Magnetized manganese oxide nanocomposite for effective decontamination of Cd(II) from wastewaters
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ABSTRACT
In this study, a composite with magnetic properties has been successfully synthesized by a novel and environmentally friendly route and is applied to Cd(II) adsorption for water decontamination. The quantification of the phases obtained by Rietveld refinement has shown the presence of 84% of Mn$_3$O$_4$ and 16% of Fe$_3$O$_4$. Transmission electron microscopy image shows an aggregate of Mn$_3$O$_4$ nanoparticles without specific orientation and the predominance of octahedral morphology with nanoparticles size estimated around 25–30 nm. The Cd(II) adsorption isotherm is fitted using the Langmuir–Freundlich model. The estimated maximum adsorption capacities of Cd(II) at pH 6 and 7 are similar (0.28 ± 0.02 and 0.31 ± 0.02 mg/m$^2$, respectively). The kinetic results show that the studied system follows the pseudo-second-order model. The Raman results indicate that Cd is being specifically adsorbed by the Mn$_3$O$_4$ in the composite. The hysteresis curve of the composite Mn$_3$O$_4$/Fe$_3$O$_4$ has changed when compared to the pure magnetite; however, the coercive field after the addition of manganese oxide remains unaltered and does not change with a value around 158 Oe. The turbidity tests showed that the magnetic sedimentation was efficient and promising for wastewater treatment in large scale. These materials can be conveniently recovered by magnetic separation, avoiding the filtration steps, which will make easier the solid–liquid separation operation that follows the adsorption process.

Key words | adsorption, cadmium, hausmannite, magnetic nanoadsorbent, manganese oxide

INTRODUCTION
Cadmium is one of the most toxic elements to humans even at low concentrations, especially when ingested or inhaled. It can be deposited and accumulated in various tissues of the body causing serious diseases (Esen et al. 2014). This metal has been used in various industrial activities such as alloy manufacturing, smelting, electroplating, pigments, plastics and batteries (Rao et al. 2011). With the increasing wastewater generation it is essential to study alternatives for water decontamination and to develop new treatment technologies that are economically viable and meet the...

As an efficient and economical alternative for metal ions removal from wastewater, the adsorption process has been investigated intensively for a long time (Venkatesan et al. 2013). The manganese oxide is one of the most effective adsorbents in removing trace metal contaminants, such as lead, cadmium, copper and nickel, from aqueous systems, due to its high adsorption capacity, selectivity and natural abundance (Lisha et al. 2010; Qin et al. 2011). The adsorption capacity of these materials is associated with the microporous structure, surface area and OH functional groups capable of reacting with different chemical species (Calderon Rosas et al. 2010).

In general, the best performance of adsorbents is associated with smaller particles, which possess large specific surface areas. Nanosized sorbents have then been designed and evaluated in view of their superior sorption capacity and reactivity. However, the smaller the particles of the adsorbent, the more difficult their separation from the aqueous solution. Therefore, the challenge of separating high specific surface area powder adsorbents from solution could be addressed with the use of magnetic composites, instead of using granular filters and nanoparticles immobilized on a support, which have reduced surface areas.

Magnetic separation is an effective technique for separating magnetic particles and has been used for several applications in areas such as biochemistry, analytical chemistry, mining and environmental engineering. It has the advantage of being rapid, easily applied in large scale operations and easily automated. Therefore, the challenge of separating high specific surface area powder adsorbents from solution could be addressed with the use of magnetic composites. Magnetic composites can be conveniently recovered by magnetic separation, avoiding the filtration steps, which may represent a barrier to the application of high performance advanced materials in environmental remediation processes and treatment of great volumes of aqueous solutions.

