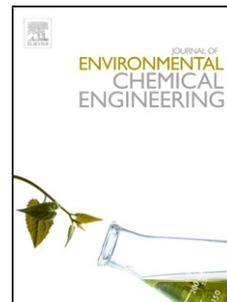


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CADMIUM REMOVAL BY A LOW-COST MAGADIITE-BASED MATERIAL: CHARACTERIZATION AND SORPTION APPLICATIONS

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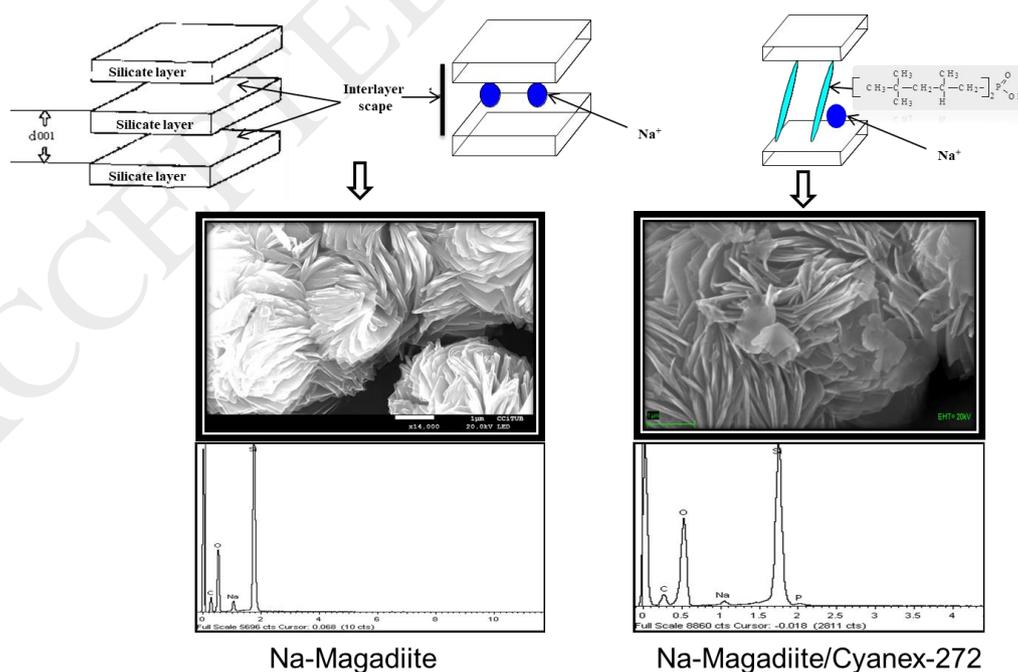
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Graphical abstract



HIGHLIGHTS

- Na-magadiite-based materials have been studied for Cd(II) removal from waters
- The sorbents were characterized with different techniques (XRD, FTIR, TGA, SEM-EDX)
- The introduction of Cyanex-272 into the interlayers of Na-Magadiite was studied
- The introduction of Cyanex-272 improves the selectivity towards cadmium ions

Abstract

The sorption of cadmium from nitrate medium at room temperature was carried out using solid phase magadiite and magadiite impregnated with Cyanex 272 [bis(2,4,4-trimethylpentyl)phosphinic acid]. The sorbent materials have been characterized by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscopy-energy dispersive X-ray analyses (SEM-EDX) and thermogravimetric analysis (TGA/DTG). The UV-Visible spectrophotometry technique was used to determine the amount of Cyanex-272 inserted into the solid support. Various parameters such as pH of the aqueous solution, initial Cd(II) concentration and equilibrium time were studied. The sorption data fitted the Sips sorption equation, and the sorption kinetics follows the model of the pseudo-second order. The maximum sorption capacity of Cd(II) was found to be 64.06 mg g⁻¹ and 49.45 mg g⁻¹ (i.e., 0.57 and 0.44 mmol g⁻¹) from magadiite and magadiite-Cyanex 272, respectively. The elution of the materials was performed with 0.1 M HNO₃ solution, and 80% of the initial sorbed cadmium was recovered.

Abbreviations: Mag: Sodium magadiite; Cyanex 272: bis(2,4,4-trimethylpentyl)phosphinic acid; Mag-C: Sodium magadiite impregnated with Cyanex 272

Keywords: Cadmium; Cyanex-272; sorption; heavy metals; Na-magadiite

1. Introduction

The wide use of heavy metal solutions in many industrial activities (battery manufacturing, refining and production of textiles, paints, dyes and mining) results in the generation of large quantities of effluent that contain high levels

of heavy metals. Most of them are toxic or carcinogenic agents and their presence in the aquatic ecosystems poses tremendous human health risks due to their non-degradable or persistent nature. Cadmium is one of these hazardous heavy metal species, which affects the kidneys, the lungs, the liver, renal damage, emphysema and even the reproductive organs in humans [1-3]. According to the World Health Organization (WHO) guidelines, cadmium is considered to be an extremely toxic metal without known biological benefits to any organism; the permissible limit of Cd(II) in drinking water is $3 \mu\text{g L}^{-1}$ [4]. Further research is required in order to create innovative technologies for separating this hazardous heavy metal element from waters and wastewaters.

Different technologies have been proposed for heavy metal removal over recent years; however, the sorption technique has attracted considerable attention because of its easy availability of materials, low operating costs, and the simplicity of the engineering design process. The performance of the sorption systems is directly associated with the functional groups present in the sorbent; several materials (such as Zeolites [5], activated carbon [6,7], chitosan [8], clay minerals [9], tea waste [10], lignocelluloses [11,12], nanoparticles [13], and modified polymers [14–17]) have all been developed for commercial applications. However, the cost/efficiency ratio of the manufacturing process of these materials could significantly increase depending on the amount of steps involved in their synthesis. Therefore, the simplicity of the sorbent production system is crucial in making the process feasible and enhancing any up-scaling to a major industrial production [18, 19].

Solvent extraction is considered an efficient technique for metal removal from concentrated wastewaters, but it may not be cost-effective for treating diluted effluents due to several drawbacks [20]: i) large organic solvent consumption; ii) difficult to recycle, and iii) an additional step is necessary in eluent treatments. One way to improve this metal separation (in terms of selectivity and sorption uptake) is the impregnation of organic acids onto the solid supports. The impregnation of different materials by organophosphorus extractants has been the scope of previous well-documented studies [21–24]. Among some of the studied organic acids, Cyanex 272 has been extensively used in liquid-liquid applications [25–28]. This present work investigates (for the first time) the removal of Cd(II) ions from aqueous solutions using Mag-C.

Mag is a crystalline layer polysilicates composed of SiO_4 tetrahedral, in which the negative charge is compensated by inter-layer sodium ions. This mineral has a large exchange capacity and presents a wide range of properties, including interlamellar water sorption and the exchange of inter-layer sodium cations, intracrystalline swelling, making this material suitable for sorption, catalysis, and molecular sieving applications

[29]. Additionally, a number of chemical species have been intercalated in the lamellar space of magadiite to produce the corresponding host-intercalating compounds for many uses [30].

A sorbent selected for specific metals with a high sorption capacity is essential for industrial applications. Mag-C was obtained by dry impregnation of Mag particles with bis(2,2,4-trimethylpentyl)phosphinic acid in order to increase the selectivity for target metals; this extractant was reported in recent literature to have a high affinity to Cd(II) ions [31,32]. The results were compared with those obtained in our previous works/studies along with those reported in the literature (concerning cadmium sorption with different sorbent materials) [33–37]. The effects of the key parameters (i.e., pH, contact time and initial metal concentration) as well as the influence of the temperature on the sorption process were all investigated.

2. Experimental

2.1. Materials

The silica gel (Ludox 40 % w/w suspension in H₂O) used for the sorbent preparation was supplied by Sigma-Aldrich (Steinheim, Germany). Cyanex® 272 (purity > 85%) was provided by Cytec (Rotterdam, Holland) and was used without any further purification. Organic solvents of chloroform (99% purity) and ethanol (96% purity) were obtained from Panreac (Bordeaux-Pessac, France). Inorganic reagents of nitric acid and sodium hydroxide were provided by Prolabo (Barcelona, Spain). Cadmium solutions were prepared using Cd(NO₃)₂·4H₂O (molecular weight 308.42 g mol⁻¹), and sodium nitrate were supplied by Probus (Badalona, Spain). Demineralized water was used in all experimental tests. The ionic strength of the solution was maintained at a constant 0.1 M by adding nitrate salt. The pH was adjusted using dilute solutions of HNO₃ or NaOH (as required).

2.2. Synthesis of sodium magadiite

The layered silicate Mag was prepared by means of reaction of NaOH with SiO₂ under hydrothermal conditions. A typical procedure is as follows: 1.2 g of NaOH pellets (purity 97.5%) is dissolved into 21.06 g of deionized water; then, 13.5 g of silica is added into the solution under continuous stirring. The procedure is carried out in a hydrothermal medium according to the method of Fletcher et al [38]. The mixture is then stirred for 2 hours at room temperature. The resulting homogenous gel (with a pH of 11.5) is placed in a Teflon-lined pressure vessel

and is heated at 150 °C for 48 hours. The final crystallized product is separated by filtration, and then it is washed and dried at 70 °C for 12 hours.

2.3. Preparation of impregnated sorbents

Cyanex 272 was introduced into Mag support by using the dry impregnation method [21]. An appropriate amount of Mag (1 g) was mixed with a high (96%) purity solution of ethyl alcohol (10 mL); containing 1 mmol of Cyanex 272. The mixture was stirred under atmospheric pressure until total solvent evaporation. The obtained solid was washed with 0.1 M HNO₃ solution to avoid release of the extractant molecule, and then dried in an oven at 80 °C for 24 hours [21, 22].

To determine the maximum amount of Cyanex 272 that could be inserted into the solid, several impregnations were carried out by means of varying the concentration of Cyanex 272. Finally, the residues of the washing waters of the various solids are preserved for the determination of the ligand by UV-visible spectrophotometry [14, 39]. The maximum amount of Cyanex 272 inserted into Mag was 1.14 mmol Cyanex per gram of magadiite support (Fig. SM1 of the supplementary materials section); this value is the same amount of Cyanex inserted into the resins and clays [21, 23]. The standard Mag-C material used in this work contains 0.68 mmol of Cyanex per gram of magadiite.

