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Magnetic poly(glycidyl methacrylate-co-divinylbenzene) with amino groups for chromium VI removal

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Abstract

Superparamagnetic microspheres of poly(glycidyl methacrylate-*co*-divinylbenzene) were produced via suspension polymerization and were functionalized with ethylenediamine, diethylenetriamine and triethylenetetramine. The results of Cr(VI) adsorption showed better removal at pH 2. The adsorptive process was best described by the pseudo-second order model, and an equilibrium isotherm study indicated the best suitability of the Langmuir model. The microspheres modified with ethylenediamine had greater adsorption capacity and the highest ΔH value at pH=2 and 318 K. The choice among EDA, DETA, and TETA as substituent groups depends on balancing adsorption efficiency, selectivity and process kinetics. In these studies, R14-DETA showed better performance than the others. The adsorbents had ΔH around 40-45 kJ/mol and ΔS between 148-159 J/mol.K. The results indicated an endothermic process, of chemical nature, with negative ΔG values. This study indicates the potential for applications in Cr(VI) removal.

Keywords: *amino functionalization, Cr(VI) removal, divinylbenzene, glycidyl methacrylate, magnetic microspheres.*

Data Availability: Research data is available upon request from the corresponding author.

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1. Introduction

Industrial wastewater often contains heavy metals. These pollutants can accumulate when discharged in the environment, where they pose a threat to the survival of many animal and plant species, including cancer and other diseases. Among these pollutants, chromium and its compounds directly contribute to industrial wastewater contamination, derived from the leather tanning, textile, electroplating, paint and pigment industries[1,2]. Chromium naturally occurs in two valence states, Cr(III) and Cr(VI). While Cr(III) is generally regarded as less toxic, Cr(VI) is widely recognized as a human carcinogen and an environmental pollutant. According to the International Agency for Research on Cancer (IARC), Cr(VI) is classified as a Group 1 human carcinogen[2,3].

There are several possible treatments for chromium-containing wastewater, such as reduction, precipitation, ion exchange, and reverse osmosis, among others. However, the adsorption process has the benefit of easy and quick removal, so it has strong potential to eliminate Cr(VI) ions from wastewater. Moreover, adsorption also does not produce any additional harmful substances[4,5].

Recently, numerous adsorbents have been developed to remove Cr(VI) ions, like iron-based adsorbents, metal hydroxides, clay and cellulose[1,4,5]. Some of these approaches can be costly and less effective at low pollutant concentrations. In addition, they may have low adsorption capacities or difficulty to achieve this target due to poor thermal stability, regeneration, and weak mechanical properties[1,5].

Polymeric resins are an interesting class of adsorbents. Their advantage over other adsorbent classes is that in addition to being easily manufactured with a wide range of physical-chemical properties (particle size, size distribution, porosity, hydrophobicity, etc.), they also can be chemically modified to introduce functional groups, producing specific sorbents[6]. Copolymers based on glycidyl methacrylate (GMA) have attracted attention due to the presence of the epoxy group. It is possible by opening the epoxide ring to introduce iminodiacetate, thiol, azole, and pyrazole groups, among others. Sorbents with amine groups are also possible and stand out for their high adsorption, fast kinetics and good selectivity for heavy metal ions, as well as chemical and mechanical stability[7].

Maksin et al.[6] synthesized porous and nonporous poly(metacrylate glydidyl-*co*-ethylene glycol dimetacrylate) (P(GMA-*co*-EGDMA)) by suspension copolymerization and functionalization with diethylenetriamine (DETA).

They found monolayer adsorption capacity at pH 1.8 and 25◦C for porous materials of this species ranging from 132 to 143 mg.g^{-1} , and 25.6 mg.g^{-1} for nonporous materials. Besides this, the thermodynamic parameters revealed that the Cr(VI) adsorption on polymers was endothermic and spontaneous.

Malović et al.[7] also synthesized P(GMA-*co*-EGDMA) by suspension polymerization with the amine groups ethylene diamine (EDA), diethylene triamine (DETA) and triethylene tetramine (TETA). The most pronounced increase in specific surface area (75%) was observed for P(GMA-*co*-EGDMA)-TETA. At pH 1.8. The selectivity of P(GMA-*co*-EGDMA)-TETA with smaller particles of Cr(VI) involving other heavy metal ions was 8.5:1.

