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Preparation of Magnetic Poly(glycidyl Methacrylate-Co-Divinylbenzene) Microspheres with amino or Quaternary Groups for Cr(VI) Removal from Aqueous Solutions

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ABSTRACT

This paper describes the preparation and characterization of magnetic poly(glycidylmetacrylate-co-divinylbenzene) with amino (R14-en) or quaternary (R14-enQ) groups on the surface for chromium removal from aqueous solutions. The adsorption process of the Cr (VI) with R14-en was dependent on the pH, and the highest adsorption values occurred in a pH range of 4 to 6s. In contrast, the adsorption of R14-enQ, because of its quaternary group (a strong base), was practically independent of the solution's pH. The kinetic studies showed that the experimental data on adsorption of Cr (VI) best fitted the pseudo second-order model, for both copolymers, suggesting that the interaction between the adsorbent and adsorbate occurs by chemisorption. The Langmuir isotherm model presented the best fit to the experimental data in equilibrium, indicating that the adsorption de Cr (VI) occurs on a monolayer of the heterogeneous surface of the adsorbent.

Keywords: Poly(glycidylmethacrylate-co-divinylbenzene), magnetic microbeads, chromium (VI), adsorption

I. INTRODUCTION

Heavy metal pollution is one of the most important environmental problems today. Toxic heavy metals such as Cr, Ni, Cd, Pb, Hg, Zn, Co and Cu contained in untreated or poorly treated industrial wastewater discharged into water bodies tend to accumulate through the food chain [1]. Chromium is considered to be the priority toxic pollutant. It is widely used in industrial activities such as electronic components manufacturing, paint manufacturing, mechanical alloying, tanning of animal hides, metallurgical alloying, and pulp processing [2,3]. Hexavalent chromium, which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), possesses significantly higher level of toxicity than the other valence states [4] due to its carcinogenic properties. Thus, it causes many health problems for people [2,3,5]. The World Health Organization (WHO) recommends a limit of 0.05 mg L-1 in drinking water (World Health Organization, 2006), a value adopted by several national environmental agencies [5].

Many methods are used to remove Cr(VI), including chemical precipitation, ion-exchange, adsorption, membrane filtration and electrochemical treatment technologies, among others. When large volumes of effluents contain relatively low concentrations, the capital and operational costs often limit the efficiency and the effectiveness of these methods [1,2]. Compared with other methods, adsorption is generally recognized as the most promising and widely used technique due to its low cost, high efficiency, regeneration ability and environmental friendliness [6]. It is commonly applied to remove heavy metal ions from water samples and aqueous solutions [5]. Several adsorbents have been studied for Cr(VI) removal, such as activated charcoal, metal oxide nanoparticles, synthesized polymer beads, and farm wastes [6,7].

Synthesized polymer beads based on glycidyl methacrylate (GMA) have been studied as adsorbents for removal of toxic heavy metal ions because their surface properties can be modified by the available functional groups to promote their adsorption ability [8–

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11]. The epoxide group of GMA has high reactivity with amine compounds, and amino-functionalized adsorbents have shown outstanding ability to remove Cr(VI) from wastewater. The amino groups are easily protonated under acidic condition. Thus, the Cr (VI) can be adsorbed onto the adsorbent by electrostatic interaction and ion exchange [6,11].

The use of magnetic beads in separation processes has many advantages. They can be easily separated from the reaction medium by applying a magnetic field [10,12–14]. Wang et al. [6] prepared polymer beads with amino groups by using GMA as functional monomer in the presence of Fe_3O_4. The Langmuir equation was appropriate to describe the chromium removal from an aqueous solution. Sun et al. [15] obtained microbeads of superparamagnetic polyethylenimine-functionalized poly(glycidyl methacrylate) with good properties to remove chromium VI from aqueous solutions. The adsorption isotherm of the adsorbent was found to fit the Langmuir model, with the maximum adsorption capacity of 492.61 mg/g.

