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Nanomagnetic Polymeric Absorbent Based on Alginate and Gamma-Maghemite Synthesized In Situ for Wastewater Treatment from Metallurgical Industry

Ivana Lourenço de Mello Ferreira,

Rodrigo Ferreira Bittencourt and Clenilson Sousa Júnior

Abstract

A nanomagnetic absorbent based on calcium alginate was produced successfully with the maghemite nanoparticles synthesized in situ, i.e., together with the polysaccharide crosslinking reaction. Physicochemical properties of the absorbent were analyzed and its ability to remove Ni(II) and Mn(II) ions from a real metallurgical industry wastewater was evaluated. Kinetic studies of the adsorption of these heavy metals were realized. To ascertain the most suitable quantity of absorbent to remove Ni(II) and Mn(II) from the wastewater, the absorbent mass was varied and adsorption kinetics was also evaluated. The competitiveness between the metals was evaluated to understand the adsorption mechanism. The samples were characterized by transmission electron microscopy, vibrating sample magnetometry, X-ray diffractometry and Mössbauer spectroscopy. The absorbent prepared, in this work, can be classified as a hydrogel. It presented predominant spherical morphology and micrometric dimension, containing atoms of iron and calcium dispersed uniformly in their internal and external surfaces. The synthesized maghemite nanoparticles presented superparamagnetic behavior. Results showed that the adsorption equilibrium time for both ions was about 60 min. The removal percentages from wastewater were 60.5% for nickel and 56.6% for manganese, using 300 mg of hydrogel. Results revealed that the adsorption mechanism is by ionic change between calcium and heavy metals.

Keywords: Nanomagnetic absorbent, hydrogel, calcium alginate, gamma-maghemite, adsorption mechanism, metallurgical wastewater

1. Introduction

Environmental pollution caused by heavy metals is a serious problem and has been the focus of worldwide concern. The chemical effect of these metals has been of great environmental interest due the fact these metals are not biodegradable, which means they have cumulative effects in organisms, causing serious damage to

health [1, 2]. Among several metals, manganese and nickel are considered highly toxic. Both are contained in wastewater from galvanoplasty as a consequence of the electrodeposition processes and other metallic surface treatments to prevent corrosion [3]. The main harmful effects caused by these metals are cancer, pulmonary lesions and central nervous system damages [4].

There are several methods for the removal of ions from aqueous solutions, such as reverse osmosis, ion exchange, precipitation, electrodialysis and adsorption [5]. Among these methods, adsorption is the most versatile and widely used to remove various pollutants [6]. Methods to remove heavy metals using low-cost adsorbents have been successfully developed, as shown in the literature [7–9].

Natural polymers like alginate (polyanion) are receiving growing attention due to their strong affinity for heavy metal ions. The absorption capacity, specifically of hydrogel in particle form, is comparable to or even better than commercial ion exchange resins. Furthermore, these materials are abundant, biocompatible and environmentally friendly, which make them potential adsorbents for removal of pollutants from wastewater [10].

Accordingly, economically feasible materials that provide efficient removal of these metals from wastewater are being widely studied. The adsorption described in this article is used as a cost-effective way to remove heavy metals, making it competitive with the conventional technology. The proposed adsorbent, consisting of hydrogel based on alginate, a natural anionic polymer, is widely studied to remove heavy metals, since it is nontoxic, inexpensive and highly efficient regarding adsorption [2].

Alginate is a linear copolymer composed of β -D-mannuronic acid (M) and α -L-guluronic acid (G) subunits. It can be used in several fields, like the food, pharmaceutical biomedical industries, for purposes such as drug delivery, sensorial enzyme encapsulation and development of contrast agents for diagnostic imaging. Moreover, alginates have been proven to be outstanding for water purification. Research has also demonstrated that gel beads of calcium alginate can remove heavy metals from wastewater [11].

