

Chromium (III) Ions Uptake from Aqueous Solutions by Chelating Resin Containing Pendant Multidentate Ligand

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ABSTRACT

From serious problems of environmental is contamination with heavy metals which have toxic nature and other harmful effects. Many heavy metal ions, such as chromium ions are detected in industrial wastewaters originating from metal plating, mining activities, paint manufacture, etc. This ion isn't biodegradable and tends to accumulate in living organisms, causing various diseases and disorders. Therefore, it should be removed from aqueous solution before discharge. In this paper it has been done an experimental work regarding the optimal conditions of removing chromium (III) ion from water using ion exchange resins namely XAD-4 amine-N-polycarboxylate-resin. The adsorption behavior of chromium (III) ions on XAD-4 amine-N-polycarboxylate-resin was studied as a function of the following variables: contact time, pH solutions, initial concentration of metal ions, resin dosage, and ionic strength. Equilibrium studies showed that, the total maximum adsorption capacity of adsorbent for chromium ions was: 0.75 mmol/g XAD-4 amine- N-polycarboxylate-resin. The results show that, XAD-4 amine- N-polycarboxylate resin resin holds great potential to remove chromium ions from polluted wastewater.

Keywords: Chromium ions, uptake, aqueous solutions, chelating resin

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INTRODUCTION

In the fields of environmental and analytical chemistry, the global research interest by extraction and remove toxic and polluting metal ions from wastewater generated from industrial activity is the main reason for avoiding pollution of water and soil. Consequently, great potentials of research were carried out for preparing, applying the chelating ion exchange resins, which have ability and selectivity for extraction, and preconcentration of toxic metal ions [1] Technology of Ion exchange has been well established, however novel resources, uses and methods are developing at a fast pace. The fact is some metals have several hurtful effects on the various forms of life. Many metals have toxicity to the human's environmental include copper, lead, cadmium, mercury, chromium, manganese etc. Main sources of metals in our environment are come from metals manufacturing and tanning surface finishing, paints and dyes extracted in addition to the battery factories. [2-6] In order to reach nothing or close to nothing of contaminants in wastewater of industrial should make treatment operations. Flexible ion-interchange chromatography nature and adsorption routes create them mainly suitable for these implementations. According to the nature of the samples, a wide variety of techniques have been proposed and used to determine the heavy metal-ions in different ecological specimens with solvent extraction, ion- interchange, coprecipitation, and absorption .[7-9]. Amongst these approaches, ion exchange was very common and practiced on a large scale in the industrial wastewater treatment operations. Although widely used of ion-exchange in the metallic finishing industry, tanning etc., there needing to improve and expand ion-exchange techniques. [10-12]. The incorporated ligands to chelating resins to bond with confident kinds of cations. The affinity for chelating-copolymer for a particular mineral is depend on hydrated of ionic charge, the radius of ionic and atoms of chelated ligand attachment by electron pairs for oxygen, and nitrogen.[13]. In ion exchange chromatography, the chelating resins employed

are selective and have an affinity for the transition metals. The iminodiacetate, and aminophosphonic resins are commonly chelating polymer using. In addition, picyeamine, poly-ethylenimine and amidoxime resins are available commercially to remove heavy metal ions. [7,14-17] Separation and enrichment of ions by the chelating resins are widely used and well understood. However, development today is mostly to improve the particularity of the chelating resins and their uses. Resins of Carboxylated are a specific type of weak cation interchange chelating-resins, which are suitable to recovery requests of the metal chromium. pH variety is less for many of the metals and takes advantage of lower over the pH is that the metal does not precipitate as hydroxides or oxides. Many studies were achieved of the adsorption properties for some metals on iminodiacetic acid (IDA) resins at temperatures and pH diverse. [3,18-21]. The use of chelating ion exchange resins such as Chelex-100 (commonly used) is fast interest as a simple and effective means to address the economic and wastewater containing heavy metals. The chelating resins are abundant, easy to prepare, cheap and available. They likewise own some properties that make them effective media to remove dissolved metal contaminants [13]. Due to chromium (Cr^{+5}) is cancer-causing, in sewage an extreme allowable limit for chromium (Cr^{+3}) of 0.5 mg/L, and for chromium (Cr^{+5}) of 0.05 mg / L is approved by law.[11,18]. In our study, chromium (III) has been selected since it is as an essential contaminate. Consequently, the monitoring of the amount of chromium in the polluted water is crucial. The study aim is to examine the action of resins to remove chromium (Cr^{+3}) from the watery samples and reducing chromium toxicity from environmental sources. Many experiments were done during a variety of pH, temperature and concentration. The batch vessels were used to remove heavy metals.