Hausmannite (Mn$_3$O$_4$) is one of the most stable manganese oxides in soils that have been shown to be capable of sorbing large amounts of trace metal ions (Backes et al. 1995; Vázquez-Olmos et al. 2005). A few works have investigated cadmium adsorption capacity by hausmannite (Feng et al. 2007). In a previous work (Silva et al. 2012), we have synthesized Mn$_3$O$_4$ magnetic composites to remove As(III) from solutions and have shown that the magnetic composite presents high affinity for arsenic. Also, Raman and infrared spectroscopy have been used to understand the arsenic complexation by a magnetic Mn$_3$O$_4$ composite (Silva et al. 2013). Mn$_3$O$_4$ magnetic composites combine the oxidative property of Mn$_3$O$_4$ with the magnetic property of ferromagnetic iron oxides, such as magnetite (Fe$_3$O$_4$) and maghemite ($\gamma$-Fe$_2$O$_3$), which will help the solid–liquid separation process that follows the adsorption process.

Given that context, the present work aims to study cadmium adsorption in a magnetic Mn$_3$O$_4$ composite previously developed by a simplified synthesis method (Silva et al. 2012, 2013).

EXPERIMENTAL

All chemicals were of analytical grade and used without further purification. All solutions were prepared with deionized water with a conductivity of 18.2 $\mu$S/cm obtained with a Milli-Q water purification system (Millipore). To remove contaminants that had been potentially adsorbed onto the glass and plastic walls, all vessels and instruments were cleaned by soaking in detergent solution, then in 1.0 mol/L HNO$_3$ solution, and subsequently in deionized water, in each case for at least 24 hours. All parts of the spectroscopic equipment used to extract and fill the sample cells was cleaned and rinsed properly with acetone. The pH electrode (713 pH Meter, Metrohm) was calibrated with three pH buffers (pH 4.0, 7.0, and 10.0).

Preparation and characterization of the Mn$_3$O$_4$ magnetic composite

For the preparation of the composite, the procedure described in Silva et al. (2012, 2013) was followed. Briefly, 1,000 mL of deionized water was placed in contact with 1.0 g of commercial magnetite particles (Sigma-Aldrich, <5 $\mu$m) and 45 mL of 1.0 mol/L MnCl$_2$.4H$_2$O (Sigma-Aldrich) solution at pH 12 (1.0 mol/L KOH Sigma-Aldrich) in a 2,000 mL Pyrex beaker under stirring (mechanical stirrer, Fisatom 713 D) and constant air input (aquarium pump Power 500).

Transmission electron microscopy (TEM) images of the magnetic composite were obtained using a Tecnai-G2-20-PEI 2006 microscope equipped with a silicon-lithium energy dispersive spectroscopy (EDS) detector (EDAX) in the Center of Microscopy at the Universidade Federal de Minas Gerais (UFMG). Samples were prepared by dispersing the powdery material onto a lacy carbon film supported by a Cu grid. Selected area electron diffraction...
(SAED) was used in order to identify the presence of both Mn$_3$O$_4$ and Fe$_3$O$_4$ phases. The SAED pattern was indexed using JEMS software. Measurements of the specific surface area were made by the Brunauer–Emmett–Teller (BET)–Multipoint method using a nitrogen gas sorption analyzer NOVA 1000 Quantachrome. Prior to measurement, the samples were weighed, degassed by placing them into a glass cell under vacuum for at least 24 h at 100 °C, and weighed again. The BET analyzer’s Dewar flask was filled with liquid nitrogen and set into place. Each degassed sample was loaded and the results of the analysis collected. The pH$_{PZC}$ (point of zero charge) of magnetic composite was estimated with potentiometric titration (Bourikas et al. 1996). The acid and base titrations were carried out by taking 0.1 g of the solid sample in 25 mL of distilled water and titrated against the 0.01 mol/L of HCl or NaOH solutions, and the corresponding pH was recorded using a pH meter (HANNA pH 213, microprocessor pH meter, USA). The titration data were further utilized to evaluate the pH$_{PZC}$.

**Adsorption experiments**

The adsorption studies were performed batchwise. The Cd solutions were prepared by dissolving cadmium nitrate (Cd(NO$_3$)$_2$·4H$_2$O, Vetec) in Milli-Q water. The adsorption studies were carried out in 250 mL Pyrex vessels sealed with laboratory parafilm (Pechiney Plastic Packaging, USA). All the results were averaged values of duplicate tests, which are commonly acceptable in adsorption experiments.