2.4. Characterization

The crystallinity of the prepared sorbents was determined by powder X-ray diffraction (XRD). Spectra were measured from powdered samples in a Bragg-Brentano diffractometer D8 Focus (Bruker, Horsaalzentrums, Germany), with copper anticathode CuK α radiation ($\lambda = 1.54 \text{ \AA}$). All the samples were scanned in the 2θ range of 2- 60° at a scan rate 2° min⁻¹. The Fourier Transform Infrared Spectroscopy (FTIR) was used to record the FTIR spectra with an Alpha instrument (Bruker, Ettlingen, Germany) within a frequency range of 400-4000 cm⁻¹ using potassium bromide pellets in order to identify the chemical functional groups on the surface of Mag and Mag-C. Morphology, micrographs and elemental analysis of Mag and Mag-C were obtained by SEM and EDX using a JEOL JSM 7100F Schottky Field Emission Scanning Electron Microscope (JEOL Ltd., Peabody MA, USA). This microscope is equipped with an Energy Dispersive X-ray (EDX) spectrometer (INCA 250, Oxford instruments,

Oxford, UK) for use in chemical analysis. The samples were coated with carbon before observations. The apparatus was operated at 20 keV. Thermogravimetric analysis (TGA/DTG) of Mag and Mag-C were performed on a TGA model Q50 V6.7 Build 203 (Peabody MA, USA) using dry nitrogen flux (60 mL min⁻¹) where 14.42 mg of samples were heated from 25 to 1000 °C at a heating rate of 10 °C min⁻¹.

The amount of Cyanex 272 inserted into the Mag at different concentrations was determined using a UV-Visible spectrophotometer model SPECORD-210 (Bayern Munich, Germany) at the wavelength of 240.1 nm. The metal concentrations were analysed by using Agilent 4100 MP-AES Spectrometer (Microwave Plasma-Atomic Emission Spectrometry), Agilent Technologies, Melbourne, Australia).

2.5. Methods

2.5.1. Effect of pH

The sorption of Cd(II) was carried out with batch experiments at 298 K (room temperature), samples of 0.025 g of solid phase were mechanically mixed in polypropylene tubes with synthetic aqueous solutions containing 25 mL of cadmium (50 mg L⁻¹; i.e., 0.44 mmol L⁻¹) at different acidities (controlled by the addition of HNO₃ or NaOH, as required). The tubes were shaken at 180 rpm for 180 min, and then the solid phase was separated by a high-speed centrifuge. The equilibrium pH (pH_i) was measured by using a pH-meter from Jenco Electronics LTD (Texas, USA). The metal concentration was determined by an Agilent 4100 MP-AES Spectrometer at 228.8 nm and 588.9 nm wavelengths (for cadmium and sodium, respectively). Three sorption replicates were performed for each experimental condition, and the standard deviation was \pm 2%. The efficiency of the process was assessed by eq. 1 and eq. 2, being q_{exp} and SE (%) the experimental sorption capacity and sorption efficiency of Cd(II), respectively,

$$q_{\text{exp}} = \frac{(C_0 - C_e)V}{w} \quad (1)$$

$$\text{SE}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium metal concentrations in solution (mg L⁻¹); respectively. V is the solution volume (L) and w is the mass of sorbent (g).

The pH of zero charge (pH_{PZC}) was determined through the so-called drift method [40, 41]; 600 mL of a dilute solution of NaCl (0.1 M) was prepared and distributed into a set of twelve flasks (50 mL of solution per flask). The pH was systematically adjusted to be in the range of 1 to 12 (using 1 M HCl or 1 M NaOH solutions, as required). Then, a known amount of sorbent (0.1 g) was added to each bottle, and the system was kept under agitation for 24 h. The initial pH (before adding the solid material) and the final pH were registered and plotted.

2.5.2. Sorption isotherms

A volume of 10 mL of cadmium solutions, with initial concentrations of cadmium ranging from 10 to 1000 mg L⁻¹, were placed in contact with 0.1 g of sorbent at room temperature. The initial pH of solution was adjusted to 2 for Mag and Mag-C. The equilibrium pH was measured using the Crison microPH 2000 pH meter (Barcelona, Spain). The cadmium content in both phases was determined by an Agilent 4100 MP-AES Spectrometer (Microwave Plasma-Atomic Emission Spectrometry).

The Langmuir, the Freundlich and the Sips equations (eq. 3, eq. 4 and eq. 5), respectively) were used to describe the experimental sorption isotherm data [42]:

$$q = \frac{q_{\text{max}} b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (3)$$

$$q = K_F C_{\text{eq}}^{1/n} \quad (4)$$

$$q = \frac{q_{\text{max}} K_S C_{\text{eq}}^{1/n_S}}{1 + K_S C_{\text{eq}}^{1/n_S}} \quad (5)$$

where q is the amount of sorbed metal per gram of sorbent at equilibrium (mmol g⁻¹), q_{max} is the maximum adsorption capacity of the sorbent (mmol g⁻¹), and C_{eq} is the equilibrium concentration of the solution (mmol L⁻¹).

In the Langmuir model (eq. (3)), b is the energy of adsorption (L mmol⁻¹), whereas K_F and n are the Freundlich adsorption constants, indicative of the relative capacity and the adsorption intensity, respectively. K_S (L mmol⁻¹) and n_S are constants of Sips model.

Additional experiments were performed to verify the selectivity of Mag-C material, 10 mL of the aqueous solutions of cadmium and nickel (at equimolar concentrations of 0.1 mmol L⁻¹; 0.2 mmol L⁻¹ and 0.3 mmol L⁻¹) were

brought into contact with 0.1 g of sorbent for 3 hours at ionic strength (0.1 M NaNO_3) at room temperature. The elution experiments were performed using 0.1 M HNO_3 solution as eluent.

2.5.3. Effect of contact time

Kinetic experiments were performed by preparing different tubes containing 0.1 g of Na-magadiite and Na-magadiite-Cyanex 272 with 10 mL of a Cd(II) solution (50 mg L^{-1}); pH values of the samples were adjusted to 2 with 0.1 M HNO_3 solution. The pH was monitored and samples were collected at different contact times (these were filtered through a $0.45 \mu\text{m}$ filtration membrane previously analysed with the Agilent 4100 MP-AES Spectrometer (Microwave Plasma-Atomic Emission Spectrometry)).

2.5.4. Effect of temperature

The thermodynamic effect on the sorption process was studied by three isotherms at different temperatures (288 K, 298 K, and 328 K) using Mag-C material as the sorbent. Samples of 0.1 g of Mag-C material were put in contact with 10 mL of cadmium solutions (at different initial concentrations), under continuous stirring. The initial metal concentration was varied between 10 - 1000 mg L^{-1} , and the initial pH was set as pH 2.

3. Results and discussion

3.1. Characterization of the materials

The X-ray diffraction patterns of the synthesized Mag and impregnated Mag-C material are shown in Fig. 1. The X-ray diffraction patterns of the characteristic peaks of magadiite at 5.6° , 11.3° , and 17.11° while 2θ corresponds to (001), (002), and (003) diffraction planes, respectively. The first diffraction peak allows calculating a basal spacing of 1.56 nm (Fig. 1.a). This value is consistent with the values reported in literature for magadiite [43–46]. Following its impregnation with Cyanex 272, the material showed two basal spacing: one basal spacing of 1.56 nm was recorded but a new diffraction peak at below 2θ corresponds to a basal spacing of 1.76 nm (Fig. 1.b). This increase in the basal spacing is explained by an intercalation of Cyanex 272 between the sheets of Mag.

Fig. 2 shows the FTIR spectra of Mag and Mag-C; the IR spectrum of Mag (Fig. 2.a) is comparable to that reported in literature [45, 46]. The sharp peak at 3644 cm^{-1} may be assigned to the Si-OH free hydroxyl groups, and the broad band at 3439 cm^{-1} may be due to the hydrogen bonded hydroxyls. The shoulder band at 1250 cm^{-1}

has been assigned to the asymmetric stretching mode of Si-O-Si, and the band around 1622 cm^{-1} is due to the water deformation (which is common to all hydrated minerals). The band at 1024 cm^{-1} may be attributed to the Si-O stretching vibration. Other bands visible at 800 cm^{-1} and 450 cm^{-1} have been attributed to symmetric Si-O stretching and Si-O shear, respectively. Some additional bands appear with Mag-C (Fig. 2.c) at 2950 cm^{-1} , 2867 cm^{-1} , and 1470 cm^{-1} , which are the characteristic peaks of asymmetric and symmetric CH_2 bands and methyl asymmetrical C-H bending, respectively, from Cyanex 272 intercalated molecules. The bands around 2318 cm^{-1} and 1363 cm^{-1} have been assigned to the presence of P-OH and P=O stretching, respectively. The spectrum of pure Cyanex 272 (Fig. 2.b) also showed the same bands [47, 48].

The thermal decomposition of sodium magadiite is summarized in Fig. 3.a. The TGA/DTG curves of Mag show three different stages of thermal degradation along with the total weight loss of 14.8% which was obtained between $27\text{ }^\circ\text{C}$ and $1000\text{ }^\circ\text{C}$. The principal weight loss (first stage) between $27\text{ }^\circ\text{C}$ and $200\text{ }^\circ\text{C}$ represents 13.8% of the loss of mass, and this is attributed to the dehydration of the material. The basal spacing (001) decreases to 1.15 nm [49]. The second thermal stage was observed between $200\text{ }^\circ\text{C}$ and $350\text{ }^\circ\text{C}$, with a slight loss of mass of 0.8%. Finally, the last stage between $350\text{ }^\circ\text{C}$ and $1000\text{ }^\circ\text{C}$ shows a loss of mass of 0.2%. In the temperature range between $500\text{ }^\circ\text{C}$ and $700\text{ }^\circ\text{C}$, Mag is decomposed into crystalline quartz, as reported by Moura and Prado [44]. At $700\text{ }^\circ\text{C}$, a well-crystallized tridymite develops which is stable up to $1000\text{ }^\circ\text{C}$.