EXPRIMENTAL

Apparatus and reagents

Chromium (III) Ions Uptake from Aqueous Solutions by Chelating Resin Containing Pendant Multidentate Ligand

A flame atomic absorption spectrophotometer model A.A.630,12 (shimadzu) was used for the determination of metal ions in solutions. The pH measurements were made with (D-82362 digital pH meter, Weiheim, Germany). A mechanical shaker (SGM 3000100, Gallenkamp, Orbital Shaker) with an incubator, which had a speed of 200 strokes min⁻¹, was used for batch equilibration.

All used chemicals were of analytical grade, and deionized water was used throughout the study. An Cr (III) stock solution 1000 mg L⁻¹ was prepared by dissolving 4.57 g of chromium nitrate [Cr (NO₃)₃, Merck, Germany] in deionized water (100 mL) and diluting to 1000 mL. A fresh solution of Cr (III) was prepared with different concentrations from the stock solution directly previous to their use. The chromium (III) concentration was determined by flame atomic absorption spectrophotometer.

Preparation of the chelating XAD-4-amine-N-polycarboxylate-resin

The chelating resin was synthesised and purified by adapting the method as described in the literature [22]. A chloromethylated polystyrene beads (**1**) (25.6 g) was mixed with bis[2-(salicylideneamino) ethyl] amine (31.0

g) with (400 mL) of dioxane and refluxed for 48 hr. The product was filtered, washed with D.W, and then dioxane by a Soxhlet extractor. The product (**2**) was extracted and collected after 48 hr. Next, the product was washed (**2**) with diethyl ether and dried at 50 °C to yield (25.0 g). The hydrolysis compound (**2**) (23.0 g) was done with 6M HCl (500 mL) at 60 °C for 12 hr. created compound in hydrochloride form which was treated with 2 M aqueous ammonia to get free amine form yield (**3**) 14.5 g. Chloroacetic acid (47.3 g in 60 mL of deionized water) was neutralized with sodium carbonate at 0 °C was added to polymer (**3**) (15.0 g) and stirred at 70 °C overnight. The control on pH of reaction solution in (pH=9-10) was done by using sodium carbonate. The reaction was worked up, the yield resin was filtered off, washed with hydrochloric acid (2 M), and then water until the washings were neutral and dried at 50 °C to give (XAD-4 amine- N-polycarboxylate-resin) (**4**) (22.4 g) which showed the spectroscopic and the analytical data identical to the literature. [22] Figure 1. The desired resin was powdered in a glass mortar and particles of 200-250 mesh size (ASTM) were used for metal sorption studies.

