Magnetic chitosan grafted (alkyl acrylate) composite particles: Synthesis, characterization and evaluation as adsorbents

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Abstract An efficient process for preparing a series of magnetic chitosan grafted (alkyl acrylate) composite particles as novel adsorbent materials has been proposed. Magnetite nanoparticles (Fe3O4) were produced by co-precipitation. Modified chitosan (CSg) bearing surface vinyl groups was synthesized by glycidyl methacrylate coupling in acidic aqueous solution through an epoxide ring opening mechanism. The magnetic chitosan grafted (alkyl acrylate) composites were prepared by radical copolymerization of butyl acrylate (BA), butyl methacrylate (BMA) or hexyl acrylate (HA) with ethylene glycol dimethacrylate (EGDMA) onto the modified chitosan vinyl groups, with addition of magnetite nanoparticles in suspension. The prepared particles were characterized by TEM, SEM, XRD, VSM and FTIR. Adsorption batch experiments on the newly synthesized composites were conducted using Ni(II) ions in aqueous solutions. The variables that influence the sorption capacity, namely the solution pH, initial metal ion concentration, sorbent mass, adsorption time and temperature have been investigated. The adsorption kinetics was analyzed by fitting the data into the following models: pseudo-first-order, pseudo-second-order and intraparticle diffusion. The Langmuir, Freundlich and Dubinin–Radushkevich models were used to fit the adsorption
1. Introduction

Water contamination with heavy metal ions, such as Pb(II), Cd(II), Hg(II), and Ni(II) is a serious environmental problem threatening human health (Fu and Wang, 2011). The major concern is caused by their ability to accumulate in the environment and trigger heavy metal poisoning due to the fact that they cannot be metabolized or decomposed (Ge et al., 2012). Therefore, a great deal of effort has been devoted to developing efficient ways to remove heavy metal ions from wastewater. Various technologies for the removal of heavy metals from aqueous solutions have been utilized, such as ion exchange, chemical precipitation, reverse osmosis, membrane separation, nanofiltration and adsorption (Barakat, 2011). The adsorption process is arguably one of the most eco-friendly methods and it is generally preferred because of its simplicity, high efficiency and the availability of various adsorbents (Tran et al., 2010). Numerous types of materials have been used for nickel sorption, for example activated carbon, solid humic acid, chelating resins, haematite, goethite, attapulgite, zeolite and montmorillonite (Pivarciová et al., 2014). Most recently, many research groups have explored various bio-sorbents such as natural polymers, mainly polysaccharides, due to their low cost, availability and advantageous presence of hydroxyl, amino and other active functional groups on the backbone (Sargi et al., 2015). Compared to other renewable resources, chitosan possesses two major advantages: firstly, it is inexpensive compared to commercial adsorbents; secondly, it has strong chelating ability toward a variety of pollutants (Rinaudo, 2006). Several review articles (Kyzas and Bikaris, 2015; Wu et al., 2010) on chitosan-based biosorbents have been published. However some disadvantages that limit their use in practical wastewater treatment applications have been identified (Wang and Chen, 2014): weak mechanical properties, poor chemical stability (Dodi et al., 2012), low surface area and difficult separation from the liquid phase (Ünlü and Ersoz, 2006). To overcome these problems, recent research has been focused on magnetic separation technology (Gómez-Pastora et al., 2014; Harikishore et al., 2013; Mehta et al., 2015). Chitosan magnetic composite particulate adsorbents provide multiple advantages, among which the facile separation from the aqueous phase (Kyzas and Deliyanni, 2013; Podzus et al., 2009), followed by re-generation and re-use (Demarchi et al., 2015). The polymeric shell is usually chemically modified in order to improve its mechanical stability over a wider pH range, selectivity and batch-to-batch reproducibility (Dodi et al., 2012). On the other hand, the acrylic-based adsorbents are widely applied in removal of heavy metals (Bayramoğlu and Arica, 2008), being recognized for high sorption capacity and good selectivity, combined with chemical and mechanical stability (Mahida and Patel, 2014). The possibility of grafting acrylic monomers onto the chitosan backbone has a huge potential for improving its properties (Mun et al., 2008).

In the present work, magnetic-chitosan grafted (alkyl acrylate) composite particles were prepared with the purpose of increasing surface area, mechanical stability, sorbent separation and re-usability compared to raw chitosan. The structure and morphology of the obtained particles were evaluated using FTIR, TEM, SEM, VSM and XRD. The adsorption of Ni(II) ions from aqueous solutions onto the newly synthesized magnetic-chitosan grafted (alkyl acrylate) composite particles was also investigated.