Nevertheless, the separation of the loaded biomaterials from the medium is often a problem. So, the use of magnetic adsorbents (called here magsorbents) to solve this technical problem has received considerable attention in recent years [12].

Magnetic nanoparticles are embedded in polysaccharides to raise their capacity as biosorbents. Also, they are very useful in the isolation or recovery process of gel beads. Papers have been published describing the removal of heavy metal ions using maghemite and alginate, as magnetic and encapsulating material, respectively [13].

Idris et al. [2] prepared magnetic alginate beads by insertion of nanoparticles of maghemite in chains of sodium alginate, aiming to remove ions of Pb (II) from aqueous solutions. Physicochemical parameters, such as pH, initial metal concentration and contact time were studied. The results revealed that 95.2% of Pb (II) was removed in 2 hours at pH 7, and the maximum adsorption capacity was 50 mg g^{-1} . Furthermore, the presence of magnetic particles in hydrogel beads enabled the easy isolation of the beads after the sorption process. The results showed the potential of using magnetic beads to treat wastewater containing heavy metals.

However, to the best of our knowledge, not studies have been published about the synthesis of hydrogels based on calcium alginate along with γ -maghemite nanoparticles prepared in situ (preparation method in a single step) to remove heavy metals from industrial wastewater. The existing works first synthesize the gamma-maghemite by the co-precipitation process and then add it to the hydrogel (two-step preparation method). Moreover, in our study, the adsorption kinetic in function of hydrogel mass and the competitiveness between the metals (adsorption mechanism) were evaluated.

2. Experimental

All chemicals were bought in analytical purity and were used without further purification. The main chemicals, calcium chloride and ferrous sulfate, were purchased from Vetec. The manganese and nickel solutions (1000 mg L^{-1}) were prepared and used as stock solutions.

Sodium alginate was supplied by Sigma-Aldrich Chemicals Co. The industrial wastewater used in this work was provided by a large metallurgical company, more particularly from the E-coat painting line pretreatment, which is a water-based immersion coating process for application on metal parts.

2.1 Synthesis of nanomagnetic absorbent

The nanomagnetic absorbent were prepared according to the method described in Llanes et al. [14] with some adaptations. It was synthesized an iron oxide-alginate nanocomposites in situ, as follows. A aqueous solution of sodium alginate (50 mL) was added dropwise, at room temperature, to a degassed ferrous sulfate heptahydrate solution (0.3 mol L^{-1}) using a syringe fitted with a needle. The pale-yellow Fe(II)-crosslinked beads were formed immediately. The solution was gently stirred, during the whole addition, and remained under stirring for 45 min. The beads were separated by filtration and washed, several times, with ethanol/water (1/1), to remove the excess ferrous ions. Then an aqueous solution of sodium hydroxide (0.5 mol L^{-1}) was added to the beads, resulting in a change in the color of the beads from light orange to dark green. The suspension was stirred for 30 min. and then heated at $65 \pm 5^\circ\text{C}$ in a water bath. A solution of hydrogen peroxide (10% v/v) was added dropwise. The suspension was stirred at $65 \pm 5^\circ\text{C}$ for 60 min. Nitrogen was bubbled in the suspension before the oxidation stage. The resulting beads were washed with ethanol/water (1/1) and added to an aqueous solution of calcium chloride (0.3 mol L^{-1}) and stirred for 24 h. Finally, the beads were separated, washed some times and placed in a kiln at 40°C for 24 h, to obtain reddish-brown beads.

2.2 Characterization

The content of mannuronate (M) and guluronate (G) units of sodium alginate sample was 62.8% and 37.2%, respectively, calculated by ^{13}C CP-MAS NMR in our previous study [15]. The viscosity average molar mass ($\bar{M}_v$) of sodium alginate was calculated by applying the equation of Mark-Houwink-Sakurada, using $K = 7.3 \times 10^{-5} \text{ dL/g}$ and $a = 0.92$, obtaining a value of $4.7 \times 10^4 \text{ g mol}^{-1}$ [15].