After impregnation with Cyanex 272 (Fig. 3.b), an additional weight loss between $180\text{ }^\circ\text{C}$ and $440\text{ }^\circ\text{C}$ was observed, corresponding to the decomposition of the extractant [48]. This indicates that Cyanex 272 was introduced into the magadiite support and was in agreement with the XRD and FTIR data. No further changes were observed after $500\text{ }^\circ\text{C}$. The total mass loss was found to be 21.5%.

SEM micrographs for Mag and Mag-C are shown in Figs. 4.a and 5.a. The synthetic magadiite is known to adopt a particle morphology composed of entangled silicate layers to form spherical nodules resembling rosettes. The EDX spectrum (Fig. 4.b) confirms the presence of silicon and oxygen, which form the layers of Mag, and the presence of sodium in the interlayer [50]. After the intercalation of Cyanex 272 in the magadiite, the observed morphology is similar for both solids (Fig. 5.a). The appearance of parallel plates is consistent with the lamellar features which are kept even after the impregnation of the layered initial solid. The elemental analysis obtained

from the EDX spectrum (Fig. 5.b) indicates the presence of sodium, silicon, oxygen and especially phosphorous, confirming that Cyanex 272 was inserted successfully into the Na-magadiite [48].

3.2. Effect of pH

The pH of the solution plays an important role in the whole sorption process. The pH influences the charge surrounding the sorbent particles which is directly related to the electrostatic interactions with the sorbate molecules [51]. In order to study the effect of this parameter on the metal sorption by the Mag and Mag-C materials, the initial pH was varied within the pH range 1.0 - 5.5 (at dilute metal concentration: 50 mg L⁻¹). These operational conditions were selected in order to avoid the precipitation phenomenon (according to the speciation diagram in Fig. SM2 where the cadmium hydroxide precipitates at pH \geq 8.15).

Figures 6.a and 7.a show the sorption performance of the sorbents. The equilibrium pH is impacted as a result of the ion-exchange involved between both ions into the lamellar structure of the materials. The sorption process with Mag becomes operationally difficult, since the cation exchange leads to a strong competition involving the protons of the solution, and, as a consequence, the equilibrium pH increases. This increase in the pH is less significant for Mag-C, which is kept between pH 6 and pH 7, and no risk of precipitation exists (Figs. 6.b and 7.b). Several additional tests were performed in order to characterize the ion-exchange as a function of the proton concentration (Figs. 6.c and 7.c). Under the same operational conditions (pH 1-7), the molar ratio (Cd/Na) (calculated as the sorbed cadmium and the released sodium) followed a similar trend: at pH below 4.5, the ratio values almost negligible (which is indicative of the competition between protons), and then, it progressively increased reaching its maximum at pH 6.7.

The sodium ions were released into the solution at a higher extent with Mag than with Mag-C; the average concentration found in the solution being almost constant for each material (44 mg L⁻¹ for Mag and 29 mg L⁻¹ Mag-C, respectively). Sarangi et al. [52] found that Cyanex 272 may form complex species with sodium (so-called Na-Cyanex-272); this may affect the ion exchange of the metal ions, which directly impacts on the metal uptake, and therefore, the sorption capacity was slightly lower for Mag-C.

In addition, the pH value at the point of zero charge (pH_{PZC}) of the sorbents was determined by the drift method (Figs. SM3.a and SM3.b) [40–41]. The values of pH_{PZC} were found as pH 8.8 and pH 6.4 for Mag and Mag-C,

respectively. At $\text{pH} < \text{pH}_{\text{PZC}}$, the surfaces of the sorbents are positively charged. This justifies the low removal of cations at acidic pH, since the repulsion forces make the diffusion of metal ions onto the external surface of the materials difficult. On the contrary, by increasing the pH, the surfaces become more negative which favours the attraction of the sorbate molecules, improving the sorption of cadmium.

3.3. Equilibrium studies

Sorption isotherms are important for interpreting the sorbate/sorbent interactions, since they describe the relationship between the liquid and solid phases at equilibrium. Several model equations have been designed for studying the distribution of the sorbate molecules on the sorbent surface, including those from Langmuir, Freundlich and Sips.

Figure 8 shows the impact of the cadmium concentrations on the removal uptake by Mag and Mag-C; an increase in the Cd(II) concentration results in an increase in the sorption capacity until a saturation plateau is reached. The characteristics of a typical favorable sorption profile correspond to the asymptotic shape of the curves (which is consistent with both Langmuir and Sips equations). At dilute metal concentrations (i.e., $< 50 \text{ mg L}^{-1}$), the sorbents allow removing more than 97% of Cd(II), which is indicative of a high performance and the feasibility of separating trace metals from dilute wastewaters.

The fitting values of the Langmuir, Freundlich and Sips models are showed in Table 1. The experimental data is better described using the Sips equation (via the comparison of the coefficient determination, r^2). It is noteworthy that the fit of the data does not mean that the principles of the models are verified, but it leads to improve the understanding of the sorption mechanism. On one hand, Langmuir model assumes [53] that: i) the sorption process occurs on a structurally homogeneous surface; ii) all the active sites are energetically identical, and iii) that there are no interactions between the sorbate molecules (thus, monolayer coverage of the sorbent surface is obtained). On the other hand, Freundlich equation assumes that the sorption occurs on heterogeneous surface, and a multilayer coverage is involved [20]. Sips equation is, however, a common adaptation of both Langmuir and Freundlich models; thus, values for $1/n_s$ close to zero are generally associated with heterogeneous sorbents, while values closer to 1.0 correspond to sorbents with relatively homogeneous binding sites.

The removal uptakes of the sorbents (Fig. 8) are in agreement with the values obtained in the pH study. The maximum sorption capacities of both materials are similar, i.e. 0.57 mmol g^{-1} and 0.44 mmol g^{-1} for Mag and Mag-C, respectively. The main difference lies in the values of the affinity parameter b (Table 1) and the product $q_{\text{max}} \cdot b$ (corresponding to the initial slope of the curves). These are almost three times higher for Mag-C than for those obtained for Mag. This means that the introduction of Cyanex 272 into the lamellar material may increase the affinity of the sorbed ions. This is useful for the treatment of industrial effluents. The sorption capacity does not reflect an increase, but it is probably due to several causes: i) the protons strongly compete with cadmium ions at acidic pH (this was also evidenced in the pH study whereby the equilibrium pH and the sodium content into the solution increases, even though the cadmium concentration does not change); ii) the introduction of the extractant into the Mag material reduces the total volume of the lamellar sections which load the sorbent, and it also reduces the total volume for hosting cadmium ions, (as a consequence, the sorption uptake slightly decreased).

Moreover, the impregnation of the Mag material contributes to improving the resulting configuration of the sorbent and to enhancing the selectivity toward cadmium species, which is also the main advantage for industrial applications. Additional analyses with simulated cadmium-nickel battery effluents (in the presence of foreign ions, i.e., 0.1 M NaNO_3) were carried out with Mag-C in order to verify the metal selectivity. The experiments were performed at equimolar concentration of Cd(II) and Ni(II) (i.e., 0.1 mmol L^{-1} ; 0.2 mmol L^{-1} ; and 0.3 mmol L^{-1}), and the results in Fig. SM4.a demonstrated a better removal performance of cadmium ions. The nickel uptake is almost negligible. The recovery of the metals can be performed with 0.1 M HNO_3 solution (Fig. SM4.b); and the eluting efficiencies obtained are greater than 80% for cadmium and 50% for nickel, respectively. This is a first-time approach for an industrial applicability of this sorbent. Further experiments will be performed with real effluents so as to study the sorption/desorption cycles. This will be the scope of future research.

Table 2 shows a comparison with the maximum sorption capacities of several sorbents found in literature; Mag-C has a sorption uptake of the same order of magnitude as the reported materials. Igberase and Osifo [36] studied the removal of Cd(II) by polyaniline grafted cross-linked chitosan beads; their results are interesting due to the greater sorption capacity achieved. But from a feasibility point of view, the manufacturing of the sorbent involves several steps which are difficult to reproduce on an industrial scale. However, Mag-C is a low-cost material and it

is easy to develop in a semi-industrial pilot plant: the simplicity of the process could be conducive to reducing the high costs of energy (which are usually involved in the large-scale manufacture of industrial sorbent resins).

The effect of the temperature on the sorption capacity was also studied using Mag-C material. Three temperatures were evaluated (288K, 298 K and 328 K) at different initial concentrations. Fig. 9 shows that the isotherms curves are overlapped and the sorption capacity does not change. This suggests that the Mag-C material can be used in a wide range of thermal conditions. The stability of the sorbent was maintained and no impact on the removal uptake was obtained under these operating conditions. This could be attributed to the following causes: i) the energy provided to the system is probably not sufficient for breaking down the sorbate/sorbent binding; or ii) the high sorbent dosage (10 g L^{-1}) and the small particles size of the materials ($<0.5 \text{ mm}$), favour the rapid diffusion of the metals into the active sites. Consequently, no differences in the equilibrium concentrations are found at different temperatures.

3.4. Influence of contact time

Sorption kinetics is an important issue for the assessment of the contact time on metal recovery. Fig. 10 shows the kinetic profiles for cadmium removal from aqueous solutions. Several authors [42, 54] have reported that kinetic uptakes are controlled by different mechanisms, including: i) bulk diffusion; ii) external diffusion (so-called film diffusion); iii) intraparticle diffusion, and iv) reaction rate. It is noteworthy that by maintaining sufficient agitation speed, the contribution to the bulk diffusion could be neglected. Demey et al. [51] reported that by maintaining a continuous agitation speed greater than 150 rpm and a sorbent dosage (SD) of 1 g L^{-1} (into 1 L of metal solution), it is enough to avoid the settling of the sorbent and thus neglecting its contribution.