2. Experimental

2.1. Materials

Analytical grade chemicals were used as received, without further purification. Iron (III) chloride hexahydrate p.a. (FeCl₃·6H₂O), iron (II) chloride tetrahydrate p.a. (FeCl₂·4H₂O), glycidyl methacrylate ((2,3-epoxypropyl) methacrylate) (GMA) and ethylene glycol dimethacrylate (EGDMA) (both stabilized with hydroquinone monomethyl ether) were purchased from Merck, Germany. Low molecular weight chitosan (CS) (Mw = 50–190 kDa; degree of deacetylation 84.5%), butyl acrylate (BA), butyl methacrylate (BMA), hexyl acrylate (HA), 2,2-azobis(2-methylpropionamidine) dihydrochloride (I), nickel (II) chloride hexahydrate, sodium hydroxide p.a. grade and acetic acid were obtained from Sigma–Aldrich, Germany; hydrochloric acid (1 N), ethanol and acetone were procured from Chemical Company (Iasi, Romania). All solutions were prepared with ultrapure water.

2.2. Synthesis of magnetic-chitosan grafted (alkyl acrylate) composite particles

The magnetic-chitosan grafted (alkyl acrylate) composite particles were obtained using a three-step procedure, described below.

2.2.1. Magnetite nanoparticles preparation

Magnetite nanoparticles were prepared by chemical co-precipitation of Fe(II) and Fe(III) ions with a molar ratio of 2:1 upon addition of aqueous sodium hydroxide solution, as reported in a previous paper (Dodi et al., 2015). Briefly, the solutions of Fe(III) chloride hexahydrate (0.0551 moles) dissolved in 120 mL water and respectively Fe(II) chloride tetrahydrate (0.0275 moles) dissolved in 120 mL water, were mixed (500 rpm) under mild nitrogen blanket, in order to avoid the formation of iron oxidation products, such as hydroxides, in a temperature controlled water bath (65 °C). Aqueous sodium hydroxide solution (0.32 moles, 120 mL) was then added using a peristaltic pump (10 mL/min). The reaction was continued for 1 h under the same conditions. The obtained Fe₃O₄ nanoparticles (batch denoted Mag) were separated from the reaction medium by magnetic field, washed with ultrapure water until neutral pH and then kept in the refrigerator (5% aqueous dispersion) for the next step.

2.2.2. Synthesis of GMA modified chitosan (CSg)

Modified CS bearing surface vinyl groups was synthesized by GMA coupling in acidic aqueous solution through an epoxide opening mechanism, as described in a previous paper (Dodi et al., 2012). Briefly, 120 mL chitosan solution (1% in
acetic acid) was brought to pH 4 with sodium hydroxide and GMA (14.1 × 10⁻³ moles) was added; the reaction mixture was kept overnight at 50 °C with 150 rpm stirring in a thermostated water bath. The obtained solution was brought to pH 6 and the polymer precipitated with acetone and ethanol to separate the unreacted products, dried at 50 °C and kept for the next step.

2.2.3. Synthesis of magnetic-chitosan grafted (alkyl acrylate) composite particles

The magnetic-CS grafted (alkyl acrylate) composites were prepared by radical copolymerization of BA, BMA or HA with EGDMA onto the vinyl groups belonging to the modified CS, using a water soluble initiator (I), with addition of magnetite nanoparticles in suspension. In a typical experiment, 0.6 g of CS dissolved in 240 mL acetic acid solution (0.25 M) was thermostated at 50 °C in a three-necked round bottom flask equipped with mechanical stirring and nitrogen flow.

The monomer mixture, containing 0.15 mL alkyl acrylate (corresponding to 1 × 10⁻³ moles BA, 0.94 × 10⁻³ moles BMA or 0.84 × 10⁻³ moles HA, respectively) and 0.45 mL EGDMA (representing 2.3 × 10⁻³ moles), dissolved in 15 mL ethanol, followed by the magnetite nanoparticle suspension (15 mL Mag suspension with 5% solids, diluted with 45 mL water; 3.88 × 10⁻³ moles magnetite) was successively added. The I solution (2.2 × 10⁻³ moles in 0.6 mL water) was subsequently placed in the reaction vessel after stirring for 2 h at the same temperature, while maintaining the nitrogen blanket. The reaction was conducted at 50 °C for 24 h. The cleaning procedure involved multiple aqueous washes using dialysis membrane followed by an acid-base treatment to remove the soluble polymer unattached to the particles. Three distinct materials were obtained and designated as Mag-CSg-BA, Mag-CSg-BMA and Mag-CSg-HA, corresponding to the respective acrylic monomers used for grafting.

2.3. Characterization of composite particles

The morphology of the composite particles was analyzed by transmission electron microscope (TEM) and by scanning electron microscope (SEM) with field emission operating at 30 kV on dried sample suspension. The magnetic properties (saturation magnetization and coercivity) were measured using a VSM 7410 vibrating sample magnetometer. X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D8 diffractometer using monochromatic Cu Kα radiation (λ = 0.154 nm) and operating at 40 kV and 50 mA over a 2θ range from 4° to 70°. Qualitative chemical composition assessment of composite particles was performed by FTIR–ATR analysis (Frontier, Perkin Elmer). The hydrodynamic diameter and polydispersity index (ethanolic particle suspension) were examined on the Delsa Nano Submicron Particle Size Analyzer (Beckman Coulter) that uses photon correlation spectroscopy (PCS) for determining particle size suspensions in a range from 0.6 nm to 7 μm.