The present work describes the preparation of magnetic poly(glycidylmetacrylate-co- divinylbenzene) with amino or quaternary groups on the surface to remove chromium from aqueous solutions.

II. METHODS AND MATERIAL

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), dichromate potassium PA (Merck); ethanol (commercial grade, Sumatex Produtos Químicos, Brazil), diphenylcarbazide PA (Merck), benzoyl peroxide PA (Vetec, Brazil), ethylenediamine (Aldrich; purity - 99%) and poly(vinyl alcohol)(Air Products, hydrolysis degree of 85% and PM = 80,000 to 125,000) were used as received.

The magnetic material was obtained by chemical co-precipitation of iron (II) and iron (III) chloride. A concentrated NaOH solution (130 mL) was slowly added to an aqueous solution of 14 g of Fe^{2+} and 27 g of Fe^{3+} in 100 mL of distilled water. The reaction was carried out under stirring for 1 hour at 80 ^{o}C. After this interval, 10 mL of oleic acid was added under stirring until complete homogenization. The precipitate was isolated on a magnet and repeatedly washed with hot water and ethanol until neutral pH. The magnetic material was stored as a slurry.

Samples of magnetic poly(GMA-co-DVB) microbeads were prepared by radical suspension copolymerization. The monomer phase containing the monomer mixture (98% mol of GMA and 2% mol of DVB), benzoyl peroxide (1% mol relative to the monomers) as an initiator, and ferric oxide (10 wt%) was suspended in the aqueous phase consisting of 260 g of water and 1.2 g of poly(vinyl alcohol) (PVA). The copolymerization was carried out at 70 °C for 24 h with a stirring rate of 800 rpm. After completion of the reaction, the copolymer particles were washed with water and ethanol, kept in ethanol for 12 h and dried at 50 °C for 24 h. This copolymer was designated as R14.

The animation occurred from the reaction 4 g of poly(GMA-co-DVB) (R14) with 10.0 g of ethylene diamine and 100 mL of toluene at 70 ºC for 72 h. The modified sample was filtered, washed with ethanol, dried and labeled as R14-en (-en designating the sample modified with ethylene diamine).

The quaternization reaction was adapted from the literature [16]. Dried R14-en (5.0 g) was swelled in methanol (40 mL) for 12 hours to favor the diffusion of the reagent solution through the interior of the polymer matrix. Then methyl iodide (25 mL) was added to the flask containing swollen beads and the reaction mixture was refluxed for 72 hours. Finally, the obtained product was filtered, washed several times with hot water (70 °C, 500 mL) and acetone (250 mL). Then, the sample was dried at atmospheric pressure for 24 hours at 50 °C and labeled as R14-enQ (-enQ designating the sample modified with ethylene diamine and quaternized). Figure 1 shows the chemical modifications, amination and quaternization.

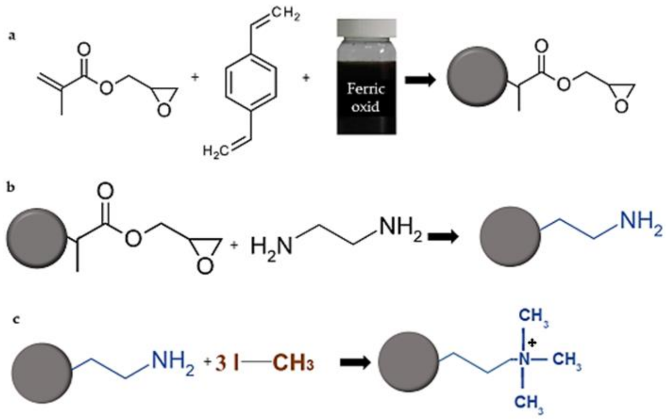


Figure 1. Synthesis scheme of copolymers. a) Magnetic poly(GMA-co-DVB)(R14); b) Magnetic poly(GMA-co-DVB) with amino groups (R14-en); c) Magnetic poly(GMA-co-DVB) with quaternized groups (R14-enQ).