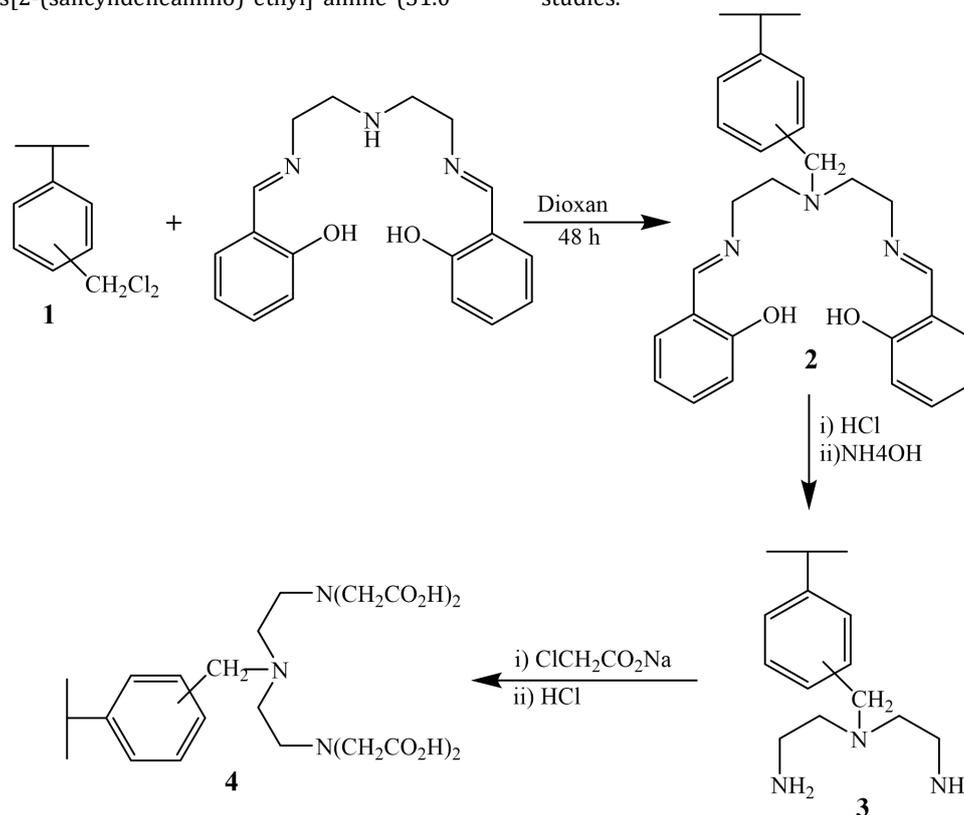


Fig.1. Synthesis of resin

The percentage chromium removal, R (%) was calculated for each run by equation:

$$(R\%) = \frac{(C_0 - C_f)V}{C_0 \times 100}$$

Where:

C₀ = (mg/L) of the initial concentration of chromium (III) ion in the solution

C_f = (mg/L) last concentrations of chromium (III) ion in the solution

V(L) = the solution size of desired ion, and m is the added mass of XAD4- amine- N-polycarboxylate-resin (g).

The metal ion uptake was calculated as mmole of chromium (III) ions/g dry resin. Each reading was done

Studies of adsorption

All the adsorption-kinetic studies were conducted by mixing a 0.1 gm sample of XAD-4 amine-N-polycarboxylate-resin and 25.0 mL of chromium (III) in 100 mL polyethylene bottles with a magnetic stirrer at room temperature. The pH value of solutions was adjusted with sodium acetate buffer or 0.1 M HCl and 0.1 M NaOH. The adsorption capacities Q (mg/g XAD-4 amine- N-polycarboxylate-resin) were calculated by using the following equation.[23]:

$$Q = \frac{(C_0 - C_f)V}{m}$$

Chromium (III) Ions Uptake from Aqueous Solutions by Chelating Resin Containing Pendant Multidentate Ligand

aqueous solution was studied in pH (1.5 to 8.5). This range was selected to prevent the precipitation of hydroxides. For these experiments, 25 mL of (Cr^{+3}) solution was agitated with 0.100 gm of resin for a period of 60 minutes. The sorption of chromium (III) ion on the resin is perceptibly very favorable and given a high affinity to the resin at pH 5.5 and 6.5.

Figure 2 revealed that the uptake of chromium (III) increases with increasing pH of aqueous solution from (3.5 -6.5) and then decreases. The total adsorption capacity of XAD-4 and amine- N-polycarboxylate resin is low at low pH because large quantities of hydrogen ions are likely to compete chromium cations for the adsorption sites. In another word, at high acidity such as pH=2, several of the chelating atoms at the chelating-site of the preparing resin might be undergone protonation ionized with protons, thus it will not coordinate with chromium(III) ions which made to diminishing in chelating adequacy. Therefore, the total capacity of adsorption will be lessening. As the pH of the solution increases, the number of protons dissociated from chelating groups on the surface of XAD-4 and amine- N-polycarboxylate resin increases and thus more negative groups for complexation of chromium cations are provided. From theoretical point of view, at pH=6 the total capacity of adsorption must be the extreme capacity of loading. This can be illustrated in that pH = 6 is close to the equivalent pH, so other atoms close to the chelation site would be available to chelate with chromium (III). At higher pH bigger than six, the hydroxyl presence will be forming the hydroxyl complexes with chromium [10,18,19].

At pH=4, the location of the chelate in the resin may be in its best steric form or the chelating atoms in resin1 may be more available to coordinate with chromium (III). This leads to making the resin more active to remove the chromium (III) ions of the solution. Consequently, the electrostatic attraction increases between the chromium (III) ions and the adsorbent, which leads to make the total adsorption capacity of the resin towards chromium (III) ions in high level. The optimum pH value, which correspond to the maximum total adsorption capacity of chromium (III), was detected at pH= 6.5.

at least in a triplicate. Metal uptake was studied at different time intervals and pH values.