The iron oxide particle size was determined by transmission electron microscopy (TEM) using an FEI Tecnai G2 F20 microscope. The samples were ground in an agate mortar along with methyl alcohol, after which the supernatant was removed from the mortar and diluted in 1 mL of methyl alcohol. The resulting solution was kept in an ultrasound bath for 10 minutes. A drop of the mixture was then deposited on a copper mesh with carbon film. The magnetic properties were analyzed by a vibrating sample magnetometer (VSM) calibrated with a nickel standard cylinder at room temperature (25°C). The total analysis time was 10 minutes and the magnetic field ranged from 2,000 to 12,000 G, and each spot was measured at 1.5 second intervals. The Mössbauer spectrum was obtained at room temperature with constant acceleration with 1024 channels, encompassing a velocity range of -11 to $+11 \text{ mm/s}$ with increments of about 0.045 mm/s per channel. Through the X-ray diffraction (XRD) it was possible to identify the metals present in the hydrogel sample. The samples were macerated with the help of pistil and gral. The diffractograms were obtained in a Shimadzu diffractometer, model XRD

6000, equipped with iron tube and graphite monochromator. The scans were made between 15 and 60° (2θ), with a goniometer speed of 2°/ min.

The morphological properties were analyzed by granulometry using a Retsch AS 200 Basic shaker with analytical sieves of 15 to 50 mesh, optical microscopy (OM) with an Olympus SZX10 microscope, for which the samples were placed on a glass slide subjected to the action of a light beam for observation, and scanning electron microscopy (SEM) with a JOEL JSM-6510LV apparatus, after coating samples with a thin gold layer. For image capture, secondary electron detectors and energy dispersive X-ray analysis (EDX) were used, with acceleration voltage of 20 kV. The metal ion concentration in the aqueous solution and industrial wastewater was determined using a Varian AA240 atomic absorption spectrophotometer (AAS), with samples diluted in order to adjust them to the calibration curve previously obtained for each metal, followed by addition of nitric acid (HNO₃) to prepare the samples for analysis.

2.3 Water uptake (WU) of nanomagnetic absorbent

The WU capacities were determined at room temperature through the Eq. (1).

$$WU = \frac{(W_w - W_d)}{W_d} \cdot 100 \quad (1)$$

W_w is the weight of swelled absorbent in water at equilibrium and W_d is the weight of dried absorbent (average weight of 100 mg). These experiments were performed in triplicate.

2.4 Adsorption experiments

The adsorption experiments were performed for 1 h contact time at room temperature by shaking with a constant weight of the nanomagnetic absorbent (100 mg). The initial concentrations of Mn(II) and Ni(II) in the solutions were varied from 50 mg L⁻¹ and then 100 to 500 mgL⁻¹ at intervals of 100 mgL⁻¹.

Adsorption experiments of the metal ions in the industrial wastewater were performed at 1 hour of contact time at room temperature by shaking with the sample natural pH (pH = 6.5). The absorbent mass ranged from 50 mg and then 100–300 mg in 100 mg intervals.

3. Results and discussion

The swelling of a polymer depends on the degree of interaction between the solvent and polymer molecules. The swelling kinetic is shown in **Figure 1**. The swelling degree at equilibrium was reached in 60 min and its value was 52%.

The size distribution curve of nanomagnetic absorbent (NA) is shown in **Figure 2(a)**. The size of the NAs produced ranged from 500 to 850 μm. The shape of the beads was mostly spherical, according to **Figure 2(b)**.

Figure 3 depicts the SEM images of NAs. In general, the beads were mostly spherical, confirming the results of OM images, and the surfaces were rough, which favors the adsorption of the NAs. The composition maps (**Figure 3**) reveal a homogeneous distribution of calcium and iron elements throughout the polymeric matrix surface. To confirm the presence of both components (calcium and iron)

Figure 1.
Swelling kinetic of nanomagnetic absorbent, in deionized water.