Elemental analysis of polymers was performed with a PerkinElmer CHNS/O analyzer (2400 Series II), applying dynamic flash combustion for sample analysis. The UV-visible spectrophotometric technique (Biospectro SP-22 spectrophotometer) was used to determine the chromium adsorbed in the copolymers. The magnetic properties of the materials were analyzed by a Lake Shore 74 vibrating sample magnetometer (VSM). The X-ray diffraction analysis was performed with a PANalytical X'Pert PRO diffractometer. The size and size distribution of particles of magnetic scaffolds were analyzed by light scattering (Malvern Mastersizer 2000) and the morphology was analyzed by SEM-EDS (FEI Inspect 550), where the microspheres were adhered on metal bases using a double-sided adhesive tape and covered with a thin layer of gold.

The conductometric titration was carried out with a Mettler MC226 conductivity meter and a Schott Gerat T80/20 automatic burette to determine the amount of immobilized quaternary groups in the magnetic copolymers. The amount of immobilized quaternary groups was determining by titration of chloride ions present in the quaternary salt with $AgNO_3$.

Sorption of metal ions from aqueous solutions was investigated in batch experiments under non-competitive room temperature. The reproducibility of the sorption experimental results were verified in triplicate. To evaluate the effect of pH on the ability to adsorb Cr (VI) by magnetic microbeads, the pH values 2, 4, 5, 6, 7, 8, 10 and 12 were tested. Thus, samples of 100 mg of microbeads were added 20 mL solutions of Cr (VI) 100 mg L-1 with different pH values previously adjusted with dilute solutions of NaOH and/or HCl. The system remained under constant stirring at 25 °C in a thermostated bath for 24 h.

The analysis of the kinetic models of the adsorption process was carried out in batch mode at 25 °C, where the mass of copolymer solution was maintained at 5.0 g.L-1 solution of Cr (VI) with different concentrations and pH values previously set at 4.0. The samples were shaken and aliquots of the supernatant were removed after different intervals (0, 5, 10, 30, 60, 90, 120, 150, 180, 210, 240 and 1400 min). The concentrations of the metal ions in the aqueous phase were measured by UV-visible spectrophotometry.

III. RESULTS AND DISCUSSION

A. Characterization of the materials

Table I shows the results of the elemental analysis of the copolymers before and after the amination reaction. The increased concentration of (8.5%) found for R14-en demonstrates the introduction of amine groups on the magnetic microspheres made of poly(glycidyl methacrylate-co-divinylbenzene).

Conductometric titration was used to determine the number of quaternary groups in the quaternized magnetic poly(methacrylate glycidyl-co-divinylbenzene) (R14-enQ). The value found was 2.18 mmol/g of polymer, confirming the presence of this new functional group in the adsorbent after the quaternization step.

TABLE I

Elemental analysis of magnetic poly(glycidyl methacrylate-co-divinylbenzene)(R14) and magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amine groups (R14-en)

Sample	% C	% H	% N	% Others
R14	54.5	11.1	0.1	34.3
R14-en	50.7	9.8	8.5	31.0

Figures 2a and 2b show the scanning electron microscope (SEM) image of a sample of magnetic poly(glycidyl methacrylate-co-divinylbenzene)(R14) and its iron distribution map. As can be seen in Figure 1a, the synthesized material is spherical, with smooth surface except for some agglomerates. The distribution of these agglomerates on the surface is not uniform and their presence was attributed to the iron oxide particles, as can be seen in the iron distribution map (Figure 2b). The presence of iron in these materials was also demonstrated by the X-ray energy dispersive analysis (Figure 3).