Nastasović et al.[8] synthesized a sample of poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) and another of poly(GMA-*co*-EGDMA) by suspension polymerization with different porosities. Subsequently, they functionalized the samples through a ring-opening reaction of the pendant epoxide groups with ethylenediamine (EDA) and diethylenetriamine (DETA). The sorption kinetics of Cr(VI), Cu(II), Co(II), Cd(II) and Ni(II) were studied under non-competitive conditions (from a single-component solution of the metal salt) and competitive conditions (mixture of different metal solutions). The adsorption of Cr(VI) ions was very fast, presumably because the sorption process occurred predominantly on the surface of the amino-functionalized granules, with no diffusion of oxyanions into the resin pores, an assumption confirmed by the poor fit of the intraparticle diffusion model.

These studies have demonstrated the potential use of aminated glycidyl methacrylate resins as adsorbents. However, these resins had no magnetic properties. The main advantage of the presence of magnetic material in polymers is that after adsorption, the spent adsorbent is easily separated from the medium by applying an external magnetic field[2]. Indeed, magnetic resins can be reused multiple times and are also suitable for use in continuous processes[9].

Wang et al.[10] synthesized a magnetic poly(GMA-*co*-EGDMA) with EDA groups. The maximum adsorption capacities obtained from the Langmuir model were 236.9, 242.1 and 253.2 mg.g^{-1} at 298, 308 and 318 K, respectively. The Cr(VI) adsorption equilibrium was achieved within 120 min. and the adsorption kinetics were compatible with the pseudo-second order equation. The thermodynamic parameters of the sorption process revealed that the adsorption was spontaneous and endothermic.

Zhao et al.[11] also studied magnetic poly(GMA-MMA-DVB)-EDA obtained by suspension polymerization. The authors evaluated the synthesized materials for the removal of Cr(VI). The adsorption data observed at the optimized condition, i.e., 35 ◦C and pH of 2.5, were well fitted by the Langmuir isotherm, and the maximum adsorption capacity increased with rising amount of the functional agent, GMA. The adsorption kinetics data were modeled by the pseudo-second order equation, and the adsorption of Cr(VI) by all the polymers reached equilibrium in 60 min.

Although there are published works describing the synthesis of magnetic polymeric microspheres based on functionalized glycidyl methacrylate (GMA)[10-12] , we found no study of the influence of the chain size of the amine groups, uptake kinetics and sorption isotherm model in amino functionalized magnetic copolymers based in GMA and DVB for chromium (VI) removal from aqueous effluents.

2. Materials and Methods

2.1 Materials

Glycidyl methacrylate (GMA) (Aldrich; purity - 97%); divinylbenzene (DVB) (commercial grade, Nitriflex, Brazil); oleic acid PA (B'Herzog, Brazil); sodium hydroxide PA (B'Herzog, Brazil); ferric chloride PA ($FeCl_3$) (Vetec, Brazil); ferrous sulfate PA ($FeSO_4$) (Vetec, Brazil)); potassium dichromate PA (Merck); ethanol (commercial grade, Sumatex, Brazil); diphenylcarbazide PA (Merck); benzoyl peroxide PA (BPO) (Vetec, Brazil); ethylenediamine (Aldrich; purity - 99%) (EDA); diethylenetetramine (DETA) (Aldrich; purity - 99%); triethylenetetramine (TETA) (Aldrich; purity - 97%); dimethylformamide (DMF) (Aldrich; purity - 99%); and poly(vinyl alcohol) (PVA) (AirProducts, hydrolysis degree of 85% and MM = 80,000 to125,000) were all used as received.

2.2 Magnetic glycidyl methacrylate-co-divinylbenzene copolymer synthesis

Poly(GMA-*co*-DVB)-M samples were prepared by radical suspension copolymerization. The monomer phase containing the mixture (98% mol of GMA and 2% mol of DVB), BPO (1% mol relative to the total monomers), as initiator, and magnetite (10% w/v) was suspended in the aqueous phase, consisting of 260 g of water and 1.2 g of PVA. The copolymerization was carried out at 70 °C for 24 h with a stirring rate of 800 rpm.

