

“Removal of heavy metals from wastewater using magnetic nanocomposites: Analysis of  
the experimental conditions”

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## **Abstract**

This contribution provides insight on the elimination of heavy metals from water resources using magnetic separation. Nanocomposites based on magnetite and chitosan were prepared. An exhaustive characterization of the magnetic adsorbents was developed. Adsorption assays were performed in batch using Cu, Zn, Cd and Cr as model heavy metals. The efficiency of magnetic adsorbents followed the order: Cu > Cd > Zn > Cr, with maximum values of 188, 159, 72 and 46 mg of Me/g of nanocomposite, respectively. Kinetics and mechanistic issues were studied. The magnetic materials were efficient for five to eight cycles using Cu(II), Cd(II) and Cr(VI) .

**Keywords:** magnetic separation, nanoadsorbents, chitosan, heavy metals, iron oxides, nanocomposites.

## **1. Introduction**

Heavy metals pollution has become a central research area among the last decades because of the grown of the industrial activities. Unlike some organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms causing harmful effects [1]. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium [2]. Many remediation technologies have been applied all over the world to deal with the contaminated aquifers [3]. It is worth mentioning filtration, centrifugation, precipitation, coagulation, oxidation, solvent extraction, ion exchange, adsorption, among others. In particular, adsorption is one of the preferred because of its simplicity, operability and versatility. A wide range of materials may be used as adsorbent, depending on the contaminant or even the environmental conditions.

Between the adsorption techniques, those involving magnetic nanotechnology have been extensively studied during the last decades [1,4-8]. Their interest is given by the combination of both magnetism and nanosize properties. Extremely small size, high surface area/volume ratio and the absence of internal diffusion resistance provide better kinetics for adsorption of metal ions from aqueous solutions. Magnetic properties allow an easy recovering of the adsorbents after use by means of an external magnetic field, thus improving the possibilities of reuse [9, 10].

In this context, chitosan is recognized by its excellent adsorption behavior toward metal ions, mainly due to the presence of a large number of primary amino and hydroxyl groups [11, 12]. Hence, this biopolymer is especially attractive to the preparation of magnetic (nano, micro and macro) adsorbents, with improved properties to water purification

operations [13,14]. Huang *et al.* [8] prepared and characterized cross-linked magnetic chitosan composites by coating the biopolymer with magnetic fluid, using epichlorohydrin as the cross-linking agent. Meanwhile, Chen Yuwei *et al.* used the same methodology to prepare magnetic chitosan nanoparticles. In this case, the maximum Cu(II) sorption capacity was about 35.5 mg/g. The authors also evaluated the regeneration of magnetic materials and reported that more than 90% of adsorbed Cu(II) could be released from the magnetic support, using EDTA as eluent [15]. Podzus *et al.* [16] also prepared magnetic chitosan crosslinked microspheres for the application in copper ions removal. They informed the adsorption ability of about 19.4 mg Cu/g chitosan-magnetite microspheres.

In this work, magnetic adsorbents based on magnetite and chitosan were prepared through direct co-precipitation of the iron oxide on polymeric moieties. The goal was to design efficient adsorbents to wastewater remediation, and correlate their physicochemical properties with the adsorption capability. Cu, Zn, Cd and Cr were selected as model contaminants due to their toxicity. Different variables, such as pH, initial concentration of heavy metal ion, and effect of contact time, inherent to adsorption process were examined. Mechanisms of adsorption were proposed as well as kinetic models for each metal. Lastly, the potential of reuse was explored performing several cycles of adsorption-purification-adsorption.