Figure 2.
Size distribution of synthesized NAs (a); optical microscopic image of NAs (b).

Figure 3.
SEM micrograph of NA external surface and composition maps of iron (Fe) and calcium (Ca) (magnification: 100X).

Figure 4.
SEM micrograph of NA internal surface and composition maps of iron (Fe) and calcium (Ca) (magnification: 300X).

Figure 5.
TEM images of maghemite nanoparticles synthesized into the NA (in situ).

inside the microspheres, a cut as made in one of the samples ($[\text{Alg-Na}] = 3\% \text{ m/v}$; $[\text{FeSO}_4] = 0.3 \text{ mol L}^{-1}$; $[\text{CaCl}_2] = 0.3 \text{ mol L}^{-1}$) as shown in **Figure 4**. It can be seen that the microsphere has a massive internal surface containing both components.

The transmission electron microscopic (TEM) images and EDX spectra (**Figure 5**) proved that the magnetic iron oxide particles were dispersed in the NA with nanometric size ($< 20 \text{ nm}$), confirming the formation of a nanocomposite with superparamagnetic behavior.

The VSM curve (**Figure 6**) demonstrates that the NA did not present a hysteresis cycle, a phenomenon that causes a delay between the magnetic flux density and the magnetic field. The saturation magnetization was found to be 9.88 emu/g . The values of coercivity (H_c) and remanence were 17.50 G and 0.30 emu/g , respectively. Besides that, all the samples were sensitive to magnetic stimulus by a magnet (**Figure 6**). A video is shown in Supplementar Material.

Figure 6.
Magnetization curve of NA and digital photograph of the samples responding to the stimulus of a magnet.

The Mössbauer spectrum (**Figure 7a**) showed the dominance of a central doublet and the presence of a low intensity diffuse sextet, typical of superparamagnetic relaxation [16].

The hyperfine parameters indicated the presence of a compound containing Fe^{3+} and maximum magnetic field probability less than 200 kOe. For the doublet, the quadrupole splitting and isomer shift of the sample were 0.70 mm/s and 0.35 mm/s, respectively. These values again indicate the presence of a phase containing Fe^{3+} [17, 18].

The superparamagnetic behavior is caused by the presence of nanometric particles, of the order of 10 nm. According to the XRD diffractogram (**Figure 7b**), the diffuse peaks of the carrier phase of iron indicate the presence of nanosized particles. The phase of iron (III) oxide (maghemite, $\gamma\text{-Fe}_2\text{O}_3$) was identified in the X-ray diffraction patterns by the rays at the approximate positions of $2\theta = 36^\circ$, 45° and 52° .

3.1 Adsorption of metallic ions from industrial wastewater by the NAs

After preparing and characterizing the nanomagnetic absorbent (NA), we investigated their adsorption capacity for removal of metallic ions from wastewater samples from the metallurgical industry.

The untreated wastewater was analyzed by atomic absorption spectrometry to ascertain the concentration of metals. The results are shown in **Table 1**.

Among the metals analyzed, manganese and nickel had the highest concentrations, both derived from surface protective coating by cathodic electrodeposition, in both cases above the thresholds allowed for discharge into the environment [19]. In view of these results, we decided to evaluate the ability of the NA to adsorb these metals (Mn and Ni) to reduce their concentration.

We first performed kinetic studies of the adsorption of these metals present in an aqueous solution prepared in the laboratory to verify the adsorption equilibrium time of each metal contaminant. The results showed that the adsorption

Figure 7.
Mössbauer spectrum (a) and XRD diffractogram (b) of NA.

equilibrium time for both ions was about 60 minutes, as shown in **Figure 8**, where the quantity of each metal adsorbed at equilibrium (Q_e) can also be seen.