2.3 Amino magnetic copolymer synthesis

The polymer particles were washed with water and ethanol, kept in ethanol for 12 h and dried at 50 °C for 24 h. The amino functionalization occurred from 2 g of poly(GMA-*co*-DVB) (R14) reacted with 10 mL of EDA, DETA or TETA and 25 mL of DMF at 55 °C, for 72 h, at 300 rpm. The amino copolymers were then washed several times with ethanol and water, filtered and dried at 50 °C for 24 hours[13].

2.4 Characterization

The magnetic amino copolymers were analyzed by scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) (FEI Inspect 55 microscope). The samples were coated with a thin layer of gold. Images were generated by secondary electron detectors with acceleration voltage of 20 kV. The thermal properties were evaluated with a Q50 V6.4 Build 193 thermogravimetric analyzer (TA Instruments). The material was heated from 10 to 500 °C in a nitrogen atmosphere with a flow rate of 100 mL min^{-1} and speed of 20 °C min^{-1}. The magnetic properties were determined by vibrating sample magnetometry (VSM) (Lake Shore 7400) with an applied field of H = ±12 kOe, under ambient conditions. The distribution and average diameter of the magnetic copolymers were obtained by light scattering detection (LSD) (Malvern Nano-ZS analyzer).

Elemental analysis was performed with a CHNS/O analyzer (PerkinElmer 2400 Series II), applying dynamic flash combustion for sample analysis. Fourier-transform infrared spectroscopy together with attenuated total reflectance (FTIR-ATR) was also used. The spectrum range ranged from 4000 to 400 cm^{-1} with resolution of 16 cm^{-1} (PerkinElmer Spectrum One). The UV-Vis spectrophotometric technique (Biospectro SP-22, λ=540 nm) was used to determine the chromium adsorbed on the copolymers.

2.5 Effect of pH on the Cr(VI) adsorption on the amino magnetic copolymers

To evaluate the effect of pH on the Cr(VI) adsorption capacity of the magnetic adsorbents, we tested pH values of 2, 4, 5, 6, 7, 8, 10 and 12. Thus, samples of 100 mg of the copolymer were added to 20 mL of 100 mg L^{-1} Cr(VI) solutions at different pH values previously adjusted with NaOH and/or HCl solutions. The systems remained under constant stirring at 25 °C for 24 h in a thermostatic bath. After this time, the resin was separated from the medium by the action of a magnet and the supernatant was analyzed by UV-Vis after reaction of these ions with 1,5-diphenylcarbazide to determine the remaining Cr(VI) content and calculate the removal rate.

2.6 Adsorption kinetics of Cr(VI) on the amino magnetic copolymers

The kinetic analysis of the adsorption process was carried out at temperatures of 25, 30, 35, 40 and 45 °C. The experiments were performed in batches with 0.25 g of copolymer at different concentrations of Cr(VI) (5, 15, 20, 25, 50, 75, 100, 150 and 200 mg.L^{-1}) at pH = 2.0. Samples were shaken and aliquots of the supernatant were removed after different intervals (0, 5, 10, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 360 and 1400 min). The Cr(VI) concentration was determined by UV-Vis after reaction of these ions with 1,5-diphenylcarbazide. The interpretation of the experimental data and the mechanisms controlling the adsorption process was adjusted to the kinetic models, investigated and validated by the correlation coefficients of their linearized equations: [log (qe - qt) vs t] for the pseudo-first order model; [t/qt vs t] for the pseudo-second order model; and [qt vs t1/2] for the intraparticle diffusion model.

2.7 Adsorption isotherm of Cr(VI) in the amino magnetic copolymers

The adsorption isotherm was analyzed in batch experiments, by placing 0.25 g of copolymer in contact with a series of Cr(VI) solutions in concentrations of 50, 100 and 200 mg Cr(VI).L^{-1}, pH = 2, for 24h. In order to evaluate the effect of temperature on the adsorption process, the isotherms were evaluated at 298.15K, 303.15K, 308.15K, 313.15K and 318.15K. The adsorption results were fitted to the Langmuir and Freundlich models. To calculate the maximum adsorbed capacity (q_{MAX}) and the adsorption constant (K_L), the Langmuir model was adopted. The experimental points were fitted to the model using the method of least squares (simple linear regression). The Cr(VI) concentration was determined by UV-Vis.