Although the articles in open literature referring to the use of magnetite and chitosan as adsorbents of contaminants in aqueous effluents are abundant [1,7,15,17-23], it is necessary to distinguish between different kinds of materials. In this sense, it is possible find: I) nanoparticles (mainly magnetite coated CS); II) microparticles MAG/CS, III) hybrid magnetic materials based on CS/MAG and other polymer/inorganic oxide/carbon based

substrate and IV) magnetic gels. Each kind of material exhibits different properties in terms of their adsorption behavior and involves diverse preparative methodologies including multiple additives and experimental variables [9]. In this context, the variation of apparently minor details (in synthetic pathways) may derive in fully different materials. In the particular case of this work, it is possible to assure that novel insight is provided in terms of the selected system adsorbent/heavy metals as well as the adsorption experimental variables that were focused on. It is also worth noting that easily prepared, low cost and versatile magnetic materials were here designed and that no extra additives (such as coupling agents, elutant, etc.) were employed ,all along the preparation and adsorption procedures, as a difference of most of the existent reports in open literature [5,24,26]. Furthermore, the analysis of the mechanisms of contaminant /adsorbent interactions was included as a way to increase the efficiency of these materials in the wastewater remediation.

## **2. Materials and Methods**

Chitosan (CS), commercialized as Chitoclear, was provided by Primex (Iceland). Magnetite (MAG,  $\text{Fe}_3\text{O}_4$ ) was synthesized in our laboratory following the procedure reported elsewhere [27]. Analytical grade solvents provided by Dorwill were used in all the procedures.

### *2.1 Synthesis of the magnetic nanocomposites*

The magnetic nanocomposites were synthesized by an adaptation of co-precipitation method earlier reported [28]. In brief, 1.627 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.8945 g  $\text{FeSO}_4$  were dissolved in distilled water with the proper amount (0.5 or 1 g) of CS scaffolds. The

suspension was stirred at 70 °C during 30 min under N<sub>2</sub> bubbling. Then, 25 cm<sup>3</sup> of 5 M NaOH were added to obtain the magnetic nanocomposites. The solid was washed several times with bi-distilled water, dried at 45 °C and gently crushed. Magnetic nanocomposites prepared from 1/0.5 and 0.5/1 Mag/CS nominal mass ratios were obtained from this procedure.

## *2.2 Characterization techniques*

The magnetic materials were characterized by FTIR spectroscopy to corroborate the presence of polymeric and magnetic moieties. A FTIR (DRIFTS) Thermo Scientific Nicolet 6700 spectrometer was used for recording spectra in the range 4000-400 cm<sup>-1</sup>.

X-ray diffraction (XRD) analyses were performed to confirm the crystalline patterns of magnetite in the nanocomposites. The assays were recorded by a PHILIPS PW1710 diffraction spectrometer with anode of Cu and curve graphite monochromator.

Composition was determined using inductively coupled plasma spectrometer (ICP-AES) Shimadzu 9000 Simultaneous High Resolution according to EPA 200.7 standard. Preparation of samples was performed by treating 1 mg of the magnetic nanocomposite with 10 cm<sup>3</sup> of 12 M HCl.

The morphology was observed by transmission electron microscopy using a microscopy JEOL 100 CX II, JEOL, TOKIO, Japan (1983).

Malvern Zetasizer was employed to measure the Z potential ( $\xi$ ) and the average hydrodynamic diameter of particles by dynamic light scattering (DLS). Dispersions of the magnetic nanocomposites, magnetite and the pure polymer were prepared using a mixture of ethanol: bi-distilled water (1:1, pH 7.6–8.0), followed by 30 min ultrasonication.

The  $\xi$  of raw materials and magnetic nanocomposites was measured in the range of pH 3.0-9.0. For this, 5 mg of solid was added into 100 cm<sup>3</sup> of a 10<sup>-2</sup> M KNO<sub>3</sub> solution, obtaining a solid/solution ratio of 20. The pH was adjusted in a range between 3 and 9 by adding 0.1 M KOH or HNO<sub>3</sub>. The IEP value or pH<sub>PZC</sub> (pH at point of zero charge) is defined here as the pH value where  $\zeta$  is equal to zero. The electrophoresis cell was washed and rinsed three times with deionized water and with the sample solution before measurements to avoid cross-contamination.

Magnetic properties were determined with a commercial vibrating sample magnetometer (VSM) at room temperature with a magnetic field in the -10 kOe to 10 kOe range.