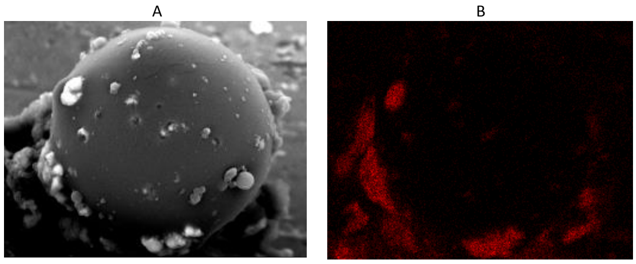
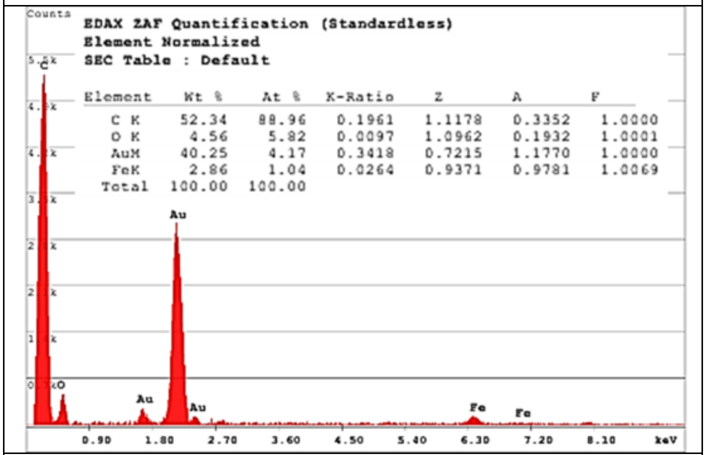


Figure 2. SEM images of: (a) magnetic poly(glycidyl methacrylate-co-divinylbenzene)(R14) and (b) its iron distribution map, both with magnification of 2500X.

Figure 4 presents the SEM images of a magnetic poly(glycidyl methacrylate-co-divinylbenzene) microsphere (R14) (Figure 4a), a magnetic poly(glycidyl methacrylate-co-divinylbenzene) microsphere after the amination reaction (R14-en) (Figure 4b) and a magnetic poly(glycidyl methacrylate-co-divinylbenzene) microsphere after the quaternization reaction (R14-enQ) (Figure 4c). As can be observed, there were no significant alterations in the microspheres' morphology after the chemical modifications. They continued to have good sphericity without cracks or breaks and with magnetic particles on the surface. This indicates that the reaction conditions used were gentle enough not to cause changes in the polymer microspheres.

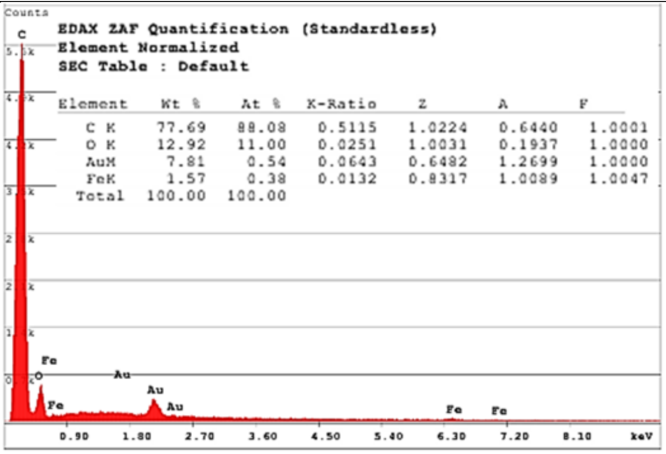
Table II reports the magnetic properties and diameter of the microspheres obtained. As can be noted, there was no significant change in the average size of the microspheres. This result indicates that no fragmentation or agglomeration occurred during the chemical modification reactions, as also observed in the SEM images (Figure 3). Copolymer R14 presented the highest saturation magnetization value (4.76 emu/g). It is possible that the lower values found for R14-en (2.25 emu/g) and R14-enQ (2.21 emu/g) were caused by leaching of the iron oxide located on the surface during the chemical reactions. The saturation magnetization is directly proportional to the quantity of magnetic material. The X-ray energy dispersive analysis (Figure 2) corroborates this hypothesis of reduced concentration of iron after the chemical reactions, since this declined from 2.86% (R14) to 1.57% (R14-en) and 1.44% (R14enQ). Lee et al. [17] also found similar saturation magnetization for chemically modified resin composed of styrene and divinylbenzene.