3. Results and Discussion

3.1 Characterization of the material

The elemental analysis (EA) results for the magnetic poly(glycidyl methacrylate-*co*-divinylbenzene) (P(GMA-*co*-DVB)-M) before modification (R14) and the samples modified with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA) are presented in Table S1, Supplementary Material. In the R14 copolymer, a substantial amount of epoxy groups was obtained, which consequently led to more amino groups attached to the surface of the copolymers, The increase in the nitrogen content in all the amino-functionalized copolymers indicated the success of the chemical modification, by demonstrating that amino groups had been introduced in the magnetic poly(GMA-*co*-DVB) microspheres. Furthermore, the amino resin functionalized with triethylenetetramine (R14-TETA) had the highest nitrogen content. This result was expected, since TETA has a greater number of amino groups[7].

FTIR-ATR spectra were obtained for all samples (Figure S1, Supplementary Material). Characteristic bands were observed between 1720-1729 cm^{-1} (υC=O), corresponding to the GMA ester carbonyl absorption band. The bands at 847 and 992 cm^{-1} were attributed to epoxide groups in copolymer R14. After the ring-opening reaction with the different amines, new bands appeared at 1560, 1559 and 1555 cm^{-1}, corresponding to the δN-H vibrations in the copolymers R14-EDA, R14-DETA and R14-TETA, respectively. These results clearly indicated that the ester groups successfully reacted with the amines. A band referring to the secondary amine appeared around 3225-3295 cm^{-1} in all amino functionalized copolymers. Although the υNH_2 vibrations appeared as a sharp band with weak intensity, the bands of υOH were broad and strong in the region between 3500-3400cm^{-1}. Thus, the vibrations for these groups may have overlapped[7]. The absorption bands found at approximately 847 and 992 cm^{-1} (epoxide ring vibrations), 1255-1259 and 1455 cm^{-1} (δ(CH) of the epoxide group) associated with the three functionalized copolymers did not completely disappear from the spectra. They can be attributed to the epoxide groups located inside the microspheres, which were inaccessible to react with the amino groups[7].

Figure S2 (Supplementary Material) shows P(GMA-*co*-DVB)-M scanning electron microscopy (SEM) images of all samples. There were no significant changes in the morphology. The spherical shape remained, indicating good structural resistance during chemical modification. Apparently, the magnetic particles were distributed over the microspheres' surface grouped into small dots, instead of being randomly distributed. We found similar results in the literature[14-16].

Table S2 in the Supplementary Material presents the diameter, magnetic properties and thermal resistance of the microspheres obtained. As can be seen, there was no significant change in the microspheres' average size (d(0.5)). This result indicates that no fragmentation or agglomeration occurred during the chemical modification reactions. With regard to magnetization, copolymer R14 had twice the saturation magnetization (M_S) as the modified copolymers.

Since M_S is directly proportional to the amount of magnetic material incorporated, it is possible that the lower values found for the chemically modified microspheres were caused by the leaching of the magnetite located on their surface during the chemical reactions[17]. Similar M_S values were also found for chemically modified copolymers based on styrene and divinylbenzene by other authors[18]. The M_R/M_S (residual magnetization/saturation magnetization) values are reported in Table S2 of the, Supplementary Material. All values are considered low and indicate an appreciable amount of superparamagnetic particles contained in the microspheres[19]. This characteristic is very important because it guarantees that the microspheres will not remain agglomerated after the magnetic field is removed subsequent to the separation process. If they remained clustered, it would make their regeneration difficult. Table S2 in the Supplementary Material also reports the P-(GMA-*co*-DVB)-M thermogravimetric analysis (TGA) results for all samples. Apparently, the amino groups' incorporation did not cause any change in the initial degradation temperature (T_{ONSET}) and also the temperature of maximum degradation rate (T_{MAX}), since the technique's error was ±4%. The mass loss can be attributed to degradation of the organic material in the copolymer. These residues were very similar, to the point of being considered equal when taking into account the random error of the equipment. The only exception was the copolymer functionalized with triethylenetetramine, for which the difference in relation to the R14 copolymer was about 31% higher. The material obtained as waste probably was iron, which was added in the form of an oxide to give the final material the required magnetic property. The *in situ* copolymerization was performed with particulate magnetite and the particles' distribution in the resin was completely random. We expected the level of incorporation of the magnetic material not to have biased behavior. Varying iron contents can even be obtained from the same series of measures.