2.4. Adsorbent characterization

The surface composition of the particles separated after the adsorption procedure was investigated by energy dispersive X-ray spectrometry (Bruker AXS Microanalysis GmbH) on a dry sample.

2.5. Adsorption studies

Magnetic-chitosan grafted (alkyl acrylate) composite particles (batches Mag-CSg-BA, Mag-CSg-BMA and Mag-CSg-HA respectively) were used as magnetic adsorbents for the adsorption of Ni(II) ions. The adsorption behavior of Ni(II) ions was investigated in aqueous solutions using a batch procedure: a volume of 10 mL aqueous sorbent dispersion (solid mass varied from 0.025 to 0.15 g) was mixed with 10 mL metal ion solution with initial concentration in the range of 0.92–4.63 mg/mL and stirred at 150 rpm in a temperature controlled shaker (temperature controlled at fixed values between 293.15 K and 313.15 K) for a specific amount of time (from 2 to 36 h) to reach adsorption equilibrium. The effects of pH, initial concentration, sorbent mass, contact time and temperature on the metal ion adsorption process were evaluated. The concentration of Ni(II) ions was determined from the absorbance peak measured at 720 nm wavelength on a UV–Vis spectrophotometer (PG T60 UV–Vis Spectrometer) using a calibration curve. The amount of Ni(II) ion uptake is described by the distribution coefficient, Kd (mL/g), calculated using Eq. (1):

\[
K_d = \frac{(C_i - C_e)}{C_e} V \times \frac{1}{m},
\]

where \( C_i \) and \( C_e \) are the initial and respectively the equilibrium concentrations of the metal ion solution (mg/L), \( V \) is the aqueous phase volume (mL) and \( m \) is the mass of solid sorbent (g).

The equilibrium adsorption capacity of Ni(II) ions, \( q_e \) (mg/g), was calculated using the mass balance equation:

\[
q_e = \frac{(C_i - C_e)V}{m},
\]

where all the symbols are the same as previously explained.

2.6. Desorption experiments

For desorption studies, composite particles bearing previously adsorbed Ni(II) ions were treated with 0.1 M aqueous solutions of hydrochloric acid. The material was left in contact with the eluting solution for a period of 24 h at 150 rpm. The desorption ratio of the metal ions from the composite particles was calculated from the amount of metal ions adsorbed and the final concentration of metal ions in the desorption medium, according to Eq. (3):

\[
\text{Recovery} \% = \frac{\text{metal}_{\text{ads}}}{\text{metal}_{\text{ads}}}, \times 100
\]

where \( \text{metal}_{\text{ads}} \) is the amount of adsorbed metal ion (mg/g), and \( \text{metal}_{\text{ads}} \) is the amount of desorbed metal ion (mg/g). This adsorption–desorption cycle was repeated five times by using the same batch of sorbent, in order to test the re-usability of the material.

3. Results and discussions

3.1. Magnetic-CS grafted (alkyl acrylate) composite particles

The composite particles were obtained in three distinct steps:

- Magnetite nanoparticles were produced by co-precipitation in an alkaline solution as described by the chemical equation:
Fe$^{2+} + 2$Fe$^{3+} + 8$OH$^- = Fe$_3$O$_4 + 4$H$_2$O

- Modified chitosan (CSg) bearing surface vinyl groups was synthesized by GMA coupling in acidic aqueous solution through an epoxide ring opening mechanism. The modified group may be either the hydroxyl or the amino group belonging to chitosan backbone, as discussed in a previous paper published by our group (Dodi et al., 2012). Vinyl groups introduced in the first step become starting points for free radical co-polymerization.
- Magnetic-CS grafted (alkyl acrylate) composite particles, namely magnetic chitosan grafted HA, magnetic chitosan grafted BMA and chitosan grafted BA and cross-linked with EGDMA were synthesized by radical polymerization of CSg, as described in Section 2.2.3 and represented in the reaction scheme (Fig. 1).

The process yield, calculated from the ratio of experimental to theoretical composite particle weight was 82% for Mag-CSg-HA, 67% for Mag-CSg-BMA and 64% for Mag-CSg-BA synthesis, respectively. The results are consistent with the magnetization measurements (discussed in Section 3.1.3) and show that some oligomeric and/or polymeric fraction was soluble and therefore removed during the washing procedure.