The effect of medium pH in Cd adsorption was studied adjusting the initial pH values (3, 4, 5, 6 and 7) with 0.5 mol/L HCl and 1.0 mol/L KOH in the Erlenmeyer flasks, filled with 50 mL of cadmium (20 mg/L) solution and 0.1 g of the adsorbent, before agitation in the thermostatic shaker (New Brunswick Scientific Edison, USA).

In the kinetic studies, suspensions of 0.1 g of adsorbent and 50 mL of cadmium (20 mg/L) solution were stirred for different periods of time (5, 10, 30, 60, 90 and 120 min) at an initial pH of 7. The equilibrium studies were conducted using the same procedure during 24 h at initial pH values of 6 and 7, varying the feed solution concentrations (from 5 mg/L to 60 mg/L). After 24 h, the pH values of the solutions were measured and the solids of each flask were separated by a magnet and the supernatant solution vacuum-filtered through a 0.22 μm membrane filter (Fisher Scientific). Subsequently, the solids were rinsed with Milli-Q water. The filtrate was assayed for cadmium directly by atomic absorption spectroscopy (Perkin-Elmer Analyst 300).

**Spectroscopic and diffraction techniques analyses**

Raman and X-ray diffraction (XRD) analyses were carried out for the solids characterization. Raman spectra were collected on a Horiba Jobin Yvon LABRAM-HR 800 spectrograph, equipped with a 635 nm helium-neon laser, 20 mW of power, attached to an Olympus BHX microscope equipped with 10, 50, and 100X lenses. The collected Raman data were baseline-corrected and curve-fitted to obtain quantitative band parameters, such as peak maxima, widths, intensities and areas, by using the software Peakfit 4.0. The diffractograms were obtained on a Shimadzu 7000 X-ray diffractometer, using a copper anode (Cu Kα1 radiation) and graphite crystal monochromator. Analyses were run by step-scanning from 4º to 90º 2θ, increments of 0.02 2θ and count time of 3 s. The Rietveld refinement was carried out using the GSAS and interface EXPGUI program. The Thompson–Cox–Hastings pseudo-voigt profile function was used and the background was adjusted by polynomial Chebyschev. Scale factor, unit cell, background radiation, profile asymmetry, the full width at half height from the instrumental broadening parameters obtained with a standard, atomic position, isotropic atomic displacements and cations occupational factors were refined. The values for R$_p$, R$_{Bragg}$, R$_{wp}$ and $\chi^2$ and the graphs obtained at every three cycles of refinement, were measured for checking quality of refinement and for a better monitoring of the results.

**Evaluation of magnetic property**

The magnetization measurements were obtained by vibrating sample magnetometer (VSM) method and is based on the change that occurred in the magnetic flux of a coil when in proximity is vibrated a sample, which is under the action of a uniform magnetic field applied. In order to evaluate the velocity of solid–liquid separation turbidity tests were performed to verify the turbidity of the materials in aqueous medium relating to the composite magnetic separation. The composite (1 g) was dispersed in water under stirring for 5 min. Then, a sample was sedimented under the influence of the magnetic field using neodymium magnet and another sample was naturally sedimented by gravity. The digital portable turbidimeter Digimed TU–DM was used for direct readings of turbidity in NTU both dispersions in the interval from 1 to 15 rpm during sedimentation.
RESULTS AND DISCUSSION

Characterization of the composite

Surface measurement of the composite via nitrogen gas absorption yielded a BET surface area of \((44 \pm 9) \text{ m}^2/\text{g}\). The morphology of the magnetic composite with TEM images indicated aggregated, octahedral nanoparticles without a specific orientation (Figure 1(a)). The EDS spectrum was taken around the particle pointed with an arrow in the image. The Mn- and Fe-peaks were identified in the EDS spectrum (Figure 1(b)), probably from Mn\(_3\)O\(_4\) and Fe\(_3\)O\(_4\) particles. The peaks of C and Cu are related to the Cu-grid coated with a carbon film. Figure 1(c) shows the zoom of a large particle pointed by an arrow in Figure 1(a). Figure 1(d) shows the SAED of this particle, which was indexed as a cubic Fe\(_3\)O\(_4\) (space group \(Fd-3m\), \(a = b = c = 8.396 \text{ Å}\)) using JEMS software. The spots inside the gray circles are the reflections of the \([1, 2, 1]\) zone axis pattern of the Mn\(_3\)O\(_4\). The \(d_{\text{hkl}}\) measure in the SAED pattern was: 
\[d_{202} = 0.2988 \pm 0.0052 \text{ nm}, \quad d_{1-11} = 0.4843 \pm 0.0211 \text{ nm}, \quad \text{and} \quad d_{1-13} = 0.2532 \pm 0.0053 \text{ nm}.\]