3.2 Effect of pH on the adsorption of Cr(VI) on the amino magnetic copolymers

Figure S3 (Supplementary Material) shows the effect of pH on the Cr(VI) adsorption (% removal and q) on the results of using the amino functionalized copolymers R14-EDA, R14-DETA and R14-TETA. As can be seen, the optimum range of adsorption of Cr(VI) ions by the three different adsorbents occurred in the acidic pH range (below 6). achieving greatest adsorption at pH=2. On the other hand, the adsorption decreased at basic pH (above 6) until pH=8 and remained constant up to pH 12. The pH value is an important factor affecting the adsorption behavior of adsorbents because of its effect on the surface charge and the protonation degree of functional groups on the active sites of the adsorbent[10].

Bayramoğlu et al.[20] reported that the adsorption of Cr(VI) ions depends on the protonation or deprotonation of amino groups on the microspheres' surface. In aqueous solutions, Cr(VI) exists in the form of chromic acid (H_2CrO_4) and dichromate ($Cr_2O_7^{2-}$) (Supplementary Material). In turn, Cr(VI) behaves like an oxyanion according to its aqueous chemistry, and these species' fraction is dependent on the chromium concentration and pH of the solution[21]. Anionic forms, such as chromate (CrO_4^{2-}), can be adsorbed at pH>6, while dichromate ($Cr_2O_7^{2-}$) and hydrogenchromate ($HCrO_4^-$) can be adsorbed at pH between 1-6[10]. Therefore, the distribution of the species of Cr(VI) might have been the main variable affecting the removal of Cr(VI) ions by the adsorbent. The amino groups on the magnetic microspheres' surface can also affect the type of electrostatic interaction between the metal ions and the sorbent surface for Cr(VI) adsorption. In addition, at lower pH values, the protonated amine group of amino magnetic microspheres causes increased electrostatic attraction between NH_3^+ and the sorbate anions[21]. Thus, at acidic pH, the amino groups of the adsorbent microspheres R14-EDA, R14-DETA and R14-TETA can be positively charged, leading to electrostatic attraction with the negatively charged chromium (VI) species, since the main species at lower pH was $HCrO_4^-$. We can thus conclude that pH dependence of Cr(VI) involves a protic equilibrium in which the protonated $HCrO_4^-$ species of the oxyanions influence the adsorption.

According to Malović et al.[7], under the same reaction conditions, the degree of conversion of epoxide groups decreased in order from ethylenediamine to triethylenetetramine. This was expected, since the limitation of the reaction occurs due to a steric hindrance effect, which is one of the main problems in the functionalization of adsorbents with large groups. The higher the degree of conversion of epoxy groups into amine groups, the greater will be the quantity of NH_2 groups to be protonated. Therefore, the expected order of the adsorption capacity (q or %removal) is R14-EDA>R14-DETA>R14-TETA. The chemical modification with EDA, DETA and TETA causes the opening of the epoxy ring, and a hydroxyl group is formed together with the amino groups. The hydroxyl comprises a chelating site. However, the number of chelating sites increases gradually according to the number of nitrogen atoms, making them nucleophilic groups, but with different molecular volumes. EDA, a secondary amine, has a nitrogen atom bonded to two alkyl groups. DETA and TETA are tertiary amines, with three and four alkyl groups bonded to the nitrogen atoms, respectively. The additional alkyl groups in DETA and TETA are responsible for increasing the electron density of the nitrogen atoms, making them more significant nucleophiles than EDA. It is known that metal ions can have difficulty diffusing into aminated microspheres due to strong steric hindrance and the cross-linking structures formed by long-chain amino groups, which in turn can result in a lower number of amino groups to be protonated. Amino groups can also easily interact with amino groups adjacent to the hydrogen bond, which leads to significant steric hindrance and an increase in the number of ineffective amino groups[22]. This may explain why R14-TETA had lower adsorption than R14-DETA, despite its higher nitrogen percentage. In metal removal, R14-DETA also had the highest efficiency, with 98.4% (pH= 2), compared to R14-EDA, with 89.6% removal at the same pH. This better result can perhaps be attributed to the presence of a substantial amount of protonated amino groups on the copolymer's surface. This is unlike the prediction of Malovic *et al.* R14-TETA had a lower sorption capacity than the others. Another possible explanation involves the relatively large size of Cr(VI) anionic species, the steric hindrances in interactions with amino group sites provoked by the rigid structure of R14-TETA, and mass transfer resistance[6].