Separation procedures

Chromium(III) was isolated from a solution containing eight additional metallic ions that is copper (II), zinc(II), manganese(II), iron(III), cobalt (II), nickel(II), palladium(II) and vanadium(V), for this purpose two different methods were used. In the first method, the pH of the model was maintained to 4.5 by hydrochloric acid and sodium acetate. The pH of the resin column was controlled on pH=4.5 through buffer solution. The sample was entered in the column by 0.5 ml/min. Thereafter, the column was washed well with pH 4.5 buffer, and the absorbent chromium (III) ions were eluted with 10 volumes of HCl (3M) at 1 mL/min. Later, the sorbed Pd^{+2} , Fe^{+2} and traces of Zn^{+2} was eluted with 2M sulphuric acid. A second method included using the same technicality, but the pH was adjusted at 6.5.

RESULT AND DISCUSSION

The resin was proposed by the following synthetic route [22]. Directly, diethylenetriamine was inserted into polymer resin through the reaction it with chloromethylated-polystyrene (1) to give resin (2), in this step of reaction direct N-alkylation has occurred. Resin (2) was reacted with chloroacetic acid followed by 2M HCl to give the desired resin (3) which revealed all the spectroscopic and the analytical data identical to the literature. [22] The formula for the chelating ligand can be abbreviated as. In this form, the benzene ring exemplifies the XAD-4 resin matrix, which is particularly poly (divinylbenzene). The amine-N-polycarboxylate copolymer XAD-4 is have a light brown color and is stable in acid and base under experimental conditions.

Effect of the initial pH

The pH value of the solution is considered an important chemical variable that can influence on metal ions removal from aqueous solutions by adsorbent materials, due to the adsorbent surface charge and the degree of ionization can be affected by the pH value. Therefore, the effect of pH on the sorption and desorption processes must be attention. In the preliminary experiment, the initial pH effect on chromium (III) ions removal from

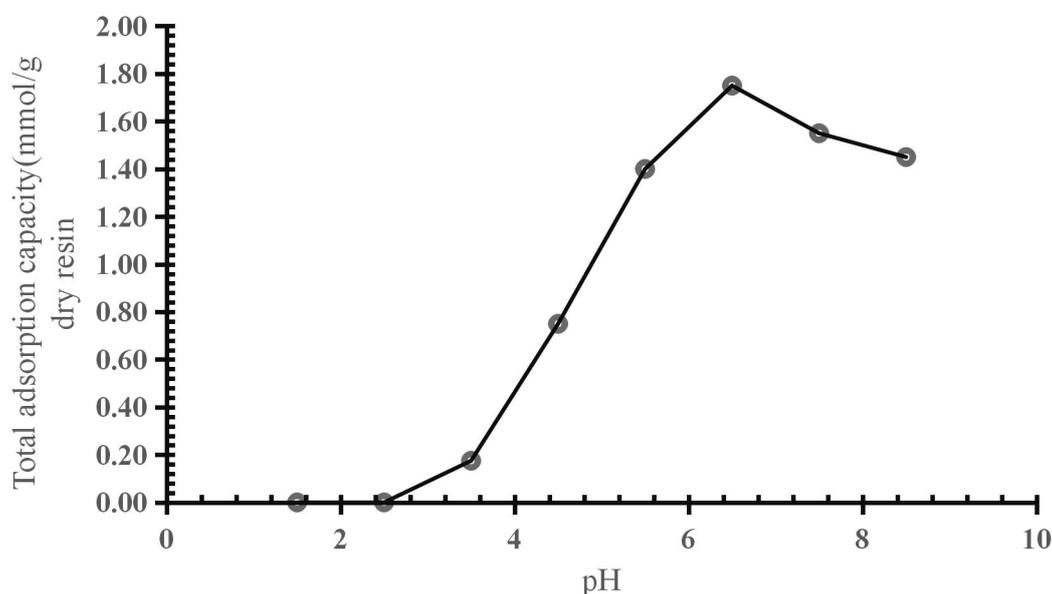


Fig. 2. The total adsorption capacity (T.C) for chromium (III) ions on XAD-4 and amine- N-polycarboxylate resin versus pH.