A


EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

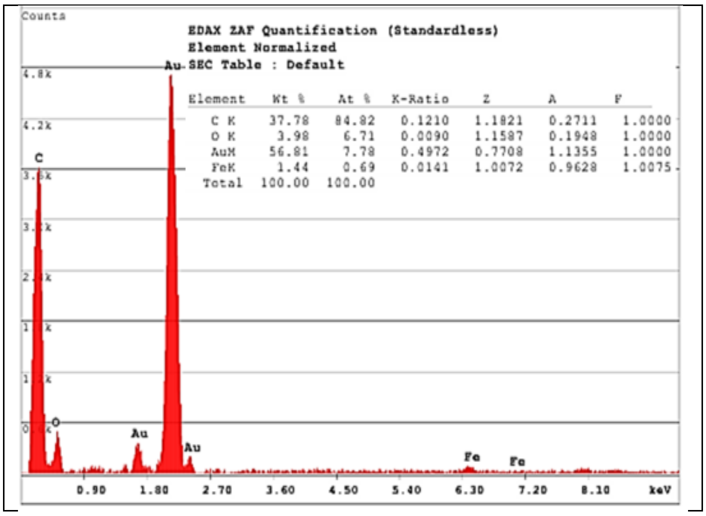
Element	Wt %	At %	K-Ratio	Z	A	F
C K	52.34	88.96	0.1961	1.1178	0.3352	1.0000
O K	4.56	5.82	0.0097	1.0962	0.1932	1.0001
AuM	40.25	4.17	0.3418	0.7215	1.1770	1.0000
FeK	2.86	1.04	0.0264	0.9371	0.9781	1.0069
Total	100.00	100.00				

B


EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	77.69	88.08	0.5115	1.0224	0.6440	1.0001
O K	12.92	11.00	0.0251	1.0031	0.1937	1.0000
AuM	7.81	0.54	0.0643	0.6482	1.2699	1.0000
FeK	1.57	0.38	0.0132	0.8317	1.0089	1.0047
Total	100.00	100.00				

C



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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z        A        F
  C K     37.78    84.82   0.1210   1.1821   0.2711   1.0000
  O K      3.98     6.71   0.0090   1.1587   0.1948   1.0000
  AuM     56.81     7.78   0.4972   0.7708   1.1355   1.0000
  FeK      1.44     0.69   0.0141   1.0072   0.9628   1.0075
 Total   100.00   100.00
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Figure 3. X-ray energy dispersive analysis: (a) magnetic poly(methacrylate glycidyl-co-divinylbenzene) (R14); (b) magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amino groups (R14-en); (c) magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ).

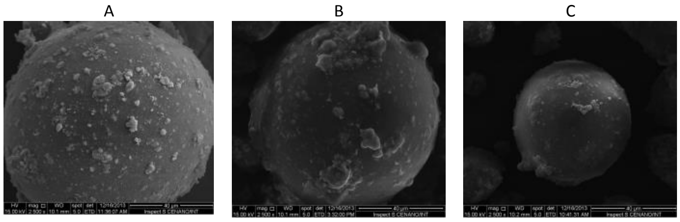

Figure 4. SEM images of: (a) magnetic poly(methacrylate glycidyl-co-divinylbenzene) (R14); (b) magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amino groups (R14-en); (c) magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ). Magnification of 2500x.