3.3 Adsorption isotherms of the amino magnetic copolymers

The experimental adsorption isotherms for different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15 K) were determined (Table S3, Supplementary Material). The experimental data fitted the Langmuir model better than the Freundlich model, because the former presented correlation coefficients closer to one. The parameters q_{MAX} (mg.g^{-1}) and K_L (L.mg^{-1}) are the Langmuir constants associated, respectively, with the capacity and energy. It is also known that the temperature increase is inversely proportional to the reaction medium's viscosity. As a consequence, there are increases in the kinetic energy and diffusion of the solute molecules into the adsorbent, thus favoring the mass transfer from molecules on the external layer and inside the adsorbent particles' internal pores[23].

We applied the Langmuir model to calculate the maximum adsorbed capacity (q_{MAX}) and the adsorption constant (K_L)[24]. Comparison of the three copolymers in the same temperature range revealed that R14-DETA showed the best results in the Cr(VI) adsorption and also the lowest values of K_Lr, indicating it is the copolymer that requires the least energy to achieve adsorption. The maximum adsorption value estimated was 78.21 mg.g^{-1}, at 45 °C (318.15 K). In general, temperature increase favored the Cr(VI) adsorption in all amino functionalized copolymers, regardless of the original amino group's size and/or the number of amino groups bonded to the copolymer (EDA – two amino groups; DETA – three amino groups; TETA – four amino groups) (Figure S4, Supplementary Material). Huang and Chen[25] reported a DETA functionalized magnetic adsorbent which was prepared by covalent bonding of polyacrylic acid (PAA) and obtained maximum Cr(VI) adsorption capacity (q_{MAX}) of 11.24 mg.g$^{–1}$ at 25 ºC. Another similar EDA functionalized adsorbent, based on magnetic glycidyl methacrylate, presented q_{MAX} = 61.35 mg.g^{-1} at 35 ºC[11]. Comparison of these results with ours at the same temperatures indicates that both the EDA copolymer (R14-EDA) and DETA copolymer (R-14-DETA) had more significant adsorption values (60.35 mg.g^{-1} at 25 ºC and 73.20 mg.g^{-1} at 35 º C, respectively). The results presented in this regard are consistent with the elemental analysis results described in Table S1 of the Supplementary Material for all amino functionalized copolymers. Of particular note, when the nitrogen percentage increased in R14-EDA (N=6.50%) and R14-DETA (N=6.98%), their q_{MAX} values also increased at all temperatures and in the same order. Although R14-TETA achieved the greatest nitrogen incorporation (N=7.71%), this result was not observed in its q_{MAX} values. This can be explained by the steric hindrance effect caused by the presence of larger groups in this copolymer[4,6]. Probably not all amino groups present in R14-TETA were available for the Cr(VI) adsorption process due to the relatively large size of Cr(VI) anionic species[6]. The higher q_{MAX} values can also indicate prominence of amino groups available in the copolymers synthesized in this work, which are promising particles for Cr(VI) removal from wastewater.

3.4 Adsorption kinetics of Cr(VI) of the amino magnetic copolymers

In order to investigate the controlling mechanism of the Cr(VI) adsorption process, we used kinetic models, validated by the correlation coefficients of their linearized equations: [log (qe - qt) vs t] for the pseudo-first order model; [t/qt vs t] for the pseudo-second order model; and [qt vs $t^{1/2}$] for the intraparticle diffusion model. All the kinetic parameters were obtained for each model, where K_{o1} (min^{-1}) represents the adsorption kinetic rate constant for the pseudo-first order model, K_{o2} (g mg^{-1}. min^{-1}) is the adsorption kinetic rate constant for the pseudo-second order model, and K_d is the rate constant in the intraparticle diffusion model. The correlation coefficients and linearized equations of these three kinetic models for the R14 copolymer functionalized by the three different amines (R14-EDA, R14-DETA and R14-TETA) are reported in Tables S4, S5 and S6 of the Supplementary Material. For all three kinetic models fitted, the reaction rates increased with rising temperature of all the functionalized copolymers studied. Furthermore, at the temperatures analyzed, the best fits of the experimental data were provided by the pseudo-second order model, with the correlation coefficients being closer to one (R^2=0.99) for most of the copolymers. Thus, the adsorption of Cr(VI) on the amino magnetic copolymers was best described by the pseudo-second order kinetic model, in which the adsorption capacity of the adsorbent is determined by the chemical bonding (chemisorption) between the Cr(VI) and functional groups on the adsorbent surface (amino magnetic copolymers)[26].