The kinetics studies were performed with Mag and Mag-C materials. Both curves in Fig. 10 are overlapped, confirming no significant influence from the contact time with the introduction of the organic solvent into the interlayer cavities of the magadiite support. The equilibrium is rapidly achieved; only ten minutes is required for reaching the sorption plateau. This can be due to several causes: i) the small particle size of the sorbent impacts on the resistance to the film diffusion, which results in more active sites available for metal removal; ii) the structure of the inorganic matrix remained relatively open after air drying and it did not affect the accessibility in the pores (this was not completely evidenced in the SEM images); and iii) the covalent radius of cadmium is

smaller than interlayer cavities of the sorbent, and no difficulties in transporting through the entrance of the pores was presented (i.e., the covalent radius of cadmium is 0.14 nm and the lamellar cavity was estimated to be between 1.56 nm and 1.76 nm). Table 3 reports the comparison of the experimental sorption capacities at equilibrium with calculated values for both pseudo-first order (PFORE) and the pseudo-second order rate equations (PSORE). The correlations confirm a much better fitting with PSORE. This easy manufacture, along with a lower time requirement for achieving equilibrium, together with its higher selectivity toward cadmium ions, ultimately transforms into Na-magadiite/Cyanex-272 material; a suitable sorbent for large-scale evaluations with real effluents.

Conclusions

Na-magadiite/Cyanex-272 sorbent is a suitable material for cadmium removal from waters. The metal sorption was strongly influenced by the pH solution. The best operating conditions were found at pH 6. The impregnation of the magadiite support with Cyanex-272 was found to increase the selectivity toward cadmium in the presence of nickel ions (at equimolar concentrations). Sips' equation fitted the equilibrium data better than Freundlich and Langmuir's models. The maximum sorption capacities were 0.57 mmol g⁻¹ and 0.44 mmol g⁻¹ for Mag and Mag-C, respectively. PSORE adjusted accurately to the kinetics data. The extraordinary advantage in using Na-magadiite/Cyanex-272 is due to its manufacturing procedure simplicity, its low cost, and its high sorption capacity. All these benefits compared with other existing more costly sorbents and time-consuming procedures. The desorption studies showed the high efficiency for cadmium recovery only using 0.1 M HNO₃ solution as eluent. 80% of the initial sorbed cadmium can be recovered speedily from the loaded material.

Acknowledgments

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References

- [1] M.P. Mahalik, H.W. Hitner, W.C. Prozialeck, Teratogenic effects and distribution of cadmium (Cd^{2+}) administered via osmotic minipumps to gravid CF-1 mice, *Toxicol. Lett.* 76 (1995) 195–202.
- [2] M.P. Waalkes, Cadmium carcinogenesis in review, *J. Inorg. Biochem.* 79 (2000) 241–244.
- [3] S. Benoff, Male infertility and environmental exposure to lead and cadmium, *Hum Reprod Update.* 6 (2000) 107–121.
- [4] H.G. Gorchev, G. Ozolins, Guidelines for drinking-water quality, WHO. 1 (2011) 564.
- [5] D.P. Quintanilla, I.D. Hierro, M. Fajardo, I. Sierra, Adsorption of cadmium (II) from aqueous media onto a mesoporous silica chemically modified with 2-mercaptopyrimidine, *J. Mater Chem.* 16 (2006) 1757–1764.
- [6] J.C. Izidoro, D.A. Fungaro, J.E. Abbott, S. Wang, Synthesis of zeolites x and a from fly ashes for cadmium and zinc removal from aqueous solutions in single and binary ion systems, *Fuel.* 103 (2013) 827–834.
- [7] I. Kula, M. Ugurlu, H. Karaoglu, A. Celik, Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl_2 activation, *Bioresour. Technol.* 99 (2008) 492–501.
- [8] T.M. Alslaibi, I. Abustan, M. Ahmad, A. Foul, Fixed-bed column study for Cu (II) removal from aqueous solutions using rice husk based activated carbon, *J. Environ Chem Eng.* 78 (2013) 589–599.
- [9] L. Huang, S. Yuan, L. Lv, G. Tan, B. Liang, S. Pehkonen, Poly (methacrylic acid)-grafted chitosan microspheres via surface-initiated ATRP for enhanced removal of Cd (II) ions from aqueous solution, *J. Colloid Interface Sci.* 405 (2013) 171–182.
- [10] V.K. Gupta, S. Sharma, Removal of cadmium and zinc from aqueous solutions using red mud, *Environ Sci Technol.* 36 (2002) 3612–3617.
- [11] S. Wan, Z. Ma, Y. Xue, M. Ma, S. Xu, L. Qian, Q. Zhang, Sorption of lead (II), cadmium (II), and copper (II) ions from aqueous solutions using tea waste, *Ind. Eng. Chem. Res.* 53 (2014) 3629–3635.
- [12] F. Y. Wang, H. Wang, J. Wei Ma, Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent-Bamboo charcoal, *J. Hazard. Mater.* 177 (2010) 300–306.
- [13] V.K. Gupta, A.Nayak, Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe_2O_3 nanoparticles, *Chem. Eng. J.* 180 (2012) 81–90.

- [14] M.T. Draa, T. Belaid, M. Benamor, Extraction of Pb (II) by XAD7 impregnated resins with organophosphorus extractants (DEHPA, IONQUEST 801, CYANEX 272), *Sep. Purif. Technol.* 40 (2004)77–86.
- [15] N. Kabay, J.L. Cortina, A. Trochimczuk, Solvent-impregnated resins (SIRs) – methods of preparation and their applications, *React. Funct. Polym.* 70 (2010) 484–496.
- [16] M. T. Sikder, T. Kikuchi, J. Suzuki, T. Hosokawa, T. Saito, M. Kurasaki, Removal of cadmium and chromium ions using modified a, b, and c-Cyclodextrin polymers, *Sep. Sci. Technol.* 48 (2013) 587–597.
- [17] M.T. Sikder, M. Jakariya, M. Mostafizur Rahman, S. Fujita, T. Saito, M. Kurasaki, Facile synthesis, characterization, and adsorption properties of Cd (II) from aqueous solution using β -cyclodextrin polymer impregnated in functionalized chitosan beads as a novel adsorbent, *JECE.* 5 (2017) 3395–3404.
- [18] H. Demey, T. Vincent, M. Ruiz, M. Nogueras, A.M. Sastre, E. Guibal, Boron recovery from seawater with a new low-cost adsorbent material, *Chem. Eng. J.* 254 (2014) 463–471.
- [19] H. Demey, T. Vincent, M. Ruiz, A.M. Sastre, E. Guibal, Development of a new chitosan/Ni(OH)₂-based sorbent for boron removal, *Chem. Eng. J.* 244 (2014) 576–586.
- [20] W.R. Mohamed, S.S. Metwally, H.A. Ibrahim, E.A. El-sherief, H.S. Mekhamer, I.M. Moustafa, E.M. Mabrouk, Impregnation of task-specific ionic liquid into a solid support for removal of neodymium and gadolinium ions from aqueous solution, *J. Mol. Liq.* 236 (2017) 9–17.
- [21] D. Bouazza, A. Boos, A. Tayeb, A. Bengueddach, Recovery of Zinc from sulphate medium by purified bentonite of Maghnia impregnated by an organophosphorus acid, *J. Mater. Environ. Sci.* 5 (2014) 2499–2503.
- [22] D. Bouazza, H. Miloudi, M. Sassi, A. Boos, G. Goetz, A. Tayeb, A. Bengueddach, Preparation of montmorillonite clays containing DTMPPA for Zinc extraction, *J. Phys. Chem. Solids.* 67 (2006) 1032–1036.
- [23] J.L. Cortina, N. Miralles, M. Aguilar, A.M. Sastre, Distribution studies of Zn (II), Cu (II) and Cd (II) with Levextrel resins containing di (2, 4, 4-trimethylpentyl) phosphinic acid, *Hydrometallurgy.* 40 (1996) 195–206.
- [24] H. Miloudi, A. Tayeb, A. Boos, G. Goetz, A. Bengueddach, Solid-liquid extraction of Cu (II) and Zn (II) by organic-inorganic hybrid silicas doped by acidic ligands, *J. Mater. Environ. Sci.* 5 (2014) 2590–2594.
- [25] N. Begum, F. Bari, S.B. Jamaludin, K. Hussin, Solvent extraction of copper, nickel and zinc by Cyanex 272, *Int. J. Phys. Sci.* 7 (2012) 2905–2910.

- [26] D. Das, V.A. Juvekar, V.H. Rupawate, K. Ramprasad, R. Bhattacharya, Effect of the nature of organophosphorous acid moiety on co- extraction of U(VI) and mineral acid from aqueous solutions using D2EHPA, PC88A and Cyanex 272, *Hydrometallurgy*. 152 (2015) 129–138.
- [27] B. Swain, C. Mishra, J. Jeong, J. Lee, H.S. Hong, B.D. Pandey, Separation of Co (II) and Li (I) with Cyanex 272 using hollow fiber supported liquid membrane: A comparison with flat sheet supported liquid membrane and dispersive solvent extraction process, *Chem. Eng. J.* 271 (2015) 61–70.
- [28] E. James, H. Quinn, Process for uranium recovery using Cyanex 272, *Hydrometallurgy*. 152 (2015) 7–12.
- [29] C.S. Kim, D.M. Yates, P.J. Heaney, The layered sodium silicate magadiite: An analog to smectite for benzene sorption for water, *Clays Clay Miner.* 45 (1997) 881–885.
- [30] D.L. Guerra, A. Azevedo Pinto, C. Airoidi, R. Ribeiro Viana, Adsorption of arsenic (III) into modified lamellar Na-magadiite in aqueous medium thermodynamic of adsorption process, *J. Solid State Chem.* 181 (2008) 3374–3379.
- [31] V. Manuel, J. Pinto, C. Mendiguchía, C. Moreno, Solvent extraction with organophosphorus extractants in environmental samples: determination of cadmium (II) in natural water, *Cent Eur J Chem.* 12 (2014) 348–353.
- [32] D.P. Mantuano, G. Dorella, R.C. Alves Elias, M.B. Mansur, Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid-liquid extraction with Cyanex 272, *J. Power Sources.* 159 (2006) 1510–1518.
- [33] P.O. Boamah, Y. Huang, M. Hua, Q. Zhang, Y. Liu, J. Onumah, W. Wang, Y. Song, Removal of cadmium from aqueous solution using low molecular weight chitosan derivative, *Carbohydr. Polym.* 122 (2015) 255–264.
- [34] S. Pandey, S. Tiwari, Facile approach to synthesize chitosan based composite--characterization and cadmium (II) ion adsorption studies, *Carbohydr. Polym.* 134 (2015) 646–656.
- [35] S. Hydari, H. Shariffard, M. Nabavinia, M.R. Parvizi, A comparative investigation on removal performances of commercial activated carbon, chitosan biosorbent and chitosan/activated carbon composite for cadmium, *Chem. Eng. J.* 193–194 (2012) 276–282.
- [36] E. Igberase, P. Osifo, Equilibrium, kinetic, thermodynamic and desorption studies of cadmium and lead by polyaniline grafted cross-linked chitosan beads from aqueous solution, *J. Ind. Eng. Chem.* 26 (2015) 340–347.
- [37] K. Srinivasa Rao, G. Roy Chaudhury, B.K. Mishra, Kinetics and equilibrium studies for the removal of cadmium ions from aqueous solutions using Duolite ES 467 resin, *Int. J. Miner. Process.* 97 (2010) 68–73.