TABLE II

Magnetic properties and diameter of copolymer beads

Copolymer	M_S (emu/g)	M_R (emu/g)	d(0.5) (μm)
R14	4.76	0.43	10.62
R14-en	2.25	0.25	100.61
R14-enQ	2.21	0.24	99.78

M_s – saturation magnetization; M_R – remanent magnetization; d-diameter

Figure 5 shows the magnetic hysteresis loops of magnetic poly(methacrylate glycidyl-co-divinylbenzene) (R14), magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amino groups (R14-en), and magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ). These do not present hysteresis cycles, a phenomenon that causes a lag between the magnetic flux density (B) and magnetic field (H). The MR values, shown in Table II, are very near zero. These observations indicate the material has superparamagnetic behavior. This characteristic is very important in separation processes, because after applying the magnetic field, it needs to be removed without leaving residual magnetization.

B. Effect of pH on the adsorption of Cr (VI) in the magnetic copolymers

Figure 6 presents the results of sorption of Cr (VI) in function of pH for the R14-en and R14enQ copolymers. R14en was strongly dependent on the pH. In the lowest pH range (2-5), the quantity of Cr(VI) adsorbed increased with rising pH, until reaching a maximum at pH = 5, after which the quantity of Cr(VI) adsorbed declined with increasing pH. The adsorption of Cr(VI) ions depended on the protonation or unprotonation of amino groups on the surface of the microbeads. In aqueous solutions, Cr (VI) exists in the form of chromic acid (H_2CrO_4) and in the form of dichromate ($Cr_2O_7^{2-}$). Several anionic forms, such as chromate CrO_4^{2-} (pH>6), dichromate $Cr2O_7^{2-}$ and $HCrO_4^-$ (pH =1-6), can exist, depending on the pH [6,18]. Thus, at acidic pH, the amino groups of the R14-en microbeads are positively charged, which leads to an electrostatic attraction with the negatively charged chromium species, since the major species at lower pH is $HCrO_4^{2-}$. This allows removing more chromium atoms per exchange site than CrO_4^{2-}, which is the main species at alkaline pH. On the other hand, the chromium sorption was only slightly sensitive to pH changes when R4-enQ (with quaternary groups) was employed. The quaternary groups, strong base anion exchangers, have greater chromate removal capacity at acidic pH compared to alkaline pH. However, they showed good adsorption capacity by Cr(VI) at alkali pH as well as at acidic pH. This is an advantage of R14-enQ because it can be used without correction of pH.

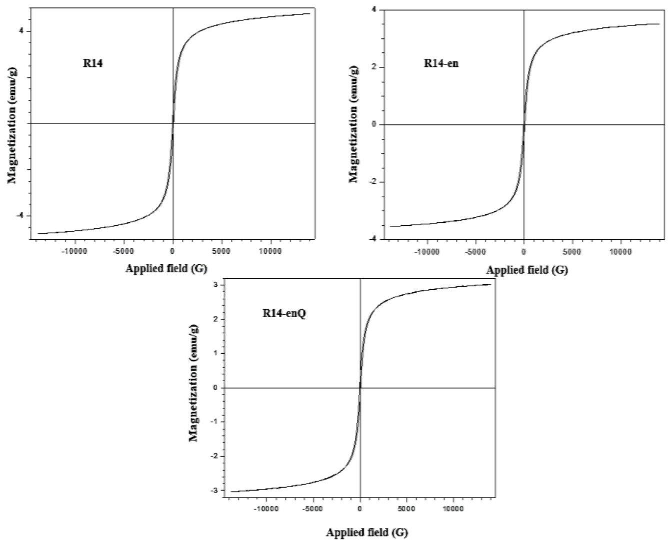

Figure 5. Magnetic hysteresis loops of (a) magnetic poly(methacrylate glycidyl-co-divinylbenzene)(R14); (b) magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amine groups (R14-en); (c) magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ).