Figure S5 (Supplementary Material) shows the variation of Cr(VI) concentrations in the liquid phase (C/C_O) as a function of the contact time of the different amino magnetic copolymers. C and C_O correspond to the concentration of the metals at time *t* and at the initial concentration. According to Sun and Xu[27], the first stage of adsorption can be affected by the adsorbate concentration and agitation. Therefore, increasing the concentration of the adsorbate in the initial part can accelerate its diffusion from the solution to the surface of the adsorbent. Next, adsorption becomes dependent on the nature of the adsorbate molecules. At the end of the process, the third stage is generally considered the determining stage, which depends on the nature of the adsorbent as its reactive sites become saturated. We observed that the adsorption of Cr(VI) followed this pattern as described in the literature. It was faster in the initial stage and became slower when approaching the final equilibrium. Moreover, equilibrium for Cr(VI) removal occurred in approximately 300 min for all amino-functionalized copolymers. Equilibrium occurs because over time, the number of empty sites decreases, which progressively reduces the percentage of Cr(VI) removal. Otherwise, the adsorbent sites became saturated, and from that moment on, the sorption becomes slow in longer time intervals[28]. The adsorption speed was directly proportional to the concentration gradient. As the saturation of the adsorption sites occurred, the concentration decreased[29]. The control of the adsorption mechanism of this process is chemisorption, involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate[4].

3.5 Determination of thermodynamic parameters of Cr(VI) in the amino magnetic copolymers

We studied the thermodynamic parameters of adsorption in a range of 298.15 to 318.15 K (Table S7, Supplementary Material). The increase in temperature favored the removal of Cr(VI) oxyanions from the solution, considering that the free energy values increased in modulus. Among the three copolymers evaluated, the adsorbent R14-EDA was the most favored by the increase in temperature from 25 to 45 °C, with an increase in free energy of 123%. The negative $\Delta G°$ values confirmed its spontaneous nature, and the adsorption process was feasible because the increase in $\Delta G°$ modulus was directly proportional to temperature. This indicated that the affinity of Cr(VI) for amino magnetic copolymers was greater at higher temperature. The standard enthalpy values ($\Delta H°$) for the adsorption of Cr(VI) were 41.51 kJ/mol (R14-EDA), 44.80 kJ/mol (R14-DETA) and 41.85 kJ/mol (R14-TETA), while the standard entropy ($\Delta S°$) values were 148.32 J/mol.K, 159.42 J/mol.K and 150.55 J/mol.K, respectively. The positive value showed that Cr(VI) adsorption was an endothermic process, in agreement with the increase in adsorption capacity with rising temperature observed (Item 3.3). In addition, we also noted that the values of the Langmuir constant (K_L) increased with rising temperature, confirming the endothermic nature of the adsorption (Table S3, Supplementary Material). Furthermore, the positive results indicated that randomness increased at the solid/solution interface during the Cr(VI) adsorption on the magnetic amino copolymers. The R14-DETA adsorbent presented the highest $\Delta H°$ value, indicating its greater binding energy with the Cr(VI). The positive values of $\Delta H°$ and $\Delta S°$ suggest that entropy contributed more than enthalpy to obtain negative values of $\Delta G°$. The magnitudes of $\Delta H°$ of R14-EDA, R14-DETA and R14-TETA were above 20.9 kJ.mol^{-1}. This confirmed that the nature of the adsorption was by chemisorption, in agreement with the results obtained in the study of kinetic models[30]. These results show that all amino magnetic copolymers synthesized in this work can be used as adsorbents in conventional processes for decontamination of water or effluents containing hexavalent chromium (Cr(VI)).