From the adsorption kinetic curves of Ni(II) and Mn(II), it can be seen that the nanomagnetic absorbent presented satisfactory removal potential. After 60 minutes, the adsorption capacity (Q_e) of nickel 12.9 mg/g of NA, which corresponds to removal potential of 52%, while for manganese it was 12.3 mg/g of NA, corresponding to removal potential of 49%.

The fact that the adsorption capacity was much more pronounced in the first 30 minutes can be explained by the adsorption mechanism, which occurs in three steps [20, 21]:

1. Transfer of external mass of molecules of the solute, from the body of the solution, to the surface of the adsorbent particles (transport of the adsorbate to the outside surface of the adsorbent);
2. Diffusion to the adsorption sites inside the particles' structure;

Metal	Concentration (mg L ⁻¹)
Al	0.20
Cd	0.06
Ca	5.46
Pb	0.07
Cu	0.06
Cr	0.00
Fe	1.38
Mna	26.88
Nia	17.02
Zn	1.50

^aLimits for discharge set by Brazil's National Environmental Council [19]: Ni = 2 mg L⁻¹; Mn = 1 mg L⁻¹.

Table 1.
Concentration of the metals presented in the industrial wastewater sample.

Figure 8.
Adsorption capacity (Q_e) and removal percentage (%) of ions from aqueous solutions by NAs in function of time: (a) $[Ni^{2+}]_{onset} = 50\text{ mg L}^{-1}$; $V = 50\text{ mL}$; $m = 100\text{ mg}$ e (b) $[Mn^{2+}]_{onset} = 50\text{ mg L}^{-1}$; $V = 50\text{ mL}$; $mMHB = 100\text{ mg}$ ($pH = 6.5$).

a)

b)

Figure 9.

Effect of NA mass on adsorption of Ni(II) (a) and Mn(II) from industrial wastewater (b) [experimental condition: pH = 6.5 and V = 50 mL].

3. Immeasurably fast step, when the adsorption itself takes place (adsorption of the adsorbate on the internal surface of the adsorbent particles). The third step does not offer any resistance to the process, so that the mass transfer and intra-particle diffusion are the steps that determine the adsorption speed.

The maximum adsorption equilibrium times observed for the two metals in question were short (60 minutes), indicating rapid reaction between the adsorbent material and the metallic ions in solution. This means the NA prepared in this study has good potential for application on industrial scale.

Two experiments were performed with the industrial wastewater, one to analyze the kinetics in function of the NA mass and the other to assess the adsorption mechanism of these ions. The intention of applying the NA for commercial treatment of wastewater is to remove metallic ions without the need to adjust the pH. Therefore, all the experiments were performed at the natural pH of the sample, 6.5.

3.2 Analysis of the adsorption kinetics in function of NA mass (for treatment of wastewater)

To ascertain the most suitable quantity of nanomagnetic absorbent to remove Ni²⁺ and Mn²⁺ from the industrial wastewater, we performed studies in which the

NA mass was varied (**Figure 9**). The results showed that 300 mg of NAs removed 60.5% and 56.6% of Ni (II) and Mn (II), respectively. Also, the higher the NA mass, the greater the removal percentages of Ni (II) and Mn (II) were. That was expected, considering that with the increase of NA mass, the availability of binding sites with metals also increases.

3.3 Competitiveness between the metals: adsorption mechanism

We performed analysis by atomic absorption spectrometry of calcium, iron, nickel and manganese ions after application of the hydrogel in the wastewater sample, for the purpose of determining the interaction between these ions and the alginate (**Figure 10**). Both nickel and manganese were adsorbed by the hydrogel (concentrations in the wastewater diminished) while calcium was desorbed by

Figure 10. Concentration of Ni²⁺ (a), Mn²⁺ (b), Ca²⁺ and Fe²⁺ ions in the wastewater as a function of contact time with the nanomagnetic absorbent (experimental conditions: mNA = 300 mg; pH = 6.5 and V = 50 mL).

the hydrogel (concentration in the medium increased). This indicates the occurrence of ionic exchange of Ni^{2+} and Mn^{2+} with Ca^{2+} . The iron concentration remained unchanged, proving no loss of magnetic material occurred from the hydrogel.