### 2.3 Adsorption assays

Adsorption of heavy metal ions on Mag/CS nanocomposites and raw materials were performed in batch. In a typical experience, 30 or 50 mg of nanocomposite was kept in contact with 30-50 mL of metal solution; the resulting suspension was magnetically stirred for 6 h at 30 °C. After adsorption, the solution was decanted under magnetic field. Then, aliquots of 1 mL were withdrawn to measure the concentration of unadsorbed metal ion by atomic absorption spectroscopy using a GBC Avanta 932. The adsorbed amount was calculated as follows:

$$q(t) = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where  $C_0$  and  $C_t$  (mg) are the initial amount of metal ion and the amount of metal ion unadsorbed in the solution, respectively;  $V$  is the volume of the Me(II) ion solution and  $m$  is the mass of magnetic nanocomposite.

### 2.3.1 Effect of pH

The effect of pH on the cadmium adsorption (chosen as model heavy metal in this case) was investigated in the range 3.0-7.0. The pH of the heavy metal solution was adjusted using 1 M HCl or NaOH.

### 2.3.2 Effect of initial concentration

The effect of the initial concentration of the metal ion on the uptake by Mag/CS was carried out by placing 50 mg of magnetic adsorbent in a series of flasks containing 50 mL of Cd(II) solution with concentrations in the range of 30-200 mg L<sup>-1</sup> at pH 7. The selected range of initial concentration of metal ion was based on data on the literature. The suspensions were equilibrated on magnetic stirred at 30 °C for 6 h.

### 2.3.3 Effect of contact time

The effect of contact time was evaluated using all the heavy metals solutions. The pH fixed in each assay was chosen based on the species present in the medium, as found in the literature depending on the heavy metal [29].

Experimental data was fitted with pseudo-first order and pseudo-second order kinetic models in order to predict the adsorption kinetics. The pseudo-first order equation was represented by:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (2)$$

where  $k_1$  is the pseudo-first order rate constant (min<sup>-1</sup>) of adsorption and  $q_e$  and  $q_t$  are the amounts of metal ion adsorbed at equilibrium and time  $t$  (min), respectively. The value of  $1/q_t$  was calculated from experimental results and plotted against  $1/t$  (min<sup>-1</sup>).

The linear form of pseudo-second order equation can be written as:



$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}} + \left(\frac{1}{q_e}\right)t \quad (3)$$

where  $k_2$  is the pseudo-second order rate constant of adsorption ( $\text{g/mg}^{-1} \text{min}^{-1}$ ).

#### 2.3.4 Regeneration studies

The reuse of the adsorbents was investigated using chromium, cadmium and copper ions as models. The adsorbent (30 mg) was contacted with the 100 mL metal solution. The adsorption was allowed under the conditions of pH and time detailed in sections 2.3 and 2.2.3. This procedure was repeated for four to eight cycles depending of the metal. After each cycle desorption or purification assays were performed by incubating the magnetic nanocomposites (30 mg) in 100 mL of distilled water under magnetic stirring during 10 min. The solid was decanted by means of a magnet. The supernatant was removed and analyzed for measure Me concentration. This procedure was repeated for three times by each cycle, measuring the desorbed metal in the washing water.

### 3. Results and discussion

#### 3.1-Characterization of magnetic nanocomposites

Figure 1-a shows the FTIR-DRIFTS spectra of chitosan and magnetite/chitosan nanocomposites. In the polymer spectrum, a band at  $3400 \text{ cm}^{-1}$  attributable mainly to  $-\text{OH}$  stretching vibration ( $\nu\text{OH}$ ) was observed, whereas signals corresponding to  $\nu\text{N-H}$  and  $\nu\text{COC}$  appeared at  $1640$  and  $1100 \text{ cm}^{-1}$ , respectively [5,28]. The spectra of magnetic nanocomposites exhibited typical bands of the biopolymer, and a strong band in the low-frequency region near  $1000\text{-}500 \text{ cm}^{-1}$ , associated to the iron oxide skeleton. In particular, the band located at  $570 \text{ cm}^{-1}$  is typical of Mag [30].