- [38] R.A. Fletcher, D.M. Bibby, Synthesis of kenyaite and magadiite in the presence of various anions, *Clays Clay Miner.* 35(4) (1987) 318–320.
- [39] J.L. Cortina, N. Miralles, A.M. Sastre, M. Aguilar, Solid-liquid extraction studies of divalent metals with impregnated resins containing mixtures of organophosphorus extractants, *React. Funct. Polym.* 32 (1997) 221–229.
- [40] M. Nasiruddin-Khan, A. Sarwar, Determination of points of zero charge of natural and treated adsorbents, *Surf. Rev. Lett.* 14 (3) (2007) 461–469.
- [41] A. Benettayeb, E. Guibal, A. Morsli, R. Kessas, Chemical modification of alginate for enhanced sorption of Cd(II), Cu(II) and Pb(II), *Chem. Eng. J.* 316 (2017) 704–714.
- [42] H. Demey, T. Vincent, Guibal E, A novel algal-based sorbent for heavy metal removal, *Chem. Eng. J.* 332 (2018) 582–595.
- [43] T. Selvam, G.P. Mabande, W. Schwieger, Y. Sugi, I. Toyama, Y. Kubota, H.S. Lee, J.H. Kim, Selective isopropylation of biphenyl to 4, 4'-DIPB over mordenite (MOR) type zeolite obtained from a layered sodium silicate magadiite, *Catal. Lett.* 94 (2004) 17–24.
- [44] A.O. Moura, A.G.S. Prado, Effect of thermal dehydration and rehydration on Na- magadiite structure, *J. Colloid Interface Sci.* 330 (2009) 392–398.
- [45] Y. Guo, Y. Wang, Q.X. Yang, G.D Li, C.S. Wang, Z.C. Cui, J.S. Chen, Preparation and characterization of magadiite grafted with an azobenzene derivative, *Solid State Sciences.* 6 (2004) 1001–1006.
- [46] D.L. Guerra, A. Pinto, R. Viana, C. Airoidi, Modification of magadiite surface by organofunctionalization for application in removing As(V) from aqueous media: kinetic And thermodynamic, *Appl. Surf. Sci.* 256 (2009) 702–709.
- [47] D. Bouazza, H. Miloudi, M. Adjdir, A. Tayeb, A. Boos, Competitive adsorption of Cu(II) and Zn(II) on impregnate raw Algerian bentonite and efficiency of extraction, *Appl Clay Sci.* 151(2018) 118-123.
- [48] F. Bari, N. Begum, S. Baharin, K. Hussin, Extraction and separation of Cu (II), Ni (II) and Zn (II) by sol-gel silica immobilized with Cyanex 272, *Hydrometallurgy.* 96 (2009) 140–147.
- [49] G. Lagaly, K. Beneke, Magadiite and H-Magadiite: I. Sodium magadiite and some of its derivatives, *Am. Mineral.* 60 (1975) 642–649.

- [50] F. Kooli, L. Mianhui, S.F. Alshahateet, F. Chen, Z. Yinghuai, Characterization and thermal stability properties of intercalated Na-magadiite with cetyltrimethylammonium (C16TMA) surfactants, *J. Phys. Chem. Solids*. 67 (2006) 926–931.
- [51] H. Demey, B. Lapo, M. Ruiz, A. Fortuny, M. Marchand, A. Sastre, Neodymium recovery by chitosan/Iron(III) hydroxide [ChiFer(III)] sorbent material: batch and column systems, *Polymers (Basel)*. 10 (2) (2018) 204.
- [52] K. Sarangui, B.R. Reddy, R.P. Das, Extraction of cobalt (II) and nickel (II) from chloride solutions using Na-Cyanex 272. Separation of Co (II)/Ni (II) by the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures, *Hydrometallurgy*. 52 (1999) 253–265.
- [53] S.S. Metwally, M.A. Hassan, R.F. Aglan, Extraction of copper from ammoniacal solution using impregnated amberlite XAD-7 resin loaded with LIX-54, *J. Environ. Chem. Eng.* 1 (2013) 252–259.
- [54] B. Lapo, H. Demey, J. Zapata, C. Romero, A.M. Sastre, Sorption of Hg (II) And Pb (II) ions on chitosan-Iron(III) from Aqueous Solutions: Single and Binary Systems, *Polymers (Basel)*. 10 (4) (2018) 367.
- [55] E. Guibal. Metal ion interactions with chitosan—a review, *Sep. Purif. Technol.* 38 (2004) 43–74.
- [56] P. Tzvetkova, R. Nickolov, Modified and unmodified silica gel used for heavy metal ions removal from aqueous solutions, *J. Univ. Chem. Technol. Metallurgy*. 47(5) (2012) 498–504.
- [57] Z. Mahmood, A. Amin, U. Zafar, M. Amir Raza, I. Hafeez, A. Akram, Adsorption studies of cadmium ions on alginate–calcium carbonate composite beads, *Appl Water Sci*. 7 (2017) 915–921.
- [58] A.S. Pereira, G. Ferreira, L. Caetano, R.S.D. Castro, 4-amine-2-mercaptopyrimidine modified silica gel applied in Cd (II) And Pb (II) extraction from an aqueous medium, *J. Chem. Technol.* 12 (2010) 7–11.
- [59] K. Chen, J. He, Y. Li, X. Cai, K. Zhang, T. Liu, Removal of cadmium and lead ions from water by sulfonated magnetic nanoparticle adsorbents, *J. Colloid Interface Sci.* 494 (2017) 307–316.
- [60] N. Kabay, M. Demircioglu, H. Ekinici, M. Yuksel, M. Saglam, M. Streat, Extraction of Cd(II) and Cu(II) from phosphoric acid solutions by solvent-impregnated resins (SIR) containing Cyanex 302, *React. Funct. Polym.* 38 (1998) 219–226.
- [61] L. Hinojosa Reyes, I. Saucedo Medina, R. Navarro Mendoza, J. Revilla Vázquez, M. Avila Rodríguez, E. Guibal, Extraction of cadmium from phosphoric acid using resins impregnated with organophosphorus extractants, *Ind Eng Chem Res.* 40 (5) (2001) 1422–1433.

[62] M.P. Gonzalez, I. Saucedo, R. Navarro, M. Avila, E. Guibal, Selective separation of Fe (III), Cd (II), and Ni (II) from dilute solutions using solvent-impregnated resins, *Ind Eng Chem Res.* 40 (2001) 6004-6013.

[63] R. Navarro, I. Saucedo, A. Nunez, M. Avila, E. Guibal, Cadmium extraction from hydrochloric acid solutions using Amberlite XAD-7 impregnated with Cyanex 921 (Tri-Octyl Phosphine Oxide), *React. Funct. Polym.* 68 (2008) 557–571.

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Fig.1. XRD analyses of the sorbent materials. 1.a) Mag; 1.b) Mag-C

Fig.2. FTIR analyses of the sorbent materials. 2.a) Mag; 2.b) Cyanex272; 2.c) Mag-C

Fig.3. TGA/DTG curves of sorbent materials. 3.a) Mag; 3.b) Mag-C

**Fig.4. Scanning Electron Microscopy (SEM) images of the Mag material. 4.a) Topography of the sorbent;
4.b) Energy Dispersive X-ray (EDX) analysis on the surface area of the solid**

**Fig.5. Scanning Electron Microscopy (SEM) images of the Mag-C material. a) Topography of the sorbent;
b) Energy Dispersive X-ray (EDX) analysis on the surface area of the solid**

**Fig.6. Influence of pH on cadmium removal using Mag as sorbent. 6.a) Sorption capacity. 6.b) Variation in
pH. 6.c) Cadmium/sodium ratio into the solution as a function of the equilibrium pH**

(T: 20 °C; V: 0.025 L; m: 0.025 g; agitation speed: 180 rpm; contact time: 3 h; C₀:50 mg L⁻¹; 0.1 M NaNO₃)

**Fig.7. Influence of pH on cadmium removal using Mag-C as sorbent. 7.a) Sorption capacity. 7.b)
Variations in pH. 7.c) Cadmium/sodium ratio into the solution as a function of the equilibrium pH**

(T:20 °C; V: 0.025 L; m: 0.025 g; agitation speed: 180 rpm; contact time: 3 h; C₀:50 mg L⁻¹; 0.1 M NaNO₃)

Fig.8. Isotherm plots for cadmium removal

(Dashed line: Langmuir model; T: 20 °C; V: 0.01 L; m: 0.1 g; agitation speed: 180 rpm; contact time: 3 h; pH:
2; C₀: 10 - 1000 mg L⁻¹; 0.1 M NaNO₃)

Fig.9. Influence of the temperature on sorption removal of cadmium using Mag-C material as sorbent

(T: 288 K, 298 K, 328 K; V: 0.01 L; m: 0.1 g; agitation speed: 180 rpm; contact time: 3 h; pH: 2; C₀: 10-1000
mg L⁻¹; 0.1 M NaNO₃)