4. Conclusions

The results presented here improve the understanding of Cr(VI) adsorptive processes as well as the different magnetic adsorbent synthesis routes with a weak base (amino functionalized). During the copolymers' amino functionalization, their magnetic properties were maintained as well as their superparamagnetism and thermal resistance. The results demonstrated that the Cr(VI) adsorption process depends on the pH of amino magnetic copolymers. All amino magnetic copolymers studied have strong potential use as Cr(VI) adsorbents in aqueous media. However, R14-DETA had the highest maximum removal capacity values (q_{MAX}), of 63.95 mg.g^{-1} at 298.15 K and 77.35 mg. g^{-1} at 318.15 K. The kinetic modeling showed that the effectiveness of Cr(VI) adsorption from aqueous solutions strongly depends on the adsorption dynamics. Thermodynamic studies showed that the Cr(VI) adsorption on the functionalized copolymers presented 41.5 kJ/mol $<\Delta H<$ 44.8 kJ/mol and 148 J/mol.K $<\Delta S<$ 159 J/mol.K. The results indicated an endothermic process having a chemical nature, with energetically favorable sorption and negative ΔG values as well as growth in modulus with increasing temperature. The adsorptive process became more favorable with increasing temperature, and despite being endothermic, adsorption was spontaneous and entropically directed.

5. Authors' Contributions

- **Conceptualization** – Washington José Fernandes Formiga; Marcos Antonio da Silva Costa.
- **Data curation** – Washington José Fernandes Formiga; Marcos Antonio da Silva Costa.
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Supplementary Material

Supplementary material accompanies this paper.

Table S1. Elemental analysis of the P(GMA-co-DVB)-M before (R14) and after functionalization with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA).

Figure S1. P(GMA-co-DVB)-M FTIR-ATR spetra before (R14) and after functionalization with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA). R14: GMA/DVB = 98/2; BPO = 1% (mol BPO/mol monomers); magnetite = 10% w/v; T = 80 °C).

Figure S2. P(GMA-co-DVB)-M SEM images: a) before (R14) and after functionalization with b) ethylenediamine (R14-EDA), c) diethylenetriamine (R14-DETA), and d) triethylenetetramine (R14-TETA) (2500x magnification, R14: GMA/DVB = 98/2; BPO = 1% (mol BPO/mol of monomers); magnetite = 10%w/v; T = 80 °C).

Table S2. P(GMA-co-DVB)-M average size, magnetic properties, and thermal degradation results before (R14) and after functionalization with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA).

Figure S3. Effect of pH on the Cr(VI) adsorption by P(GMA-co-DVB)-M: functionalization with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA) (C0 = 100 mg Cr(VI).L-1; Volume = 50 mL; stirring speed = 200 rpm; temperature = 25 °C; 24h).

Table S3. Parameters of adjustments to the Langmuir and Freundlich models for different temperatures used in the Cr(VI) adsorption by P(GMA-co-DVB)-M: functionalization with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA).

Figure S4. Adsorption isotherms of Cr(VI) adsorption by P(GMA-co-DVB)-M: functionalization with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA) at different temperatures, 24h, pH=2.

Table S4. R14-EDA copolymer velocity constants obtained in the kinetic fits for temperatures of 298, 303, 308, 313 and 318K.

Table S5. R14-DETA copolymer velocity constants obtained in the kinetic fits for temperatures of 298, 303, 308, 313 and 318K.

Table S6. R14-TETA copolymer velocity constants obtained in the kinetic fits for temperatures of 298, 303, 308, 313 and 318 K.

Figure S5. Effect of contact time on Cr(VI) adsorption by P(GMA-co-DVB)-M (5,0g.L^{-1}) functionalization with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA). (Co – initial concentration of Cr(VI); C - concentration at any given time; at 25°C; pH=2; 200rpm; C_0=100mg/L).

Table S7. Equilibrium parameters for calculating the Gibbs free energy of the assortative process and analysis of the thermodynamic parameters of the Gibbs equation in the Cr(VI) adsorption by P(GMA-co-DVB)-M: functionalization with ethylenediamine (R14-EDA), diethylenetriamine (R14-DETA) and triethylenetetramine (R14-TETA).

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