The X-ray diffraction analysis demonstrated that the crystalline pattern of magnetite was not affected by the polymeric moieties. This behavior evidenced analyzing nanocomposites with different Mag/CS ratio (Supplementary Material).

The average hydrodynamic diameters ( $D_h$ ) and chemical composition are listed in Table I. From the data, it is possible to identify a linear dependency between the nominal amount of polymer and the proportion of CS effectively incorporated on nanocomposites. This trend is in agreement with previous findings on the same polymer/iron oxide system [28].

Concerning to the  $D_h$ , it is found that the biopolymer dispersions render large aggregates when testing by DLS ( $>5 \mu\text{m}$ ). The  $D_h$  increases when increases the amount of polymer in the nanocomposite. As it was reported by Lassalle *et al.* [28], it seems that a partial dissolution of lower molecular weight CS fractions occurred during the nanocomposite formation. This could be probably induced by the ionic strength of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  solution and the co-precipitation conditions, factors that contribute to the difference in particle size of CS and Mag/CS nanocomposites [28]. The nanoparticles of Mag act as nucleation seeds of macromolecular chains of CS during co-precipitation, allowing certain control in their final sizes. This control is strongly dependent on the amount of polymer.

The evolution of surface charge as a function of pH is a useful tool to predict the capability of the adsorbents to interact with different substrates. Figure 1-b displays the  $\zeta$  of raw materials and nanocomposites as a function of pH. As can be seen,  $\zeta$  of all materials is positive in acidic conditions but negative in basic ones. The  $\text{pH}_{\text{pzc}}$  of CS is about pH 6.9, which is close to the  $\text{pK}_a$  value (about of 6.4-6.7) of its amino group as reported by other authors [31,32]. At  $\text{pH} < \text{pH}_{\text{pzc}}$ , the magnitude of  $\zeta$  increases, and this fact could be attributed to the protonation of the amino group ( $-\text{NH}_2$  to  $-\text{NH}_3^+$ ). At  $\text{pH} > \text{pH}_{\text{pzc}}$  the amino

groups were deprotonated and  $\zeta$  becomes negative. As shown in Figure 1-b the  $\text{pH}_{\text{pzc}}$  of raw magnetite was about 7.1, consistent with the values reported in literature [6, 33,34]. After chitosan bonding, the  $\text{pH}_{\text{pzc}}$  was shifted to 5.45 for Mag/CS 1/0.5 nanocomposite. This value confirms the binding of chitosan, and the  $\text{pH}_{\text{pzc}}$  shift to lower values could be attributed to the introduction of several oxygen-containing functional groups. The same behavior was also observed by Chuang-Chang *et. al* [6], who reported that the point zero charge of magnetite was shifted from 6.70 to 5.95 after chitosan bonding. In the same way, Badruddoza *et. al* [33] observed a shift of  $\text{pH}_{\text{pzc}}$  from 6.8 to 4.7 in carboxymethyl- $\beta$ -cyclodextrin modified  $\text{Fe}_3\text{O}_4$  nanoparticles.

On the other hand, the value of  $\text{pH}_{\text{pzc}}$  reported for Mag/CS 0.5/1 is 8.3. Evidently, the higher zeta potential and PZC of chitosan–magnetite particles arises as a result of a higher proportion of amine groups, coming from a greater amount of chitosan in the nanocomposite. This result is also in agreement with a previous study reported in the literature [35].

Quantitative measurements of magnetism were obtained from VSM. From this assay, the magnetization (M) of each nanocomposite as a function of the applied magnetic field (H) at room temperature was obtained. The saturation magnetization ( $M_s$ ) values of nanocomposites were satisfactory in relation to the value recorded with pure magnetite, of about 60 emu/g (data previously reported [28]). The magnetization curves reveal that the nanocomposites have superparamagnetic behavior at this temperature, with reversible curves following a Langevin like function. This could be attributed to the size of magnetic cores of few nanometers in agreement with TEM analysis. Besides, the higher,  $M_s$  value (40 emu/g) was observed for the material with larger iron oxide content, as can be seen in

Table I. Anyway, data on Figure 1-c suggest that both nanocomposites developed suitable magnetic properties for the desired applications.