### 3.1.2. Structural properties by XRD

XRD patterns of pure Fe$_3$O$_4$ and of the three types of magnetic chitosan composite particles are shown in Fig. 4A. The reflection peak positions and their relative intensities on the patterns recorded for the composite particles are similar with those recorded for pure magnetite. Seven peaks for characteristic Fe$_3$O$_4$, corresponding to (111), (220), (311), (400), (422), (511) and respectively (440) planes, were observed in all samples. Peaks related to the lattice planes at (210) and (213), characteristic to the tetragonal structure of maghemite phase (Parmar et al., 2015), are missing from all the samples.

The relative weak diffraction lines on the composite patterns indicated that the Fe$_3$O$_4$ particles were coated with an amorphous chitosan-acrylate copolymeric shell, without any phase change. An estimate of the average crystallite sizes in the pattern was attained by the widely used Scherrer equation (Ayala-Valenzuela et al., 2005) using the strongest diffraction peak at $2\theta = 35.6^\circ$, that corresponds to the (311) lattice plane:  
$$\tau = 0.92/\beta \cos \theta,$$

where $\tau$ is the average crystal grain size of the ordered (crystalline) domains, $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg angle (in degrees) and $\beta$ is the measured full-width of the strongest (311) reflection peak measured at its half maximum intensity (in radian).

The size determined with the Scherrer equation is estimated at 10 nm for the uncoated Fe$_3$O$_4$ particles, while for the magnetite particles embedded in the copolymer shell the diameter is 10.8 nm (Mag-CSg-HA), 11.3 nm (Mag-CSg-BMA) and 13.4 nm (Mag-CSg-BA), respectively. These results are consistent with those obtained by TEM technique (see above).

### 3.1.3. Magnetization measurements

Fig. 4B shows the magnetization curves of the composite particles compared with raw magnetite at room temperature. The data indicate that bare magnetite nanoparticles attained magnetizations around 66.0 emu/g. The intense black color and the high saturation magnetization suggest the absence of iron hydroxide impurity, as described by Hernández et al. (2009). The FTIR spectrum (discussed below) is consistent with this result.
The composite particles obtained in the presence of chitosan-acrylate shell show saturation magnetization values lower than those of bare nanoparticles, namely 32.3 emu/g for batch Mag-CSg-HA, 30.1 emu/g for batch Mag-CSg-BMA and 33.7 emu/g for batch Mag-CSg-BA. The results show that the added polymeric shell, non magnetic in nature, constitutes about half of the composite particle by weight. Considering the ratio between magnetite and the CS plus monomers mixture as introduced in the synthesis (0.75 g/1.2 g), the theoretical magnetite content should be about 38.5%. The resulted higher percentage is due to the fact that some polymer formed in solution or was weakly adsorbed on the particle surface and was subsequently removed during the washing step.

Another important aspect of the magnetic properties is the superparamagnetic character (zero coercivity) of the obtained composites, an advantageous feature that allows their re-use, due to the fact that magnetic interaction between particles occurs only in the presence of magnetic field.

3.1.4. FTIR analysis

Comparative FTIR spectra of bare magnetite and of the composite particles are presented in Fig. 4C. Peaks located in the range of 564–566 cm⁻¹, associated with the presence of magnetite are evidenced in all four samples. On the bare magnetite spectrum we also note the absence of peaks located either around 900 cm⁻¹, or in the 620–700 cm⁻¹ range. The first one is associated with the iron hydroxides (Montes Atenas et al., 2005) and the second one with maghemite (Namduri and Nasrazadani, 2008). The result confirms the purity of the synthesized magnetite and it is in agreement with the evidenced high saturation magnetization and the observed intense black color.

The surface modification of the Fe₂O₃ particles is confirmed by FT-IR. The absorption bands characteristic to chitosan appear at 3361 and 3353 (O–H and N–H stretching vibrations), 1459 and 1454 cm⁻¹ (C–N stretching vibrations) and respectively in the region of 1260–1144 cm⁻¹ (C–O–C and C–O stretching vibrations). The peaks at 1725, 1726 and 1727 cm⁻¹ (ester type COO⁻), 2952 cm⁻¹ (C–H) and 1459 and 1454 cm⁻¹ (C–H aliphatic) are related to the presence of acrylates (El-Fadl and El-Mohdy, 2015). The results are consistent with the presence of both magnetite and acrylate-grafted chitosan in the composite particles.

3.1.5. Particles size distribution

The hydrodynamic diameters and polydispersity index of magnetic-CS grafted (alkyl acrylate) composite particles were calculated by the CONTIN method (Durdureanu-Angheluta et al., 2012) and are reported in Table 1. The average diameters indicate a relatively polydisperse distribution evidenced by the observed differences in \(d_{10}, d_{50}\) and \(d_{90}\) values. The composites containing CS grafted with hexyl acrylate are smaller and more uniform in size. The result may be explained by the low solubility of hexyl acrylate compared to the other two monomers. The reaction system contains no surfactant and a water-soluble initiator, under monomer saturated conditions. The monomers with

![Figure 2](https://example.com/figure2.png)

**Figure 2** TEM pictures of magnetic-CS grafted (alkyl acrylate)s composite particles: batch Mag-CSg-HA (A), batch Mag-CSg-BMA (B) and batch Mag-CSg-BA (C).