The synthesis of Mn\(_3\)O\(_4\) in the presence of magnetite is confirmed both by EDS and electron diffraction and by the presence of diffraction peaks corresponding to a cubic structure of Fe\(_3\)O\(_4\). Rietveld refinement of the composite shows the Mn\(_3\)O\(_4\) structure in the tetragonal space group \(I41/amd\), with the following cell parameters: lattice constants, 
\[a = b = 5.7640 \pm 0.0001 \text{ Å}, \quad c = 9.4620 \pm 0.0005 \text{ Å} \quad \text{and cell volume,} \quad V = 314.36 \text{ Å}^3; \quad \text{and the Fe}_3\text{O}_4 \text{ structure in the cubic space group, } Fd\bar{3}m, \quad \text{with the following cell parameters: } \quad a_0 = 8.3910 \pm 0.0003 \text{ Å}, \quad \text{and cell volume, } V = 590.80 \text{ Å}^3 \quad (\text{Figure 2}).\]

The quantification of the phases in the composite obtained by Rietveld refinement has shown the presence of \(83.7 \pm 0.9\%\) of hausmannite and \(16.4 \pm 0.2\%\) of magnetite. The composite sample
presents Mn$_3$O$_4$ crystallite size $d_{XRD}$ of 33 nm, estimated using the Scherrer equation (Equation (1)):

$$d_{XRD} = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$  \hspace{1cm} (1)

where $\theta$ is the Bragg angle, $\beta$ is the expanse of the diffraction line width (integral width), $\lambda$ is the wavelength of the X-ray and $K$ is the Scherrer’s constant which is different depending on the crystal (1.05 is typical). Using these equations, the average crystallite size, $d_{XRD}$, is calculated. The $\beta$ value to be substituted for this equation is the value obtained by correcting the integral width according to the integral width curve using the ‘Jones Correction’ method by which the inherent expansion of the system is corrected. Fe$_3$O$_4$ crystallite size could not be calculated since the Scherrer equation is not proper for particles with diameters in the micrometer scale.

The Figure 3 shows Mn$_3$O$_4$ particles in the composite. Fe$_3$O$_4$ particles were not identified in this TEM image. However, an aggregate of Mn$_3$O$_4$ nanoparticles without specific orientation and the predominance of octahedral morphology were observed. The size of nanoparticles was estimated around 25–30 nm (Figure 3) similar to the value of 33 nm for the Mn$_3$O$_4$ phase in the magnetic composite calculated by XRD.

**Cd adsorption**

**Effect of solution pH**

The effect of solution pH on cadmium removal by the magnetic composite was examined. Due to the dissolution of manganese oxide at pH lower than 3.0 and cadmium precipitation at pH higher than approximately 8.0 (for a range of Cd concentration 20–50 mg/L), the pH range of 3.0–7.0 was selected for this study. The results presented in Figure 4 show that the uptake capacity, $q_e$ (quantity of Cd adsorbed at equilibrium) is linearly increasing with increasing solution pH. Therefore, solution pH is a crucial factor to affect the extent of Cd(II) adsorption onto magnetic composite. The estimated value of the pH$_{PZC}$ (point of zero charge) for the composite was 6.2 (Figure 5) which is consistent with some values described in the literature. Bhushan
et al. (2012) have determined pH$_{PZC}$ values close to 7 for hausmannite. However, Wilk et al. (2005) determined pH$_{PZC}$ values higher than 10 and Backes et al. (1995) found pH$_{PZC}$ values less than 5 for synthesized hausmannite. The differences in the pH$_{PZC}$ values for hausmannite are due to the origin of the samples, materials synthesis, crystallinity, temperature and degree of hydration (Huang & Stumm 1973).