4. Conclusion

Nanomagnetic absorbent (NA) based on calcium alginate along with gamma-maghemite nanoparticles were synthesized in situ and applied for the removal of metals present in industrial wastewater. The NA presented, predominantly, spherical morphology, with homogeneous distribution of the elements iron and calcium, both on the internal and external surfaces of the NA particles, and responded to the stimulus of a magnet. The XRD diffractogram demonstrated that the synthesized magnetic material was maghemite. The transmission electron microscopic images proved that the maghemite particles had diameters smaller than 20 nm. The NAs were good adsorbents of the metals from the wastewater. The adsorption equilibrium was achieved in 1 hour at pH of 6.5. By using 300 mg of NA, it was possible to remove simultaneously 60.5% of Ni (II) and 56.6% of Mn (II). Based on the results, we can propose that the adsorption mechanism of the metals occurred by exchange of Ca^{2+} ions (crosslinker) with Ni^{2+} and Mn^{2+} ions present in the wastewater.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author details

Ivana Lourenço de Mello Ferreira^{1*}, Rodrigo Ferreira Bittencourt¹
and Clenilson Sousa Júnior²

¹ State University of Rio de Janeiro, Rio de Janeiro, Brasil

² Federal Institute of Education, Science and Technology of Rio de Janeiro,
Rio de Janeiro, Brazil

*Address all correspondence to: ivanalmellof@gmail.com

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References

- [1] C. Liu, R. Bai, L. Hong, Diethylenetriamine-grafted poly(glycidyl methacrylate) adsorbent for effective copper ion adsorption *Journal of Colloid and Interface Science*, 303, 99-108 (2006). DOI: 10.1016/j.jcis.2006.07.057
- [2] Idris, A.; Ismail, N. S. M.; Hassan, N.; Misran, E.; Ngomsik, A. Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb(II) removal in aqueous solution. *Journal of Industrial and Engineering Chemistry*, 18, 1582-1589 (2012). DOI: 10.1016/j.jiec.2012.02.018
- [3] V. M. Nurchi, I. Villaescusa, Agricultural biomasses as sorbents of some trace metals *Coordination Chemistry Reviews.*, 252, 1178-1188 (2008). DOI: 10.1016/j.ccr.2007.09.023
- [4] Bhattacharyya K. G., Gupta S. S., Removal of Hazardous Metals from Water by Clays, in: *Hazardous Materials and Wastewater: Treatment, Removal and Analysis*, 79-125 (2007).
- [5] L. V. A. Gurgel, R. P. Freitas, L. F. Gil, Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride. *Carbohydrate Polymers*, 74, 922-929 (2008). DOI: 10.1016/j.carbpol.2008.05.023
- [6] Gupta, V.; Ali, I. Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste. *Journal of Colloid and Interface Science*, 271, 321-328 (2004). DOI: 10.1016/j.jcis.2003.11.007
- [7] M. Arami, N. Y. Limaee, N.M. Mahmoodi, N.S. Tabrizi, Removal of dyes from colored textile wastewater by orange peel adsorbent: Equilibrium and kinetic studies *Journal of Colloid and Interface Science.*, 288, 371-376 (2005). DOI: 10.1016/j.jcis.2005.03.020
- [8] Paulino, A. T., Guilherme, M. R., Reis, A. V., Campese, G. M., Muniz, E. C., Nozaki, J. Removal of methylene blue dye from an aqueous media using superabsorbent hydrogel supported on modified polysaccharide. *Journal of Colloid and Interface Science*, 301, 55-62 (2006). DOI: 10.1016/j.jcis.2006.04.036
- [9] V. K. Gupta, A. Mittal, V. Gajbe, Adsorption and desorption studies of a water soluble dye, Quinoline Yellow, using waste materials *Journal of Colloid and Interface Science.*, 284, 89-98 (2005). DOI: 10.1016/j.jcis.2004.09.055
- [10] Yu, K.; Ho, J.; Mccandlish, E.; Buckley, B.; Patel, R.; Li, Z.; Shapley, N. C. Copper ion adsorption by chitosan nanoparticles and alginate microparticles for water purification applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 425, 31-41 (2013). DOI: 10.1016/j.colsurfa.2012.12.043
- [11] Wu, D.; Zhang, L.; Wang, L.; Zhu, B.; Fan, L. Adsorption of lanthanum by magnetic alginate-chitosan gel beads. *Journal Chemical Technology and Biotechnology*, 86, 345-352 (2001). DOI: 10.1002/jctb.2522
- [12] Bee, A.; Talbot, D.; Abramson, S.; Dupuis, V. Magnetic alginate beads for Pb(II) ions removal from wastewater. *Journal of Colloid and Interface Science*, 362, 486-492 (2011). DOI: 10.1016/j.jcis.2011.06.036
- [13] S. F. Lim, Y. M. Zheng, S. W. Zou, J. P. Chen, Removal of copper by calcium alginate encapsulated magnetic sorbent. *Chemical Engineering Journal*, 152, 509-513 (2009). DOI: 10.1016/j.cej.2009.05.029