Fig.10. Effect of contact time on sorbent materials

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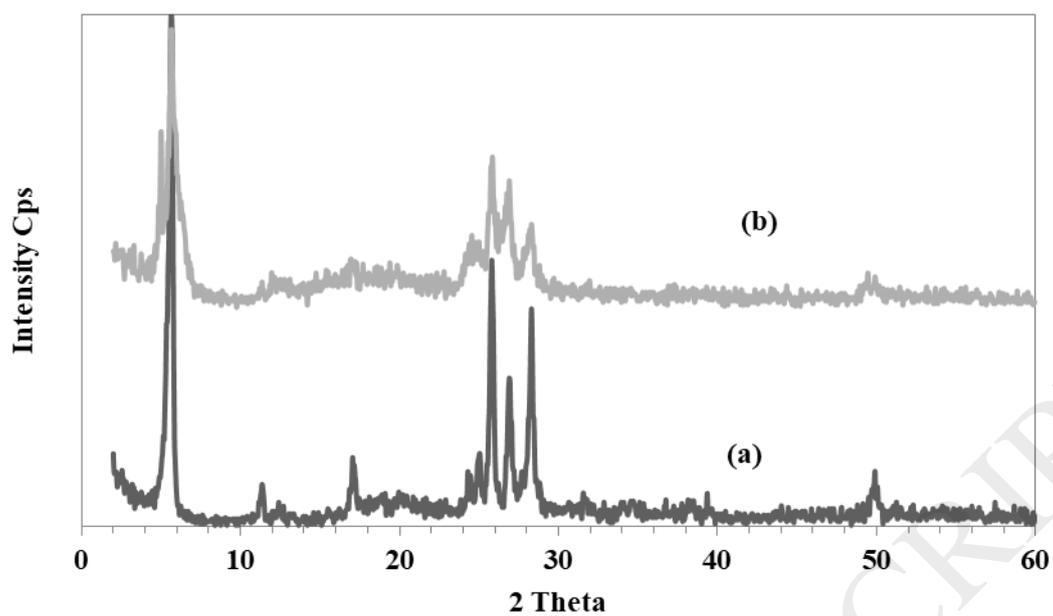


Fig.1. XRD analyses of the sorbent materials. 1.a) Mag; 1.b) Mag-C

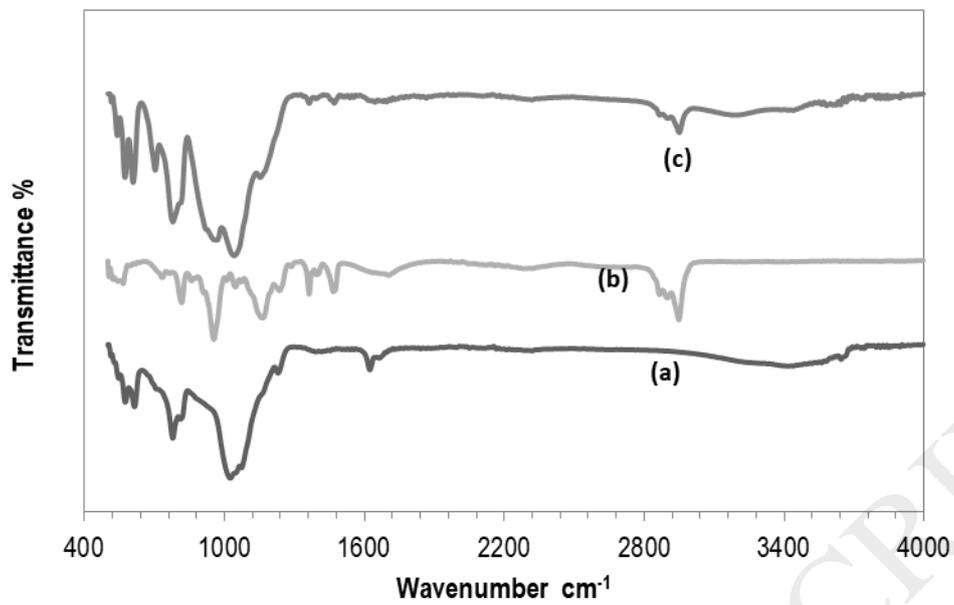


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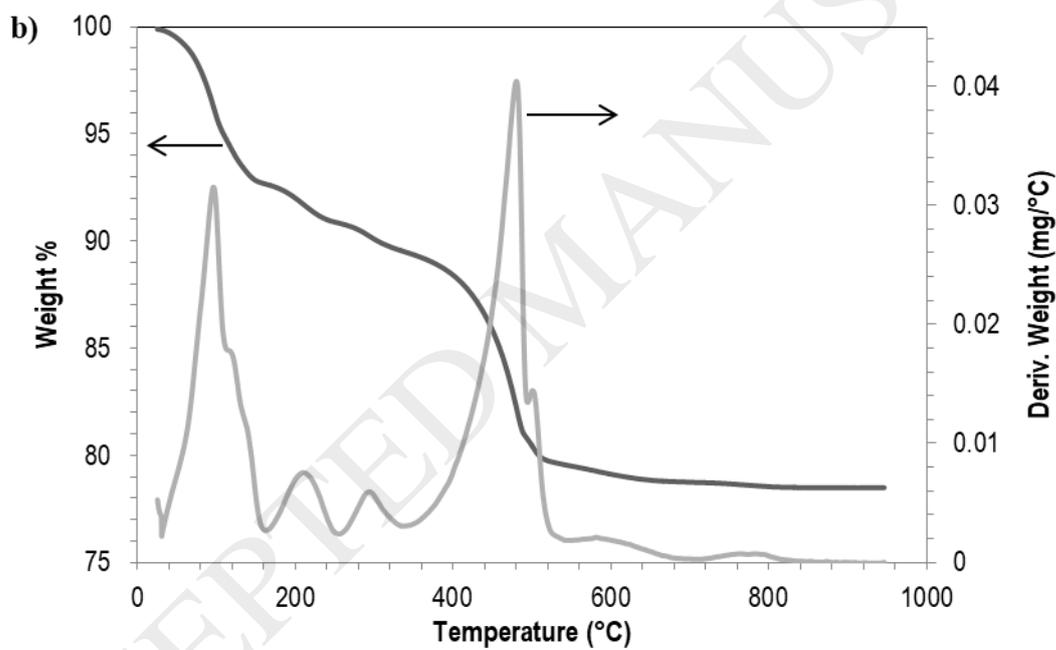
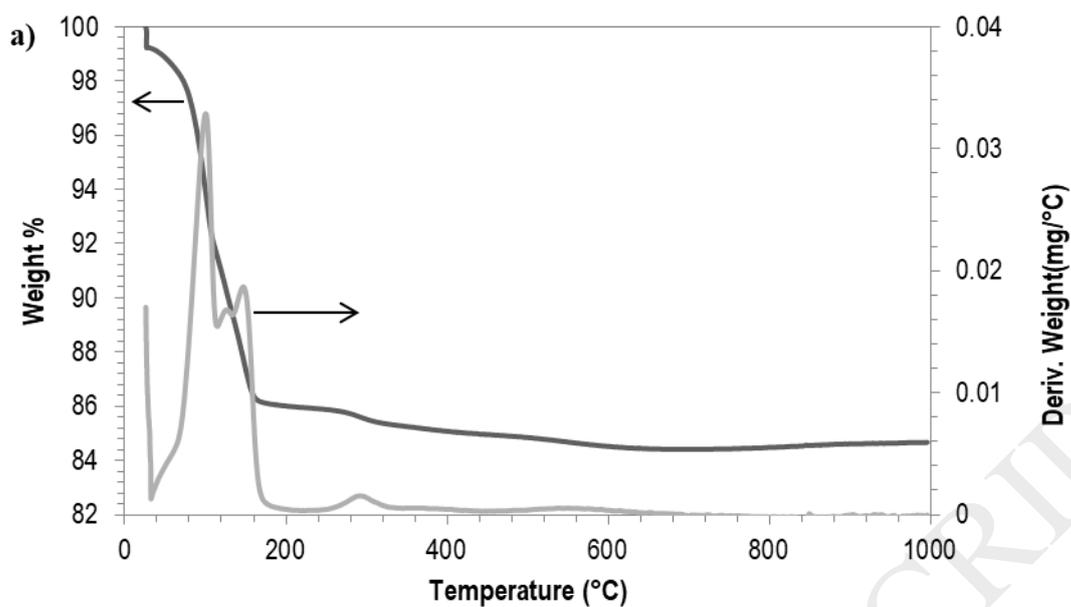


