs, 8000X, of precipitates obtained by manganese oxidation by KMnO_4 at pH 7.0: (a) MnSO_4 solution; (b) effluent A1; (c) effluent A2.

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