![Figure 3](https://example.com/figure3.png)

**Figure 3** SEM images of composite particles (Mag-CSg-HA (A), Mag-CSg-BMA (B) and Mag-CSg-BA (C)).
higher solubility (BA and BMA) are characterized by high nucleation rate and are prone to initially produce a larger number of particles that are not colloidally stable and will therefore coagulate into larger aggregates (Chen and Sajjadi, 2009).

3.2. EDX analysis after metal ion adsorption

EDX spectra of dried samples following Ni(II) ion adsorption in optimum conditions (Fig. 5 and Table 2) evidence the peak specific to nickel element. The mapping image shows uniformly distributed adsorbate on the composite surface. The results confirmed that Ni(II) ion was efficiently adsorbed onto the surface of all three samples, with lower percentages by weight than the values calculated from the experimental adsorption capacities (as discussed in Section 3.3.3), due to the fact that EDX method is only semi-quantitative since it detects only the elements located in close proximity to the surface. The highest amount of adsorbed Ni(II) ion is present on the sample grafted with HA. This result is in agreement with the one reported below in the adsorption study section.

3.3. Adsorption study

3.3.1. Effect of the pH

The effect of the pH on the adsorption of Ni(II) ions by the magnetic composite adsorbents at 293.15 K, initial Ni (II) concentration of 2.7 mg/mL and contact time of 24 h, using 0.1 g of each material, is illustrated in Fig. 6A. The particles grafted with HA show slightly higher affinity for Ni(II) than the ones with BA and BMA at all pH values. All three materials show low adsorption capacity at low pH due to electrostatic repulsion between the metal ion and the protonated amino groups belonging to...
chitosan backbone. As the pH increases between 4.0 and 7.0, more binding sites become available and Ni(II) ion adsorption increases steeply due to less frequent competition between metal ions and protons present in solution. A relative slow increase in the range of 7.0–8.5 was observed for all three materials, with the maximum adsorption occurring at pH 8.5, probably due to simultaneous adsorption and precipitation processes. It should be noted that Ni(II) ions start to precipitate at pH > 8.5 (Pivarcˇiova´ et al., 2014). Considering these issues, we selected for the next optimization experiments a pH value situated below the Ni(II) metal ion precipitation limit, namely pH 7.

3.3.2. Effect of initial metal ion concentration

As shown in Fig. 6B, the adsorption capacity increased with increasing equilibrium metal ions concentration in the range of 0.92–4.63 mg/mL for all samples, while keeping the pH, contact time, temperature and the sorbent mass constant at 7.0, 24 h, 293.15 K and 0.1 g, respectively. This increase in loading capacity of the sorbent with respect to the metal ions concentration can be explained by the high driving force for mass transfer, as described by Konaganti et al. (2010). The same trend was observed on chitosan grafted poly(alkyl methacrylate), poly(ethyl methacrylate), poly(butyl methacrylate) and poly(hexyl methacrylate) derivatives used for Orange-G removal in adsorption batch experiments, where the authors explain that the driving force to overcome liquid and solid phase mass transfer resistances for the adsorption process increases with increasing the dye concentration.

3.3.3. Effect of sorbent mass

As shown in Fig. 6C, with the raise of adsorbent dosage in the range of 0.025–0.15 g, while keeping the pH, contact time, temperature and the initial metal concentration constant at 7, 24 h, 293.15 K and 2.7 mg/mL, respectively, the Ni(II) ions removal steadily decreases for all samples. This result can be attributed to overlap or aggregation of adsorption sites by increasing the magnetic composite particles quantity, resulting in a decrease in the total surface area available for Ni(II) ions.

3.3.4. Effect of contact time

Fig. 6D shows the removal of Ni(II) ions as a function of contact time, a parameter used to assess the potential for practical applications. A rapid increase in the adsorbed amount of the ions occurred within the first hour during the adsorption process for all three samples. The plots indicate that the adsorption equilibrium of Ni(II) ions on magnetic CS grafted (alkyl acrylate) composites is attained within 12 h with almost 90% efficiency. Away from the equilibrium time, adsorption is found to be nearly constant for up to 36 h. The results indicated that the adsorption occurred mainly on the surface of the particle sorbent and it is driven by van der Waals forces. Accordingly, in order to ensure adsorption equilibrium had been reached, all the later experiments were carried out at a contact time of 24 h.

3.3.5. Adsorption kinetic study

Adsorption kinetic models, namely pseudo-first order, pseudo-second order and intraparticle diffusion were utilized to identify what type of adsorption mechanism occurs on the magnetic CS grafted (alkyl acrylate) composites.