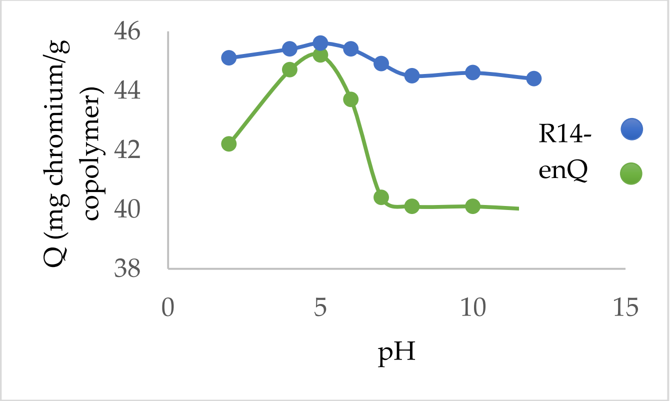

Figure 6. Effect of pH on chromium sorption.

C_0 = 100 mg/L; V = 50 mL; mechanical stirring speed = 200 RPM; time(t) = 240 min

C. Adsorption kinetics of Cr (VI) on magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amine groups (R14-en) and magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ).

To understand the mechanism that controls the adsorption phenomenon, we evaluated three kinetic models: pseudo first-order, pseudo second-order and intraparticle diffusion. Figure 7 shows the effect of contact time on the capacity to adsorb Cr(VI) of the magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amine groups (R14-en) and the magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ). As can be seen, the adsorption rate of chromium(VI) increased with contact time until equilibrium was reached at 200 min. After this time, the active sites of the adsorbent became saturated when equilibrium was reached, so the sorption became slow in the later stages [2].

The validity of the models was investigated by the correlation coefficients of the linearized equations: log(qe – qt) vs t for the pseudo first-order, t/qt vs t for the pseudo second-order and qt vs t1/2 for the intraparticle diffusion models, respectively. Table III shows the correlation coefficients and linearized equations of the three kinetic models for the R14en and R14enQ copolymers. It can be observed that for the two copolymers, the pseudo second-order had the best fit, since the correlation coefficients for both were near one. In this model, the quantity of ions adsorbed in equilibrium is a function of the initial concentration of metals and the nature of the interaction between the adsorbate and adsorbent. The limitation mechanism of this process of adsorption of metals is the chemical adsorption, involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate [19].

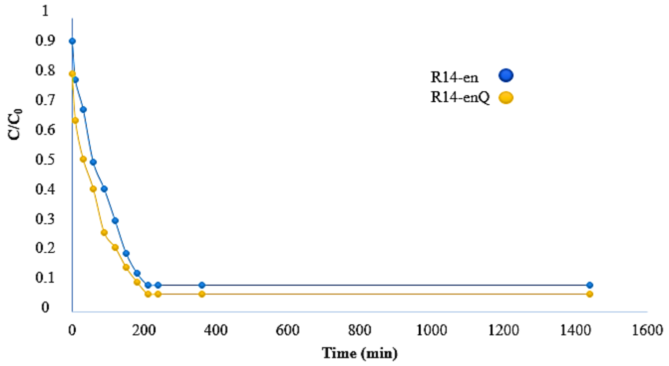

Figure 7. Effect of contact time on chromium adsorption capacity

C_o – initial concentration of Cr(VI); C - concentration at any given time

TABLE III

Correlation coefficients and linearized equations of the three kinetic models.

Copolymer	Model	Correlation coefficient
	Pseudo first-order	r^2
R14-en	y = 1.0705 – 0.0024*x	0.8643
R14-enQ	y = 1.0673 – 0.0023*x	0.9501

	Pseudo second-order	
R14-en	y = 0.9882 + 0.0136*x	0.9932
R14-enQ	y = 0.6074 + 0,0153*x	0.9996
	Intraparticle diffusion	
R14-en	y = 0.1295 + 3.9366*x	0.9777
R14-enQ	y = 0.1765 + 3.9880*x	0.9798

The values of the velocity constants determined for removal of Cr (VI) by the copolymers R14-en and R14-enQ, for the kinetic pseudo second-order model, were 1.37 x 10^{-2} g.(mg.min)-1 and 2.52 x 10^{-2} g.(mg.min)$^{-1}$, respectively. The adsorption velocity constant of the magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ) was almost twice that of the magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amine groups (R14-en).