Complementary data of the morphology and size of the nanocomposites and raw materials was achieved by TEM. The images of  $\text{Fe}_3\text{O}_4$ , CS and magnetic nanocomposites are shown in Figure 2. The images of raw magnetite show highly aggregated nanoparticles with individual sizes lower than 20 nm (Figure 2b). The CS (Figure 2a) morphology coincides with the one expected to a typical amorphous polymer. The morphology of the magnetic nanocomposites is homogeneous and the two components are clearly distinguished: the dark areas correspond to the magnetic phase and the white ones to the polymeric moieties. It is also possible to observe the iron oxide nanoparticles finely dispersed within the polymeric matrix. The sizes of such nanoparticles are on the order of 20 nm, similarly to the raw magnetite. These results are in agreement with those reported by Chen Yuwei and Wang Jianlong [15], who observed particle sizes in the range of 8-40 nm in magnetic chitosan nanoparticles.

### *3.2-Adsorption experiments*

Nanocomposite with ratio Mag/CS 0.5/1 resulted the best adsorbent for the removal of copper and zinc. This could be attributed to the presence of more available linking sites due to the CS functional groups but also to the great surface area of the polymer.

Adsorption assays on raw materials (Mag and chitosan) were also performed using Cu as model heavy metal. In both cases the adsorption was gradual, achieving around 120 mg/g of solid after 240 minutes.

Thus, in-depth adsorption studies were carried out using this nanomaterial as adsorbent. Then, the results presented here in after are related to the use of this material as adsorbent.

The maximum adsorption levels are shown in Figure 3 as a function of the assayed metal.

### *3.2.1-Effect of contact time*

Cu(II) and Zn(II) adsorption –

The Cu(II) adsorption occurred rapidly at early stages when Mag/CS nanocomposite was tested. It was probably due to the abundant availability of active sites over the surface. An almost constant adsorption percentage was reached at approximately 240 min; after that period of time, a partial desorption of the metal ion was observed.

The maximum adsorption was about 190 mg/g of solid, which represents an improvement of roughly 60% with respect to raw materials' performance. The efficiency of adsorption of the synthesized materials was thus demonstrated.

Zn(II) adsorption was also carried on the raw materials and the selected nanocomposite. The profiles show slight differences in the adsorption capability. It is worth noting that the maximum adsorbed amounts were in the range 70 – 87 mg/g using any of the tested adsorbents. The kinetic profiles revealed that adsorption occurred rapidly during the first ten minutes and then remained almost constant up to the end of the experience.

Furthermore, a random trend was observed in the earlier stages of the adsorption process by using either the magnetic adsorbent or the raw materials. This behavior was more accentuated in the case of magnetic nanocomposite as adsorbent. This fact could be explained considering the formation of heavy metal ion derivatives in aqueous solution during adsorption. According to the literature, precipitation of Zn(OH)<sub>2</sub> occurs at pH 6.2 without any solid support. However, when an adsorbent such as chitosan, is present, precipitation of chitosan–Zn<sup>2+</sup> complexes could occur at pH < 6.2 [36]. Then it is feasible that these kinds of species contribute to the random observed behavior [4,7,37].

#### Cr(VI) adsorption –

The results of the kinetics of Cr(VI) removal on Mag/CS nanocomposite suggested a relatively fast initial uptake and a subsequent stable stage. The maximum adsorption capacity was around 46 mg Cr/g of solid (ca. 39 %) and this value was reached at 45 min, and kept stable for 4 h. After that period of time, a little ion desorption was detected. The kinetic results here obtained are in concordance with a recent report using a similar magnetic adsorbent synthesized using glutaraldehyde as crosslinking agent [38].