The pseudo-first order equation is expressed as follows:

\[ q_t = q_e (1 - e^{-k_1t}), \]  

and the linear form given is as follows:

\[ \ln(q_e - q_t) = \ln q_e - k_1t, \]
where \( q_e \) and \( q_t \) (mg/g) are the amounts adsorbed at equilibrium and at any time (h) respectively, and \( k_1 \) (h\(^{-1}\)) is the adsorption rate constant of pseudo-first-order reaction. The values of \( k_1 \) were calculated from the plots of \( \ln(q_e - q_t) \) versus \( t \) (He et al., 2015).

The pseudo-second order kinetic equation is given by

\[
\frac{t}{q_t} = \frac{1}{k_2q_0^2} + \frac{1}{q_0}
\]

where \( k_2 \) (g/mg/h) is the kinetic constant; its value was determined from the plots of \( \frac{t}{q_t} \) against \( t \) (Dinu and Dragan, 2010).

The third kinetic equation is the intraparticle diffusion model, given by the equation

\[
q_t = k_{id}t^{0.5} + c_i,
\]

where \( k_{id} \) (mg/g h\(^{0.5}\)) is the rate constant of intraparticle diffusion controlled sorption, and \( c_i \) is the thickness of the boundary layer (Hameed et al., 2008).

The fitting kinetic parameters of magnetic CS grafted (alkyl acrylate) composites according to pseudo-first-order, pseudo-second-order and intraparticle diffusion models are shown in Table 3. The results evidenced that pseudo-first-order and pseudo-second-order kinetic models were in better agreement with the experimental data. The uptake of Ni(II) ions occurred in two stages as follows:

- an initial rapid stage lasting for 4 h, in which approximately 76% of the available Ni(II) ions were adsorbed;
- a second stage, with much slower rate, starting at 4 h and lasting until the equilibrium plateau is reached (24 h).

The pseudo-first order kinetic model fits best the experimental data in the initial stage, when a lot of binding sites are available on the adsorbent. The second stage was best fitted by the pseudo-second-order kinetic model, indicating that the chemical process was the rate-limiting step for the remaining sites (Dinu and Dragan, 2010).

The experimental data were also analyzed using the intraparticle diffusion model but the correlation coefficients for all sorbents were much lower than those obtained according to the pseudo-first-order and pseudo-second-order models.

3.3.6. Effect of temperature and thermodynamic data

Fig. 6E illustrates the effect of the temperature on the adsorption process carried out at three different temperatures (293.15 K, 303.15 K and 313.15 K), while keeping all the other parameters constant, namely the pH (7.0), contact time (24 h), target ion concentration (2.7 mg/mL) and sorbent mass (0.1 g).

The thermodynamic parameters, namely the enthalpy (\( \Delta H \)) and entropy (\( \Delta S \)) associated with the adsorption process were calculated from the slope and intercept of the linear plot of \( \ln K_d \) versus the reciprocal value of the temperature (1/T) using the following equation:

\[
\ln K_d = \frac{\Delta S - \Delta H}{RT},
\]

where \( K_d \) is the distribution coefficient.

The Gibbs free energy of specific adsorption (\( \Delta G \)) was calculated using the following equation:

\[
\Delta G = \Delta H - T\Delta S.
\]

The estimated thermodynamic parameters are presented in Table 4. It was observed that the distribution coefficient \( K_d \) decreased with the increase in temperature. \( \Delta H \) values are negative for all materials (−8.17 J/mol for Mag-CSg-HA, −9.16 J/mol for Mag-CSg-BMA, respectively −11.39 J/mol for Mag-CSg-BA), evidencing the exothermic nature of the adsorption. Also, the estimated enthalpy value of less than 40 kJ/mol indicates that the sorbate binding to the surface occurs mainly by physical, rather than chemical sorption. The values of \( \Delta S \) were found to be positive due to the physical nature of the sorption process. The negative values of \( \Delta G \) indicate a spontaneous nature of the adsorption process, with a favorable contribution from both the enthalpic and the entropic components.

3.3.7. Adsorption isotherms

The analysis of the isotherm data allows the evaluation of adsorption capacities and the interaction of nickel ion species with the magnetic CS grafted (alkyl acrylate) composites. Experimental data obtained from the study of initial adsorbate concentration on adsorption capacity were evaluated with the three mostly used adsorption models, namely Langmuir, Freundlich and Dubinin–Radushkevich. The linearized forms of the equations representing the models were used. The adsorption isotherm experiments were carried out at constant pH, contact time, temperature and sorbent mass, and kept respectively at 7.0, 24 h, 293.15 K and 0.1 g.