Effect of contact time

The factor of contact time is important in esteeming the adsorption ability, which assistances to regulate the rate of maximum removal of solutes [24]. The contact time is effect on total adsorption capacity of chromium (III) ions Figure 3, which illustrates that the removal percent of chromium (III) ions rises with long contact time from 0-60 min. The concentration of chromium (III) ions in the solution decreased rapidly within 10-60 min and then becomes nearly constant until the end of the experiment. The sorption was nearly complete in 70-120 minutes and decreasing in the amount of residual chromium in the aqueous shows that strong binding of chromium (III) ions with XAD-4 and amine-N-polycarboxylate resin. The chromium binding at initial phases high and becomes almost constant after an optimum contact time of 60 min. The metal adsorption versus time curve is a single, smooth, and constantly explain saturation, which suggests possible monolayer covering of metal ions on the adsorbent surface [10]. The equilibrium adsorption

capacity was about 1.60 mmol/g dry resin for chromium (III). The optimum contact time correspond to the extreme total capacity of adsorption of chromium (III) ions was perceived to be about 60 min.

It's presumed that, adsorption of chromium (III) ions on proposed chelating resin occurs according to two mechanisms: ionic exchange between hydrogen of carboxylic groups of chelating resin and chromium (III) ions in solutions, and by internal diffusion through resin pores. The first mechanism can be supported with the fact which is a considerable increase of acidity was observed in solution after establishment of equilibrium. The other fact of ionic internal diffusion was indicated by the rapid equilibrium between ions and resin, so ions can get in and out of resin readily. Also, titration of released hydrogen ions in comparison with concentration of adsorbed ions by resin reveals that, the latter ions are in excess. The difference was attributed to presence of other adsorbed mechanisms than ionic exchange, such as internal diffusion and physical adsorption and so on.

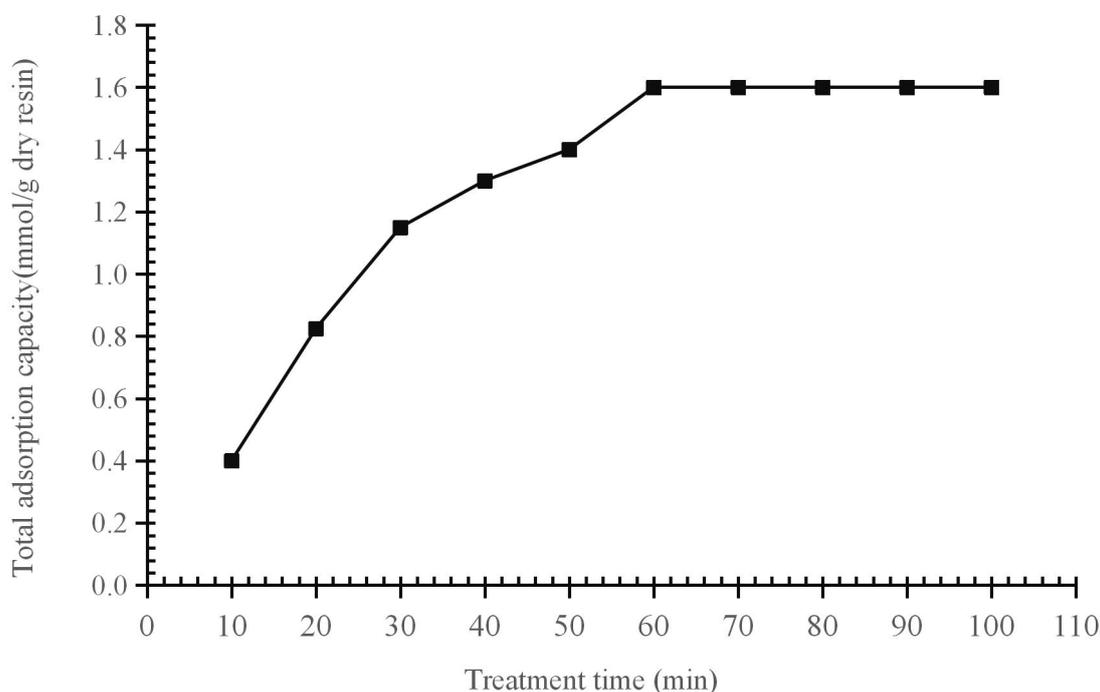


Fig. 3. Total adsorption capacity of chromium (III) ions on XAD-4 and amine- N-polycarboxylate resin versus time at pH 6.5.