Besides, it is worth noting that the levels of removed Cr, identified as % of Cr adsorbed with respect to the initial amount or mg Cr/g adsorbent, refer to total Cr eliminated from the aqueous solution. Since the method used to quantify this metal is ICP, it is not possible to discern between different ionic species (Cr(VI), Cr(III)). However, according to the data reported in open literature it is feasible that part of original Cr(VI) in the solution would be reduced to Cr(III) by means of surface exposed magnetite nanoparticles [39]. Therefore, the informed removed Cr would be a sum of both species. Consequently the purification of water from Cr(VI) using these nanoadsorbents under these experimental conditions proceeds by a dual adsorption-reduction mechanism [40].

#### Cd(II) adsorption –

The kinetics of cadmium adsorption on Mag/CS nanocomposite exhibited a similar behavior to the other analyzed heavy metals ions. A fast initial uptake and subsequent stable stage was observed. The maximum adsorption level was reached within the first 30 min. and equilibrium was attained until 120 min. After this period of time desorption was observed. Similar results were reported in open literature using chitosan-magnetic resin to remove this heavy metal [1].

Kinetic modeling demonstrated that adsorption data were well described using the pseudo second order equation. This model is based on the assumptions that the chemical sorption is the rate-limiting step and that mass transfer in solution is not involved. That means that there is an external surface mass transfer process controlling the early stages of the adsorption process. Hence, a sharp rise in the early stages is indicative that a fast initial mass transfer occurs [41].

The experimental data was analyzed according to the linearized form of pseudo-first-order and the pseudo-second-order kinetics models. The linear trend observed in plots of  $t/q_t$  vs.  $t$  further validates the pseudo-second order kinetic model, as it is shown in Figure 4.

From the data analysis, it emerges that Cr(VI) was better fitted than Zn(II), Cu(II) and Cd(II) with this model. The value of rate constant  $k_2$  increases in the order Cr < Cu < Cd < Zn, being this fact an indication of the affinity of heavy metal ions and Mag/CS nanocomposite. It has been reported that in general, the binding of metals ions on different kinds of materials depends mainly on their physicochemical properties. A more in-depth discussion on this aspect will be included later in *Mechanism of adsorption*.

### 3.2.2-Effect of pH on metal ion adsorption

Cd was selected as model metal to assess the influence of the pH on the adsorption performance because it remains available as  $\text{Cd}^{2+}$  in the range of pH that is commonly found in a real water sample (between 4 and 7). In the case of other metals, the formation of insoluble hydroxides occurs when pH is higher than 5 [42, 43].

The formation of whitish solution and the presence of solid residue were observed at pH 8, which is attributable to the formation of cadmium hydroxide. As shown in Figure 5, the adsorption capacity increases with the rising pH. The higher uptake capacity was achieved

at pH 7, with a 95% of heavy metal removal respect to the initial amount. This behavior could be justified in terms of the interactions between heavy metal and exposed functional groups on the surface of magnetic adsorbent. As it was already mentioned, the surface charge of Mag/CS nanocomposite exhibited positive values of  $\zeta$  at pH < 8.3 due to the protonation of  $-\text{NH}_2$  groups of chitosan. Therefore, there is a competition between  $\text{H}^+$  and metal ions for sites in the Mag/CS nanocomposite. This fact derived in an ion exchange process. Then, the presence of more acidic environment led to lesser amount of Cd(II) removed by the magnetic adsorbent. Nevertheless, the high efficiency of cadmium ion removal achieved at pH 7 could suggest a decrease in the competitive effect as well as a decrease in the electrostatic repulsion as the pH raises. These suggestions were also described by Paulino *et. al* [44,45] studying the cadmium adsorption in hydrogel of chitosan and magnetite.