The removal of Cd(II) increased from 35 to 70% as pH increased from 3.0 to 7.0. The variations in adsorbed amount with pH could be explained on the basis of the number of negatively charged sites on the surface of magnetic composite. The pH$_{PZC}$ (point of zero charge) of the composite is 6.2 (Figure 5). When pH increases, more hydrogen ions leave the magnetic composite surface increasing the number of negatively charged sites, which is favorable for cadmium ions adsorption due to electrostatic attraction (Qin et al. 2011). As pH increases, the net positive surface charge decreases and approaches net zero charge, close to pH$_{PZC}$, thus decreasing repulsion of the Cd cations. The uptake of Cd at pH < pH$_{PZC}$ suggests that adsorption is not solely controlled by electrostatic interactions.

**Sorption isotherms**

Cadmium sorption isotherms of the magnetic composite toward two pH values (6 and 7) are illustrated in Figure 6. The sorption isotherms were evaluated using the Langmuir–Freundlich model (Equation (2)),

$$q = \frac{bQ_m C_e^{1/n}}{1 + bC_e^{1/n}}$$  

where $q$ is the quantity of cadmium adsorbed at equilibrium (mg/g), $C_e$ is the equilibrium concentration of cadmium (mg/L), $b$ is the Langmuir adsorption constant (L/mg), $Q_m$ is the maximum adsorption capacity (mg/g) and $1/n$ is the measure of heterogeneity.

The Langmuir–Freundlich model returned the best fitting parameters in comparison to Langmuir and Freundlich models (data not shown). A noteworthy observation is that pH 7 shows a much higher binding affinity to the magnetic composite compared to pH 6, as indicated by the $b$ and $n$ values presented in Figure 6. At pH 7, the magnetic composite surface is slightly more negatively charged than at pH 6, which favors cadmium ions adsorption due to electrostatic attraction in low concentrations. The estimated maximum adsorption capacities of Cd(II) at pH 6 and 7 were similar (0.28 ± 0.02 and 0.31 ± 0.02 mg/m$^2$, respectively). This suggests that cadmium adsorption is not predominantly electrostatic, since the Cd uptake would be expected to be higher at pH 7 if the electrostatic attraction was the main adsorption mechanism.

**Kinetic studies**

The adsorption of Cd(II) on magnetic composite occurs during the first few minutes (Figure 7(a)). The results revealed that the adsorption takes place in two different steps: the first step was found to be rapid (first 10 min), the second one exhibits a subsequent removal until equilibrium is reached (60 min). The equilibrium time was 60 min. The kinetic data (Figure 7(a))

![Figure 5](https://iwaponline.com/wst/article-pdf/74/12/2762/456384/wst074122762.pdf)

**Figure 5** | Experimental curve corresponding to the potentiometric titrations for the determination of the PZC of Mn$_3$O$_4$/Fe$_3$O$_4$ magnetic composite.

![Figure 6](https://iwaponline.com/wst/article-pdf/74/12/2762/456384/wst074122762.pdf)

**Figure 6** | Isotherms for Cd(II) sorption on the Mn$_3$O$_4$ magnetic composite. Experimental conditions: pH 6 and pH 7, 200 rpm, 24 h, (25 ± 0.5) °C.
were linearized and analyzed by pseudo-first-order (Equation (3)) and pseudo-second-order (Equation (4)) models (Barka et al. 2012),

\[ \frac{dq_t}{dt} = K_1(q - q_e) \]  

\[ \frac{dq_t}{dt} = K_2(q - q_e)^2 \]  

where \( K_1 \) and \( K_2 \) (g/(mg min)) are the rate constants of pseudo-first-order and pseudo-second-order adsorption, respectively, \( q_e \) is the amount of substance adsorbed at equilibrium in mg/g and \( q_t \) is the amount of substance adsorbed at time \( t \) in mg/g.