- [14] Llanes, F.; Ryan, D. H.; Marchessault, R. H. Magnetic nanostructured composites using alginates of different M/G ratios as polymeric matrix. *International Journal of Biological Macromolecules.*, 27, 35-40 (2000). DOI: 10.1016/S0141-8130(99)00115-4
- [15] M. P. M. da Costa, M. C. Delpech, I. L. M. Ferreira, M. T. de M. Cruz, J. A. Castanharo, M. D. Cruz, Evaluation of single-point equations to determine intrinsic viscosity of sodium alginate and chitosan with high deacetylation degree *Polymer Testing*, 63, 427-433 (2017). DOI: 10.1016/j.polymertesting.2017.09.003
- [16] G. M. Costa, E. Grave, R. E. Vandenberghe, Mössbauer studies of magnetite and Al-substituted maghemites *Hyperfine Interactions*, 117, 207-24 (1998). DOI: 10.1023/A:1012691209853
- [17] G.M. Costa, C.B. Andujar, E. Grave, Q.A. Pankhurst, Magnetic Nanoparticles for in Vivo Use: A Critical Assessment of Their Composition. *Journal of Physical Chemistry B*, 118, 11738-11746 (2014). DOI: 10.1021/jp5055765
- [18] Vanderberghe, R.E.; Barrero, C.A.; Da Costa, G.M.; Van San, E.; De Grave, E. Mössbauer Characterization of Iron Oxides and (Oxy) hydroxides: the Present State of the Art. *Hyperfine Interactions* 126, 247-259 (2000). DOI: 10.1023/A:1012603603203
- [19] CONAMA Resolution, N° 430, 2011. Accessed on 11/22/2019. Available at: <http://www.mma.gov.br/port/conama/res/res11/res43011.pdf>.
- [20] K. C. Justi, M. C. M. Laranjeira, A. Neves, A. S. Mangrich, V. T. Fávere, Chitosan functionalized with 2[-bis-(pyridylmethyl) aminomethyl]4-methyl-6-formyl-phenol: equilibrium and kinetics of copper (II) adsorption. *Polymer*, 45, 6285-6290 (2004). DOI: 10.1016/j.polymer.2004.07.009
- [21] K. C. Justi, V. T. Fávere, M. C.M. Laranjeira, A. Neves, R. A. Peralta, Kinetics and equilibrium adsorption of Cu(II), Cd(II), and Ni(II) ions by chitosan functionalized with 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formylphenol *Journal of Colloid and Interface Science.*, 291, 369-374 (2005). DOI: 10.1016/j.jcis.2005.05.017