Resin dosage effect

The study of the Effect of the amount of resin on the removal of chromium (III) ions from XAD-4 and the amine-N-polycarboxylic resin was performed using a batch method at pH = 6.5. Resin amount was extended from 0.01 to 0.14 g and equilibrated until 60 min at an initial chromium (III) ions concentration of 200 $\mu\text{g mL}^{-1}$. Figure 4 reveals variation of percentage removal of chromium (III) ions as a function of resin dosage. It is clear that the concentration of equilibrium in the solution reduces with rising resin amount for original chromium (III) ions. Subsequently, the metal portion detached from

the aqueous part increases with increasing the dose of the absorbent in the batch container with a stable primary metal concentration of 0.08 g, the adsorption capacity reaches a nearly constant value. This effect was expected because for the permanent primary solute concentration, increasing the doses of the absorbent would provide a greater surface area and absorption sites for the adsorbent.[12] To determine removal of 200 $\mu\text{g mL}^{-1}$ chromium (III) ions in 25 mL, a least resin amount of 0.12 g of XAD-4 and amine-N-polycarboxylate resin is required.

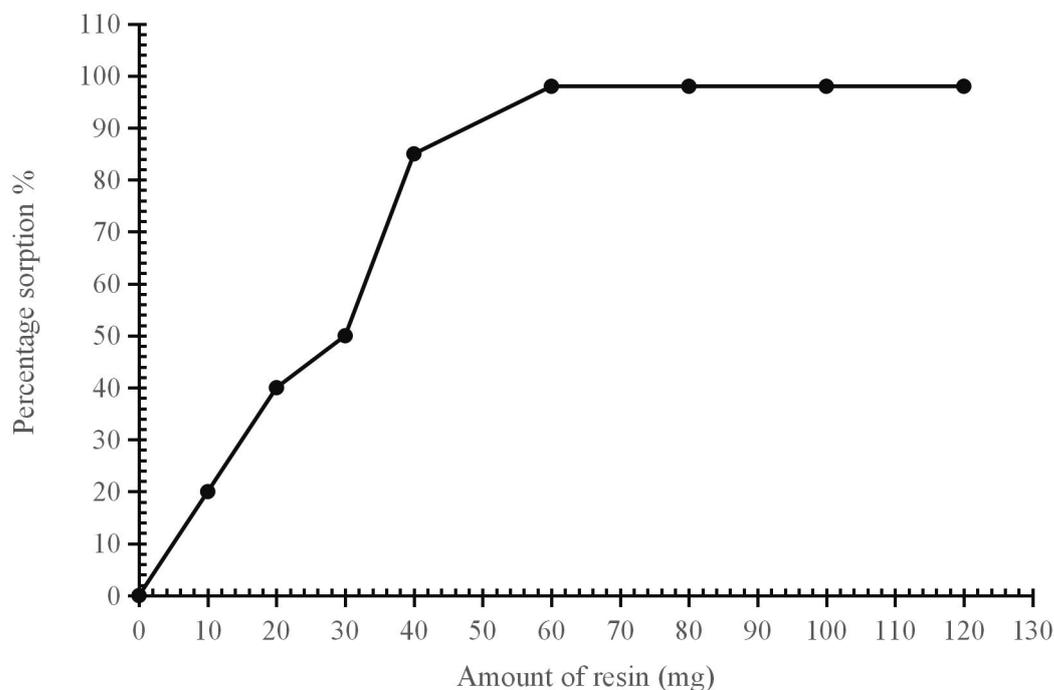
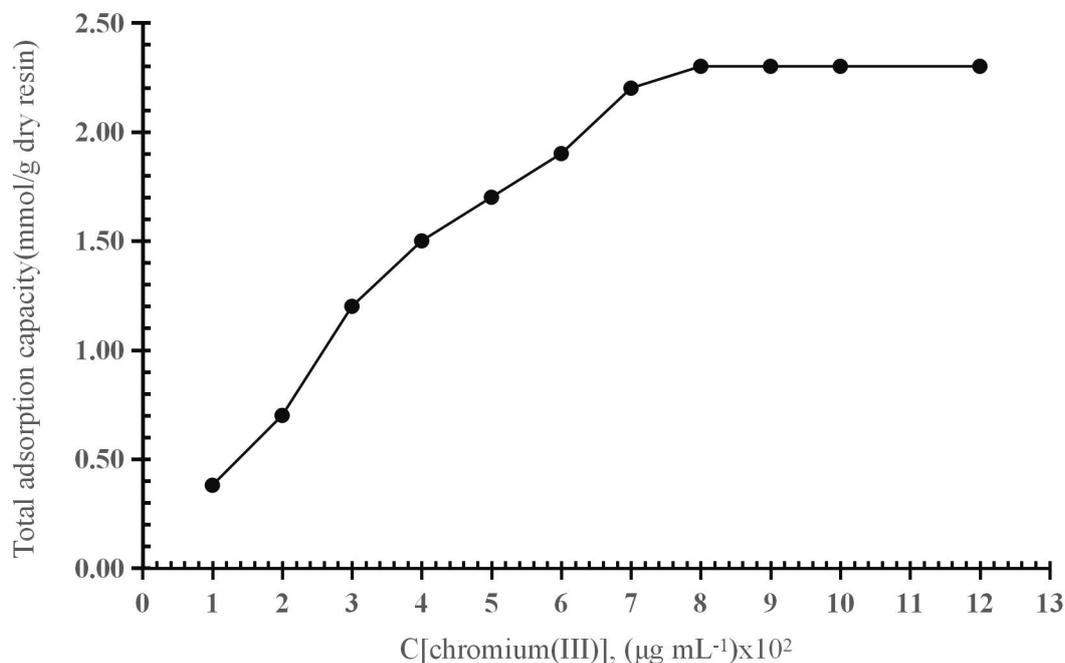