The Langmuir model predicts the formation of an adsorbed solute monolayer on a surface with a finite number of identical sites suggesting that the adsorbent surface is homogeneous, with no side interactions between the adsorbed ions (Konaganti et al., 2010). The linearized expression of the Langmuir isotherm is shown in Eq. (11):

\[
\frac{C_S}{q_e} = \frac{1}{K_L \times q_m} + \frac{C_e}{q_m},
\]

where \( C_e \) is the sorbate equilibrium concentration in the liquid phase (mg/L), \( q_e \) is the amount of solute adsorbed per mass of adsorbent (mg/g), \( q_m \) characterizes the saturated adsorption capacity (mg/g) and \( K_L \) is related to the affinity of the sorbate for the adsorbent (L/mg).
The Freundlich adsorption isotherm considers the existence of a heterogeneous multilayered adsorbing surface. The empirical equation takes the following form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e,$$

where $K_F$ represents the relative sorption capacity and $\frac{1}{n}$ characterizes the nature and the intensity of the sorption process and also the distribution of active sites.

Dubinin–Radushkevich (D–R) isotherm describes the characteristic porosity of the adsorbent and the apparent energy of adsorption.

**Figure 6**  Adsorption of Ni (II) ions from aqueous solution using magnetic CS grafted (alkyl acrylate) composite particles: (A) Effect of pH, (B) effect of initial metal ion concentration, (C) effect of sorbent mass, (D) effect of contact time, and (E) effect of temperature.
The Freundlich model describes the process better than the Langmuir or D–R models for the removal of nickel ions in the entire studied concentration range; thus, the adsorption was multilayered. The maximum adsorption capacity \( q_{\text{m}} \) of magnetic chitosan grafted (alkyl acrylate) composites obeyed the following order: Mag-CSg-HA > Mag-CSg-BMA > Mag-CSg-BA. The composite particles obtained by grafting with the monomer containing the longer, more hydrophobic side chains are more efficient as adsorbents due to their smaller size and most probably to a looser surface configuration, with larger spaces between binding sites that increase their availability.

The mean adsorption energy \( E_S \) calculated from the D–R isotherm is helpful in predicting the nature of the adsorption process: physical (at \( E_S \) values in the range of 1–8 kJ/mol) or chemical (at \( E_S \) values of more than 8 kJ/mol) (Chen and Chen, 2009). The values obtained for the studied systems (1.55 kJ/mol, 1.70 kJ/mol and 1.55 kJ/mol, for Mag-CSg-HA, Mag-CSg-BMA and Mag-CSg-BA, respectively) indicate that adsorption process is physical in nature on all three adsorbents.

A comparison of the Ni(II) adsorption capacity, \( q_{\text{m}} \) (mg/g) on magnetic chitosan grafted (alkyl acrylate) composite particles and some other chitosan-containing materials used as adsorbents and reported in the literatures (Kyzas and Kostoglou, 2015; Monier et al., 2010; Tran et al., 2010; Zeng et al., 2015; Zhou et al., 2009), is shown in Table 6. According to the values listed in Table 6, the adsorption capacities found in this work for the ion under study, are higher than most of those reported in the literature. One exception is represented by the cross-linked chitosan microspheres grafted with ethylenimine, that present a swelling–adsorption dynamic interaction with the metal ion. However, the main inconvenience of the adsorbents based on chitosan bearing imino groups is represented by the impossibility to regenerate and reuse them.

Therefore, the novel composites synthesized in this study can be recommended as an alternative material for Ni(II) ions removal from wastewater by using magnetically aided adsorption technology.

### Table 4 Thermodynamic parameters for the sorption of Ni (II) on magnetic CS grafted (alkyl acrylate) composites.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( \Delta H ) (J/mol)</th>
<th>( \Delta S ) (J/mol K)</th>
<th>( \Delta G ) (kJ/mol)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>293.15 K</td>
</tr>
<tr>
<td>Mag-CSg-HA</td>
<td>-8.17</td>
<td>60.52</td>
<td>-17.74</td>
<td>0.88</td>
</tr>
<tr>
<td>Mag-CSg-BMA</td>
<td>-9.16</td>
<td>72.83</td>
<td>-21.35</td>
<td>0.87</td>
</tr>
<tr>
<td>Mag-CSg-BA</td>
<td>-11.39</td>
<td>97.93</td>
<td>-28.72</td>
<td>0.96</td>
</tr>
</tbody>
</table>

### Table 5 Constants obtained from the Langmuir, Freundlich and Dubinin–Radushkevich sorption isotherms.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
<th>Dubinin–Radushkevich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R^2 ) ( q_m ) (mg/g) ( K_L ) (L/mg)</td>
<td>( R^2 ) ( K_F n )</td>
<td>( R^2 ) ( X_m ) (mg/g) ( K_{DR} ) (mol²/kJ²) ( E_S )</td>
</tr>
<tr>
<td>Mag-CSg-HA</td>
<td>0.92 121.96 0.16</td>
<td>0.99 38.90 0.95</td>
<td>0.96 7.81 -0.21 1.55</td>
</tr>
<tr>
<td>Mag-CSg-BMA</td>
<td>0.91 104.17 0.21</td>
<td>0.99 36.44 1</td>
<td>0.98 7.50 -0.19 1.70</td>
</tr>
<tr>
<td>Mag-CSg-BA</td>
<td>0.94 101.01 0.20</td>
<td>0.97 24.54 0.84</td>
<td>0.96 7.81 -0.21 1.55</td>
</tr>
</tbody>
</table>