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D. Adsorption isotherms

We also investigated the models according to the isotherm models of Langmuir and Freundlich. For the system in question, we put the Langmuir equation in its most suitable linear form (1) for determination of the adsorption parameters: maximum adsorption capacity (qmax.) and constant of Langmuir (K). We did the same for the Freundlich equation (2).

$$C_{eq}/q_{eq} = 1/QKL + Ceq/Q \qquad (1)$$

Where:

- q_{eq} represents the quantity of adsorbate in the adsorbent, in equilibrium (mg.g^{-1});
- C_{eq} represents the equilibrium concentration of the adsorbate in solution (mg.L^{-1});
- Q denotes the maximum adsorption capacity (mg.g^{-1}); and
- K_L is the constant of Langmuir related with the constant of equilibrium (L.mg^{-1}).

$$\text{Log } q_{eq} = \log K_F + 1/n \text{ Log } C_{eq} \qquad (2)$$

Where:

- K_F [(mg.g-1)(L.mg-1) 1/n] is the constant of Freundlich; and
- 1/n is related with the adsorption intensity.

The isotherm of Langmuir provided the best fit of the experimental adsorption data, with a correlation coefficient near one, as can be seen in Table IV. According to this model, the quantity of chromium anions (VI) adsorbed on the surface of the adsorbents and the concentration of these ions in the aqueous phase in equilibrium increases with the concentration of ions in the aqueous phase, progressively approaching saturation at higher concentrations.

Table V shows the maximum adsorption capacity (q_{max}) of the R14-en and R14enQ copolymers calculated according to the linearized model of Langmuir. The Fisher test revealed a significant difference (at 95% confidence) between the two means found. As can be observed, the maximum surface saturation capacity of the adsorbent (q_{max}) was higher for the R14-enQ copolymer (63.29 mg of Cr (VI)/g of R14enQ) than for the R14-en copolymer (60.98 mg of Cr (VI)/g of R14-en).

TABLE IV. Coefficients and linearized equations for the isotherms of Langmuir and Freundlich.

Copolymer	Model	Coefficient
	Langmuir	r^2
R14-e	y = 0.1109 – 0.0164*x	0.9990
R14-enQ	y = 0.1221 – 0.0158*x	0.9972
	Freundlich	
R14-en	y = 2.5216 + 0.3785*x	0.9400
R14-enQ	y = 2.6101 + 0.3444*x	0.9694

TABLE V. Maximum capacity of chromium adsorption qmax) on magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amine groups (R14-en) and magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ).

Copolymer	R14-en	R14-enQ
Q_{max}(mg Cr/mg)	60.98 ± 0.01	63.29 ± 0.36

For the magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ), not only was the adsorption capacity higher, it was also independent of pH, due to the presence of a cationic group as adsorption site without dependence on declining pH to protonate the amine groups found in its structure. The independence from pH reduces the number of steps in the process of removing chromium from wastewater and the consumption of chemical reagents, thus lowering the treatment costs.

IV. CONCLUSION

The results show that magnetic poly(methacrylate glycidyl-co-divinylbenzene) with amine groups (R14-en) and magnetic poly(methacrylate glycidyl-co-divinylbenzene) with quaternary groups (R14-enQ) can be used as adsorbents to remove Cr (VI) from aqueous solutions. The process of adsorbing Cr (VI) with R14-en was dependent on pH, where the highest adsorption values occurred in a pH range from 4 to 6s. In contrast, for R14-enQ, because of its quaternary group (strong base), the adsorption was practically independent of the solution's pH. The kinetics studies showed that the experimental data on adsorption of Cr (VI) best fit the pseudo second-order model, for both copolymers, suggesting that the interaction between adsorbent and adsorbate occurs by chemisorption. The Langmuir isotherm model presented the best fit to the experimental data in equilibrium, indicating that the adsorption of Cr (VI) takes place on a monolayer on the heterogeneous surface of the adsorbent.

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