Fig.3. TGA/DTG curves of sorbent materials. 3.a) Mag; 3.b) Mag-C

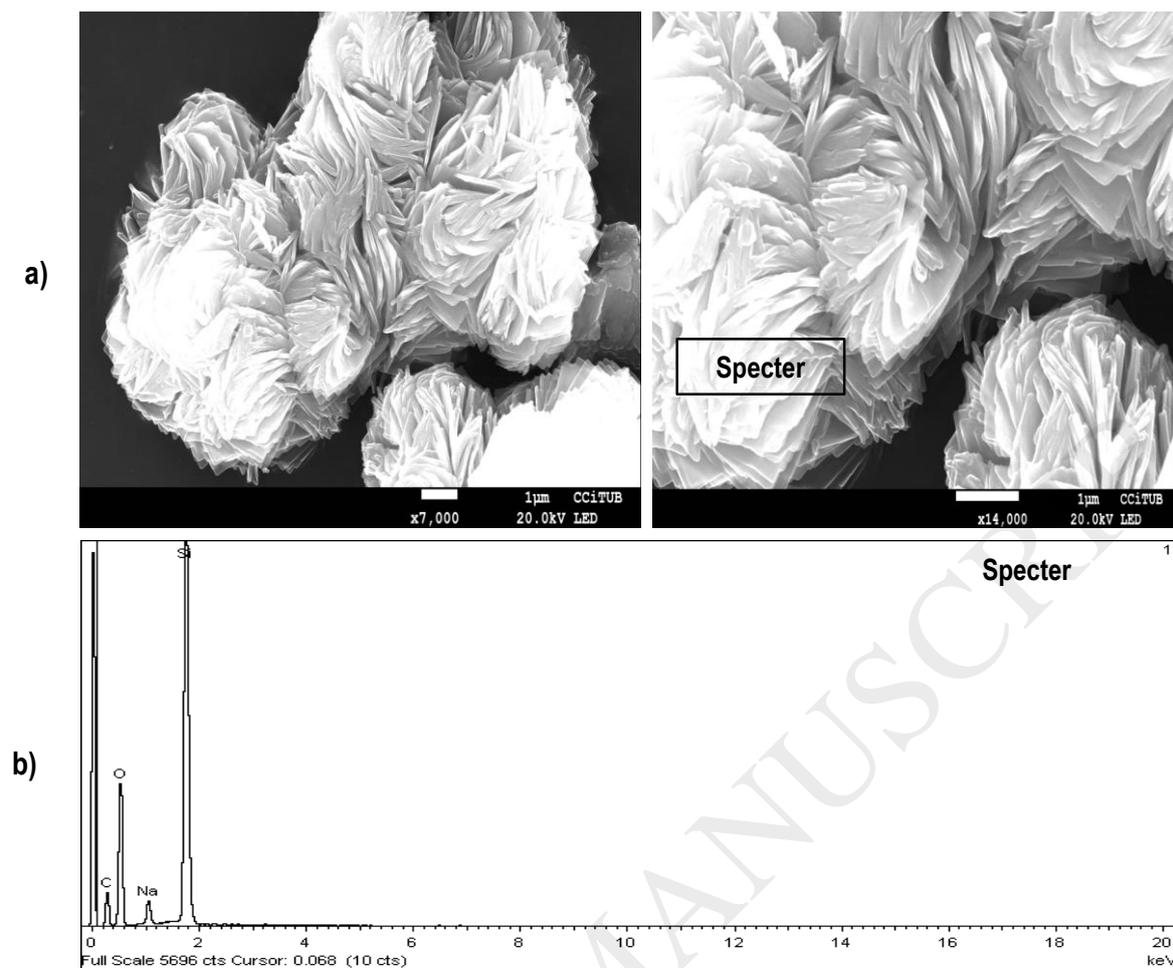


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4.b) Energy Dispersive X-ray (EDX) analysis on the surface area of the solid

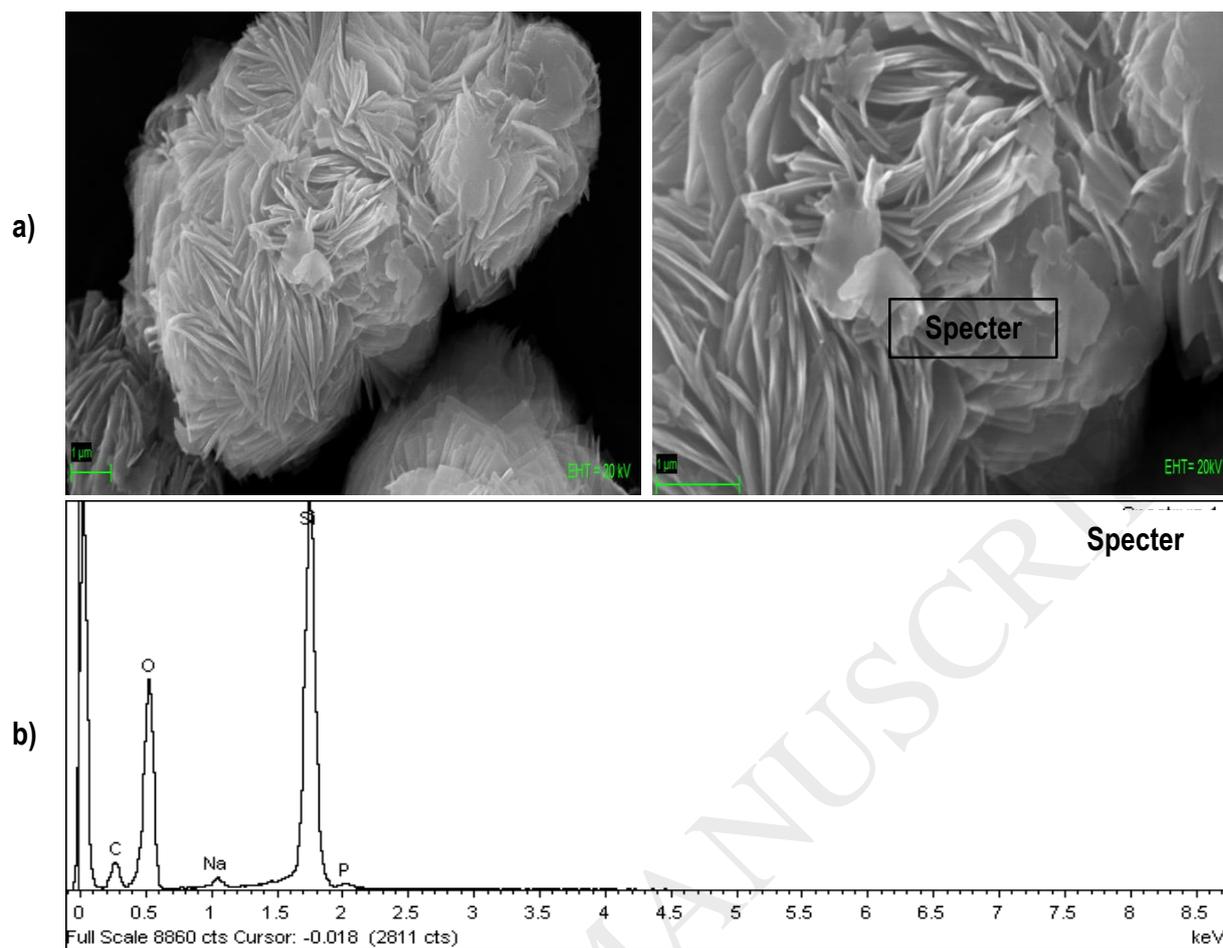


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b) Energy Dispersive X-ray (EDX) analysis on the surface area of the solid