The data could not be fitted by pseudo-first-order model (\( R^2 = 0.7652 \)), but showed a good fitting to the pseudo-second-order model (Figure 7(b)). The calculated \( q \) (6.65 mg/g) obtained in the pseudo-second-order kinetic model agrees with the experimental \( q \) (6.0 mg/g). \( V_0 \) represents initial adsorption rate (mg/(g min)), which is the same as \( K_2 q_e^2 \). The \( V_0 \) obtained value is high (5.72 mg/g min), suggesting a good affinity of the composite for cadmium, which agrees with the equilibrium isotherm results (Chang et al. 2012). The correlation coefficient for the pseudo-second-order kinetic model is close to unity. From these results, it was concluded that the studied system follows the pseudo-second-order model. Pseudo-second-order model is based on the assumption that the adsorption follows second-order chemisorption (Ho & McKay 1998). It is known that metals are specifically adsorbed on manganese oxides (Della Puppa et al. 2013). The kinetic results presented in this study support this assumption.

Characterization of Cd loaded composites

The Raman spectrum of Mn3O4 magnetic composite shows the main bands reported in literature for Mn3O4: a very sharp peak at 658 cm\(^{-1}\) corresponding to the Mn–O breathing vibration of divalent manganese ions in tetrahedral coordination; two smaller peaks located at 320 and 375 cm\(^{-1}\) corresponding to bending modes of Mn3O4; and a weak signal at 480 cm\(^{-1}\) corresponding to asymmetric stretch of \( \text{Mn}–\text{O}–\text{Mn} \) (Figure 8(a)) (Han et al. 2006; Julien et al. 2004). Raman spectra of different regions only showed the characteristic Raman bands of Mn3O4 which indicates that the magnetic particles are not exposed.

Raman spectra were obtained for cadmium adsorbed onto the synthesized Mn3O4 magnetic composite.
sample. As a result of the adsorption process the Raman bands broadened and shifted downwards. The results are compiled in Figure 8(b) and the peak fittings of the spectra are shown in Figure 9. The broadening and shifting of the bands after cadmium adsorption can be attributed to Cd binding to the oxygen of surface –OH groups, which lowers the vibration frequencies (Han et al. 2006; Zuo et al. 1999). The peak fitting results have shown that the sample loaded with Cd exhibits, in its Raman spectrum, a band centering at 339 cm⁻¹, which can be related to Cd-O vibration (Oliva et al. 2016).

The Raman results indicates that Cd is being specifically adsorbed by the Mn₃O₄ in the composite, since its presence in the loaded samples modifies the bands related to hausmannite vibrations and causes the appearance of a band related to Cd-O.

Evaluation of magnetic property

The Figure 10(a) shows the different magnetic behavior of the samples. The pure magnetite (Fe₃O₄) presents a typical magnetic response of a ferromagnetic material with the saturation magnetization around 134 emu/g (Kucheryavy et al. 2013). This value is related to the large size distribution of the magnetite. For the composite Mn₃O₄ Fe₃O₄, the hysteresis curve (Figure 10(b)) has changed and the magnetic signal decreases by one decade of magnitude, with the saturation magnetization close to 13 emu/g. The decreasing occurs by the mass increase of the non-magnetic material, which in our case is the manganese oxide. However, the coercive field after the addition of manganese oxide remains unaltered and does not change with a value around 158 Oe, which means that the

![Figure 9](https://iwaponline.com/wst/article-pdf/74/12/2762/456384/wst074122762.pdf)  
Figure 9 | Raman spectra peak fitting of the (a) non-loaded and (b) Cd-loaded (10 mg/g) synthesized magnetic composites.

![Figure 10](https://iwaponline.com/wst/article-pdf/74/12/2762/456384/wst074122762.pdf)  
Figure 10 | Room temperature magnetization curves of magnetic Mn₃O₄/Fe₃O₄ composite (a) and magnetite (b).
magnetic removal capacity of magnetite does not change after the addition of manganese oxide in the composite.