### Table 6 Comparison of theoretical adsorption capacities \( q_m \) (mg/g) for Ni(II) ions of different sorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>( q_m ) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan microspheres</td>
<td>76</td>
<td>Kyzas and</td>
</tr>
<tr>
<td>Chitosan–chlorosulfonic acid microspheres</td>
<td>85</td>
<td>Kostoglou (2015)</td>
</tr>
<tr>
<td>Chitosan-ethylenimine microspheres</td>
<td>152</td>
<td></td>
</tr>
<tr>
<td>Chitosan/rectorie nano-hybrid composite</td>
<td>13.32</td>
<td>Zeng et al. (2015)</td>
</tr>
<tr>
<td>Chitosan/magnetite nanocomposite beads</td>
<td>63.33</td>
<td>Tran et al. (2010)</td>
</tr>
<tr>
<td>Thiourea-modified magnetic chitosan microspheres</td>
<td>15.3</td>
<td>Zhou et al. (2009)</td>
</tr>
<tr>
<td>Cross-linked magnetic chitosan-isatin Schiff's base</td>
<td>40.15</td>
<td>Monier et al. (2010)</td>
</tr>
<tr>
<td>Mag-CSg-HA</td>
<td>121.96</td>
<td>This study</td>
</tr>
<tr>
<td>Mag-CSg-BMA</td>
<td>104.17</td>
<td>This study</td>
</tr>
<tr>
<td>Mag-CSg-BA</td>
<td>101.01</td>
<td>This study</td>
</tr>
</tbody>
</table>

The linear form of the D–R isotherm is represented as

\[
\ln q_e = \ln X_m - K_{DR} e^2
\]

where \( K_{DR} \) is a constant related to the adsorption energy (mol²/kJ²), \( X_m \) is a constant that indicates the sorption degree characterizing the sorbent (mg/g) and \( e \) is the Polanyi potential shown in Eq. (14):

\[
e = RT \ln(1 + 1/C_e)
\]

where \( T \) is the absolute temperature (K) and \( R \) is the ideal gas constant \((R = 8.314 \text{ J/mol K})\).

The free energy of adsorption \( E_S \) is calculated with the Eq. (15):

\[
E_S = (-2K_{DR})^{-1/2}
\]

The corresponding Langmuir, Freundlich and D–R parameters for all samples are reported in Table 5. According to the resulted correlation coefficients (Table 5), we conclude that
The results of the re-generation study are summarized in Table 7. An almost complete elution of the previously loaded Ni(II) ions was achieved within 24 h by using 0.1 M HCl solution. The materials were tested in five sorption/desorption cycles with no decrease in their capacity. The results indicated that the magnetic CS grafted (alkyl acrylate) composite particles loaded with the toxic metal ions could be regenerated and repeatedly used, a very important property for an industrial application to avoid the secondary pollution in the wastewater treatment.

3.4. Re-generation and reuse studies

The kinetic analysis shows that the process of Ni(II) ions adsorption on magnetic composite particles is a three-step procedure, namely, magnetic chitosan grafted HA, BMA and BA, crosslinked with EGDMA, were synthesized via a three-step procedure, characterized using TEM, SEM, XRD, VSM and FTIR and successfully used for the adsorption of Ni(II) ions from aqueous solutions. The optimum parameters for the adsorption process were determined for all three materials. The adsorption capacity conforms to the following order: Fe₃O₄–CSg–HA > Fe₃O₄–CSg–BA > Fe₃O₄–CSg–BMA. The kinetic analysis shows that the process of Ni(II) ions adsorption on magnetic chitosan grafted (alkyl acrylate) composite particles is a complex one, starting with a fast period described by a pseudo-first-order model and followed by a slow stage that fits a pseudo-second-order model. This behavior is probably due to the presence of binding sites with different degrees of accessibility. The adsorption isotherms for the sorption of the metal ions on magnetic composite particles were determined and modeled using the Langmuir and Dubinin–Radushkevich equation models. Results of batch equilibrium tests indicated that Freundlich isotherm describes the Ni(II) ion adsorption process in the best way. The adsorption process has been found to be exothermic and characterized by physical sorption. Desorption experiments conducted by employing diluted HCl solutions showed that the loaded materials could be easily regenerated and re-used in five cycles, without significant loss in adsorption capacity. The obtained magnetic supports demonstrated their potential use in wastewater treatment by a simple and inexpensive method.

Acknowledgment

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References