### *3.2.3-Effect of initial concentration of heavy metal*

According to WHO (2008) [46], the maximum cadmium concentration tolerable in drinking water is  $0.003 \text{ mg L}^{-1}$ . It was earlier reported that cadmium has toxic effects when the concentration exceeds the threshold limit value (TLV) of  $0.005 \text{ mg L}^{-1}$ , causing different types of acute and chronic disorders [47]. For this reason, in this work the adsorption capacity of Mag/CS nanocomposite as function of Cd(II) concentration was analyzed in the range  $30 - 200 \text{ mg L}^{-1}$ . Figure 6 shows the evolution of the metal adsorption (expressed as  $\text{mg g}^{-1}$  and % of cadmium available in solution) as a function of the initial concentration of Cd. Adsorption capacity increased with the initial metal concentration, yielding a maximum at  $200 \text{ mg L}^{-1}$ . However, percentage of removed Cd(II) was higher at lower initial Cd concentrations, reaching almost 96% of ion removal.



After a brief survey of available literature, few investigations were found studying this experimental variable related to Cd adsorption. In this sense, Paulino *et. al* [44,45] studied the removal of Cd(II) by hydrogel of chitosan and magnetite. In these studies the authors found that the maximum Cd(II) ion removal from the solution occurred with an initial concentration in the range of 200 - 300 mg L<sup>-1</sup>. The maximum adsorption capacities of Cd(II) were about 69.6 mg g<sup>-1</sup> of hydrogel [45] and 80.57 mg g<sup>-1</sup> of hydrogel [44]. Therefore, the explanation to this behavior could be related to the adsorption mechanism and the species present in the aqueous media.

#### 3.2.4-Adsorption mechanism

The mechanism and the surface interactions involved in the adsorption process were mainly elucidated through FTIR and Z potential data.

As it was previously mentioned, the adsorption assays were performed at pH < pH<sub>pzc</sub> of nanocomposites. In this condition, -NH<sub>2</sub> groups of chitosan are protonated. Thus, the binding could be achieved by replacing H<sup>+</sup> with a metal ion; meaning an ion exchange process [48-51]. In addition, similar interactions are possible to occur between the heavy metal cation and the non-coated magnetite surface in nanocomposites [51, 52]. At the studied pH, ≡FeOH became the dominating species in magnetite surface. Thus, the removal of heavy metal ions could be achieved through an ion exchange process, giving rise to the species ≡(Fe-O)<sub>m</sub>X<sup>(2-m)+</sup>. This mechanism is suitable to explain the copper, cadmium and zinc ion removal [51].

At pH = 4, the one fixed to Cr(VI) adsorption; this metal mainly exists as HCrO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>4</sub><sup>2-</sup> in aqueous solution. Then the adsorption could proceed through electrostatic attractions between these species and NH<sub>3</sub><sup>+</sup> (from CS) and/or OH<sup>+</sup> (from Mag) [53].

Besides the mentioned mechanisms, the feasibility of metals to coordinate with  $-\text{NH}_2$  and Fe has been documented [54]. In this context, the trend in the  $q_{max}$  observed in the four studied metals was closely related to the covalent index ( $X^2R_i$ ) of each ion. It is important to highlight that covalent index reflects the degree of covalent interactions in the metal–ligand complex relative to ionic interactions [52]. Hence, higher  $X^2R_i$  value implies stronger covalent interactions. A linear correlation between  $X^2R_i$  and the maximum adsorption levels of each metal was found, as it is reflected in Figure 7. Then, the adsorption efficiency is higher for the metals having higher covalent index

In view of these results, it is clear that the formation of covalent bonds represents the main interaction adsorbent–heavy metal mechanism. In these terms, the preferential order of adsorption is satisfactorily justified and is in accordance with information in open literature [55]. The Figure 8 includes a schematic representation of feasible interactions between metal ions and adsorbents.