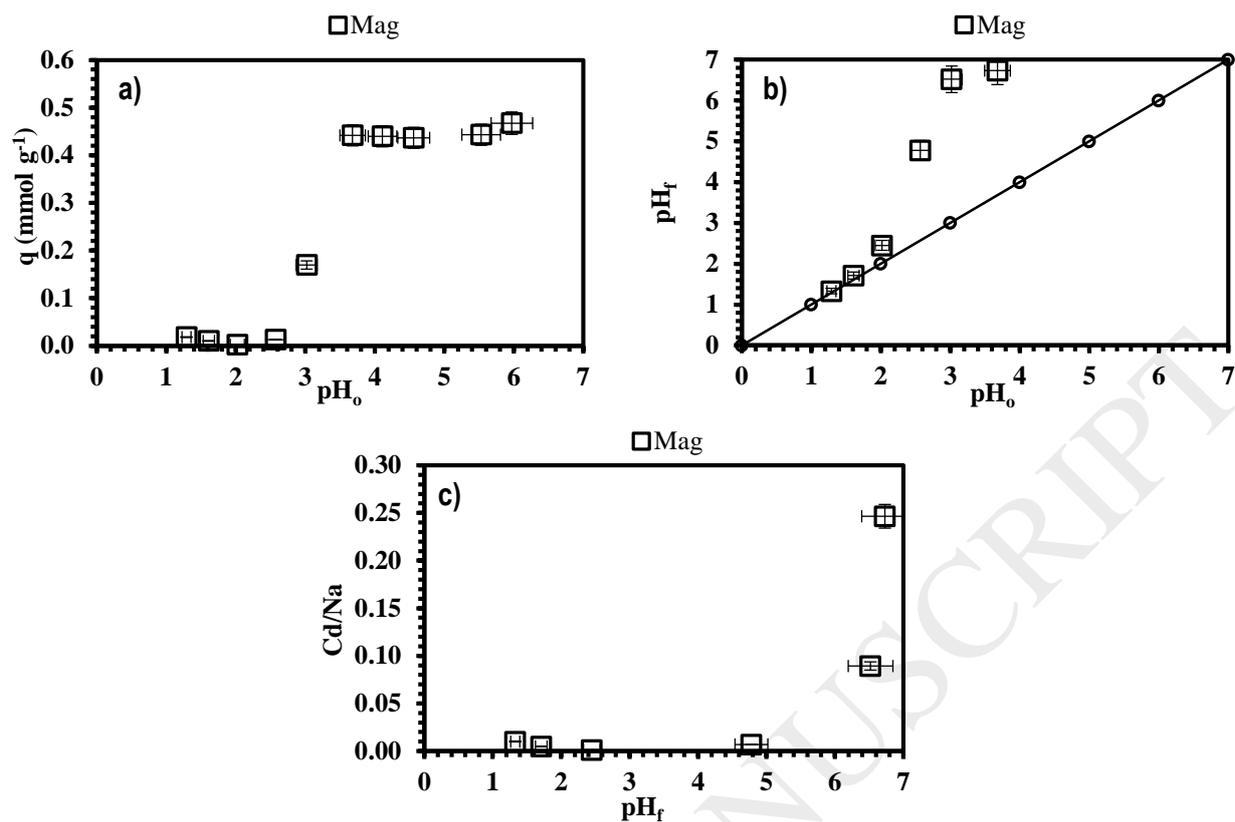


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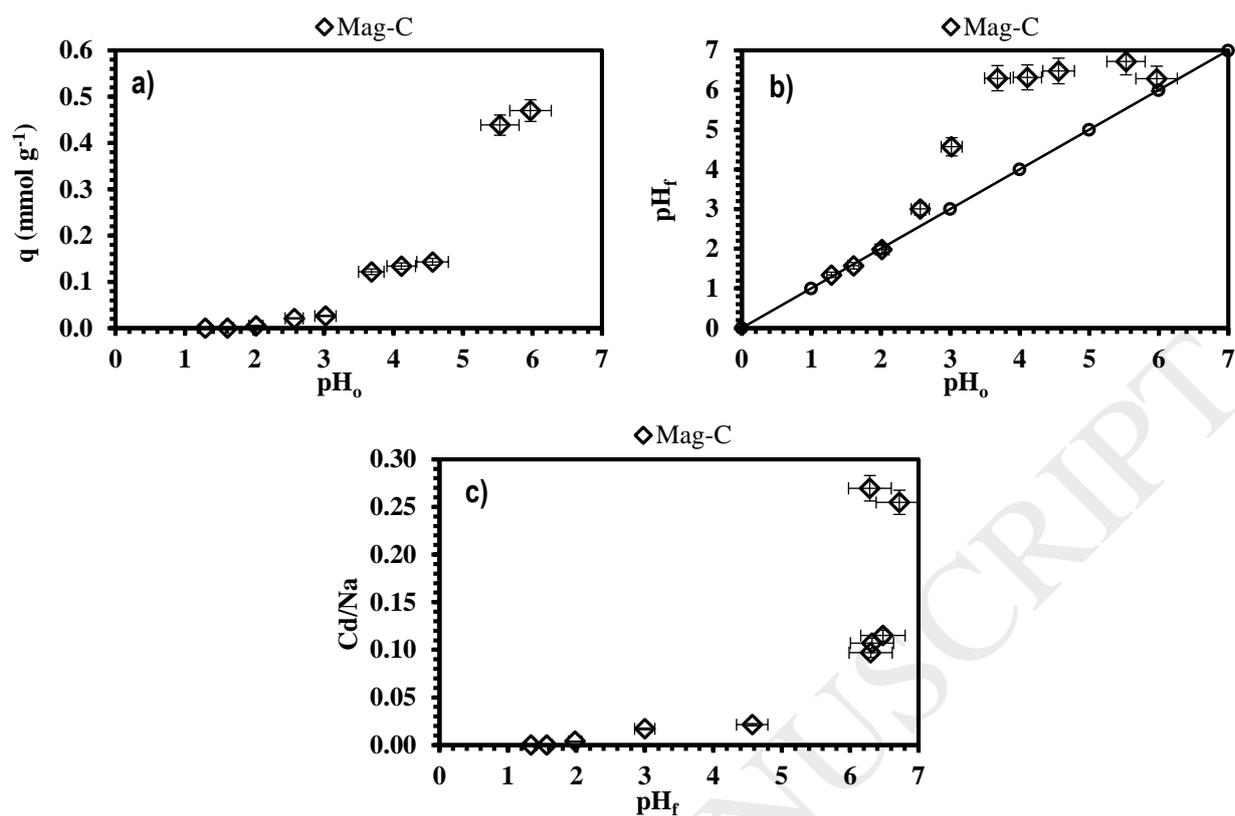


Fig.7. Influence of pH on cadmium removal using Mag-C as sorbent. 7.a) Sorption capacity. 7.b) Variations in pH. 7.c) Cadmium/sodium ratio into the solution as a function of the equilibrium pH

(T:20 °C; V: 0.025 L; m: 0.025 g; agitation speed: 180 rpm; contact time: 3 h; C₀:50 mg L⁻¹; 0.1 M NaNO₃)

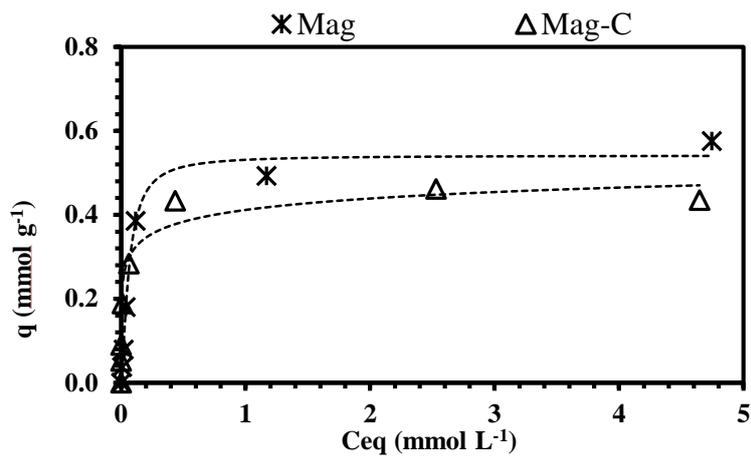


Fig.8. Isotherm plots for cadmium removal

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2; C_0 :10-1000 mg L⁻¹; 0.1 M NaNO₃)

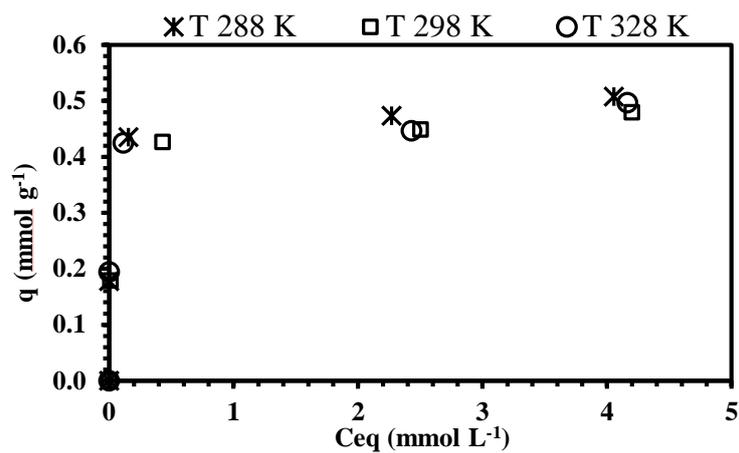


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(T: 288 K, 298 K, 328 K; V: 0.01 L; m: 0.1 g; agitation speed: 180 rpm; contact time: 3 h; pH: 2; C_0 : 10-1000 mg L⁻¹; 0.1 M NaNO₃)

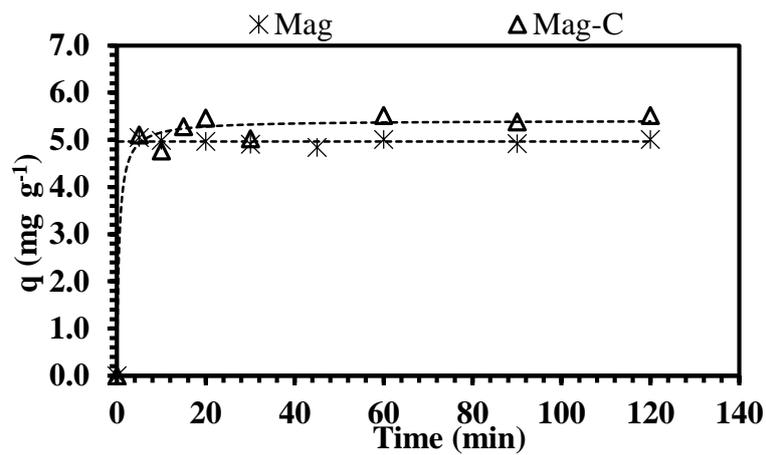


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C_0 : 50 mg L^{-1} ; 0.1 M NaNO_3)

Table 1. Langmuir, Freundlich and Sips constants of sorbent materials

Table 2. Comparison of sorption capacities of cadmium ions on different sorbents

Table 3. Kinetic parameters of sorbent materials

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Table 1. Langmuir, Freundlich and Sips constants of sorbent materials

Sorbent	Langmuir				Freundlich				Sips			
	q_{exp} (mmol g ⁻¹)	q_{max} (mmol g ⁻¹)	b (L mmol ⁻¹)	r^2	$q_{max} \cdot b$ (L g ⁻¹)	K_F (mmol ^{1-1/n} g ⁻¹ L ^{1/n})	n	r^2	q_{max} (mmol g ⁻¹)	K_s (L mmol ⁻¹)	n_s	r^2
Mag	0.57	0.57	12.88	0.977	7.34	0.42	4.05	0.85 5	0.54	51.08	0.70	0.984
Mag-C	0.44	0.45	48.14	0.928	21.66	0.40	8.20	0.94 3	0.69	1.47	4.18	0.942

Table 2. Comparison of sorption capacities of cadmium ions on different sorbents

Sorbents	Experimental conditions	Sorption capacity (mg g ⁻¹)	Sorption capacity (mmol g ⁻¹)	References
Modified silica gel (S2A)	pH= 5	1.20	0.01	[56]
Silica gel (SG)		1.13	0.10	
XAD-2- Cyanex 301	[H ₃ PO ₄] 3.2 M	1.56	0.01	[61]
XAD-7- Cyanex 301	[H ₃ PO ₄]12.7 M	11.52	0.10	
XAD-2- Cyanex 272	pH= 2	9.96	0.09	[62]
XAD-2- Cyanex 302		2.95	0.03	
Alginate–calcium carbonate	pH= 6	10.20	0.09	[57]
XAD-7- Cyanex 921	[HCl] 3 M	13.00	0.12	[63]
Duolite ES 467 Resin	pH= 4.6 T= 60	17.08	0.15	[37]
4-amine-2-mercaptopyrimidine Modified Silica Gel	pH= 3	21.69	0.19	[58]
XAD-7-Cyanex 302	[H ₃ PO ₄] 0.1 M	32.40	0.29	[60]
Chitosan-activated carbon	pH= 6	52.63	0.47	[35]
Na-magadiite	pH= 6	57.0	0.57	[Present work]
Na-magadiite-Cyanex 272		44.0	0.44	
Fe ₃ O ₄ sulfonated magnetic nanoparticle (Fe ₃ O ₄ -SO ₃ H MNP)	pH= 7	80.90	0.72	[59]
Chitosan-based materials (flakes/beads)	pH= 7	67.44 - 146.12	0.6-1.3	[55]
Chitosan-Eskom fly Ash activated	pH= 8	87.72	0.78	[34]
Algal-based material (AF-PEI)	pH= 4	97.79	0.87	[42]
Chitosan derivative	pH= 6	98.04	0.87	[33]
Polyaniline Grafted Cross-linked Chitosan Beads	pH= 6	145.0	1.29	[36]

Table 3. Kinetic parameters of sorbent materials

Experimental		PFORE			PSORE		
Sorbent	q_{exp} (mg g^{-1})	K_1 (min^{-1})	q_1 (mg g^{-1})	r^2	K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	q_2 (mg g^{-1})	r^2
Mag	5.01	20.08	4.96	0.998	25.08	4.96	0.998
Mag-C	5.51	0.63	5.29	0.978	0.37	5.41	0.984