Table 1 shows the turbidity values of the magnetic composite in water and subjected to natural sedimentation and magnetic sedimentation in an interval of 15 min. The Figure 11 shows the images of the turbidity test in the time from 1 to 15 min. The results indicate that natural sedimentation is slower than the magnetic sedimentation. In the period of 15 min, natural sedimentation shows turbidity values which are approximately doubled. Therefore, the magnetic composite when dispersed in water is presented as fine particles and the natural sedimentation is difficult. Thus, the magnetic sedimentation is a promising alternative for the treatment of effluents, since greater efficiency in separating the composite particles from the aqueous medium was observed.

**CONCLUSIONS**

Characterization results for the composite show that it is formed by aggregated, octahedral Mn₃O₄ and Fe₃O₄ particles. The quantification of the phases in the composite obtained by Rietveld refinement has shown the presence of 84% of Mn₃O₄ and 16% of Fe₃O₄. Raman spectra of different regions only showed the characteristic Raman bands of Mn₃O₄ which indicates that the magnetic particles are not exposed.

The composite was applied to Cd(II) adsorption and the results show that pH 7 presents a much higher binding affinity to the magnetic composite compared to pH 6, as indicated by the b (0.34 L/mg at pH 6 and 0.62 L/mg at pH 7) and n (0.28 at pH 6 and 0.58 at pH 7) values obtained from the adsorption isotherm fitting using the Langmuir–Freundlich model. The estimated maximum adsorption capacities of Cd(II) at pH 6 and 7 are similar (0.28 ± 0.02 and 0.31 ± 0.02 mg/m², respectively), suggesting that cadmium adsorption is not predominantly electrostatic.
However, in low concentrations, the removal is more efficient at pH 7, reaching 98% removal of Cd(II) in solution indicating that the magnetic composite shows potential for use in the removal of trace concentrations in aqueous media.

The studied system follows the pseudo-second-order kinetic model. The $V_0$ obtained value is high (5.72 mg/g min), which suggests a good affinity of the composite for cadmium. The results indicate that cadmium is being adsorbed in a specific way by the manganese oxide in the composite. Therefore, an important contribution of this work is the development a magnetic adsorbent, with high adsorption capacity and fast removal of Cd(II) from wastewater. It is important to note that the magnetic nanocomposite can be reused in the adsorption process to full saturation of the sites. Cadmium has high commercial value because it can be reused as starting material in various industrial activities such as the production of alloys, electrodeposition or metal coatings. The cadmium concentrated in nanoparticles can probably be recovered after specific chemical treatment and reused in industrial applications.

Raman spectra were obtained for cadmium adsorbed onto the synthesized Mn$_3$O$_4$ magnetic composite sample. As a result of the adsorption process, the Raman bands broadened and shifted downwards. Also, a band related to Cd-O appears. The results suggest that Cd is being specifically adsorbed by the Mn$_3$O$_4$ in the composite, binding to the –OH groups present in the surface.

The magnetic properties of this material, as shown in the magnetization hysteresis curve, make it easier to solid–liquid separation operation following the process of adsorption. The turbidity tests showed that the magnetic sedimentation has become a promising alternative. It follows that the magnetic composite Mn$_3$O$_4$/Fe$_3$O$_4$ is promising for large-scale application for the treatment of wastewater due to the efficient separation of the aqueous medium by applying a magnetic field, thereby eliminating the filtration step.

**ACKNOWLEDGEMENTS**

This work was supported by the National Institute of Science and Technology on Mineral Resources, Water and Biodiversity (INCT-Acqua), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Fundação de Amparo à Pesquisa do estado de Minas Gerais (Fapemig). We would like to thank Ms Ilda de Sousa (from the Department of Metallurgical and Materials Engineering – Universidade Federal de Minas Gerais – UFMG) for specific surface area results and Prof. Elisa Maria Baggio Saitovitch (CBPF) for magnetization measurements. The authors would like to acknowledge the Center of Microscopy at the Universidade Federal de Minas Gerais (http://www.microscopia.ufmg.br) for providing the equipment and technical support for experiments involving electron microscopy.

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First received 20 April 2016; accepted in revised form 5 September 2016. Available online 22 September 2016