To further gain insight on the adsorption mechanism, a selected magnetic adsorbent was analyzed through FTIR after Cd adsorption. Spectra of Mag/CS before and after Cd adsorption are compared in Figure 9. From the Figure, it is seen that a band located at  $3400\text{ cm}^{-1}$ , corresponding to the stretching vibration of  $-\text{OH}$  and  $-\text{NH}$  groups, shifted to lower wavenumbers ( $3300\text{ cm}^{-1}$ ); and a band broadening was also observed. This could reinforce the idea of interaction between the hydroxyl group and/or amino groups from the nanocomposite and the heavy metal ion [56]. These spectral features support chelation of Cd (and similarly the other heavy metals) with NH and OH functional groups. The weakening of the N-H bond strength by the conversion into a bonded NH group caused a downshift of the stretching as well as the bending absorption bands. According to Golcuk

*et. al* [57], the result of binding with the metal Cd leads to alteration of the hybridization type around nitrogen causing weakening of NH bond [58]. Similar findings were also reached by other authors using comparable adsorbent materials, on the adsorption of Cu(II) [59,60].

### *3.2.5-Reusability and regeneration of magnetic chitosan nanocomposite*

The reuse of the adsorbent is a key factor in improving wastewater process economics, and hence in conditioning the practical implementation of these technologies.

Cr, Cd and Cu were selected as models to evaluate reusability. The performance of magnetic adsorbents as a function of each cycle is depicted in Figure 10. It was observed that, as expected, uptake capacity decreased after each reuse cycle.

Five consecutive adsorption/desorption cycles were performed using Cu. At the end of the fifth cycle Mag/CS nanocomposite retained about 25% of the initial removal capacity for Cu.

In the case of Cr, eight consecutive cycles could be carried out, and the removal efficiency after the eighth cycle was roughly 20% of the initial removal ability. Using Cd, around 40% of the initial removal capacity was reached after the fourth cycle.

Negligible adsorbent mass loss was evidenced after each cycle; confirming the stability of the nanocomposites in the application media.

Similar results, in terms of the number of reuse cycles may be found in open literature regarding to the removal of the same heavy metals with adsorbents of different nature. However, in most of the published articles, the adsorbed metal ions were desorbed and concentrated by eluents. In fact, many authors have reported regeneration of different adsorbents by using eluents such as HCl, HNO<sub>3</sub>, acetic acid and EDTA to induce the metal

desorption. In general the level of regeneration (in terms of percentage of Me desorbed) is not reported [4,15,24,42, 60,61].

In this case, a partial desorption of the Me was achieved, remaining linked to the adsorbent almost more than 50% of the adsorbed metal. This implies that, even when mild regeneration conditions were applied (absent of eluents, roughly neutral pH, short contact time), the adsorbents retain some of their adsorption capability (between 25-40%). It is true that other strategies may be implemented in order to improve the regeneration of these materials, for instance using longer incubating times, variations of pH or incorporating chelating agents. It is important to mark that the behavior of three explored metals was comparable in terms of their regeneration and retention of adsorption capability along the cycles.

The key point in our study is to offer an ecofriendly, easy-handling and low cost adsorbent with the possibility of reuse with a simple H<sub>2</sub>O washing treatment. To better show the performance of our adsorbents with respect to the available articles in open literature, comparative data is included in Table II. Clearly, the maximum adsorption capacity found within this work is on the same order than the one informed in literature.

#### **4. Conclusion**

Successful removal of heavy metals from aqueous solutions in batch was achieved using magnetic nanocomposites. The adsorption levels were comparable to those reported in the literature with more sophisticated adsorbents and higher cost procedures. The trend of uptake followed the order Cu > Cd > Zn > Cr in single metal solutions. Kinetic results showed that the pseudo-second order equation fits well the adsorption data.

Coordination bond formation between nanocomposites functional groups ( $-NH_2$ , Fe) and metals appeared as the main mechanism governing the adsorption procedure. Ion exchange and electrostatic attraction also contributed to the linkage of heavy metals.

Satisfactory reusability capacity was found (at least five to eight reuse cycles depending on the metal) avoiding the use of solvents and/or extra additives.

The versatility of these nanomaterials would allow their application in other separation processes, including other kinds of contaminants such as organic ones.

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