Fig. 4. Resin dosage effect on the adsorption of chromium (III) ions on XAD-4 and amine- N-polycarboxylate resin at pH 6.5. chromium (III) ions $200 \mu\text{g mL}^{-1}$, temperature, 25°C .

Effect of initial ion concentration on Adsorption

The initial concentration of chromium (III) ions' affection on adsorption capacity is explained in figure 5. The above-mentioned capacity rises first with the primary concentration of minerals ion increasing, then reached the value of a plateau. At less than 800 ppm of the chromium ions concentration, the amount of the adsorption sites in XAD-4 and amine- N-polycarboxylate resin was much more than the quantity of a metal ion in tested solution. The efficiency of high adsorption was attributed to the hydrophilic nature of carboxylate (-

COO^-) groups in the above-mentioned resin, which is interested in a suitable affinity with the metal ions. Moreover, the above-mentioned resin long sidechain, which served as a spacer arm that could seized metal ion simply. [19]. Because of the metal ion quantitative' increasing, the resin adsorbed more metal ions and the polymer-chains dwindled. Chromium (III) ions would be hard to spread in the free chelating sites within the above-mentioned resin. This is the reason of the adsorption 1curves capacity divergent at height concentrations of metallic ions.



Chromium (III) Ions Uptake from Aqueous Solutions by Chelating Resin Containing Pendant Multidentate Ligand

Fig. 5. The effect of the initial concentration of chromium (III) ions on the total capacity of adsorption by XAD-4 and amine-N-polycarboxylate resin at 25 °C, pH 6.5 (adsorption time = 60 min).

Effect of ionic strength on Adsorption

In wastewater, the presence of salts is one of the important factors may impede on the adsorption capacity of chromium (III) ions. Figure 6 shows the total adsorptions capacity of chromium (III) ions as a function of NaNO₃ concentration by using XAD-4 and amine-N-polycarboxylate resin. The concentration of NaNO₃ was ranged from (0 to 1.0 mol/L) or (0 to 8.5×10⁴ µg mL⁻¹). Apparently, the total adsorption capacity of chromium

(III) ions decreased, when the concentration of NaNO₃ in aqueous solution increased from 0.1 to 0.6 mol/L, As the concentration of NaNO₃ in aqueous solution increased more than 0.60 mol/L, negative effect on the adsorption process is perceived. The charge density of chromium (III) ions isn't so great to develop high attraction between the carboxylic group and chromium (III) ions. Therefore, total adsorption capacity of chromium (III) ions is affected vastly in the presence of NaNO₃.

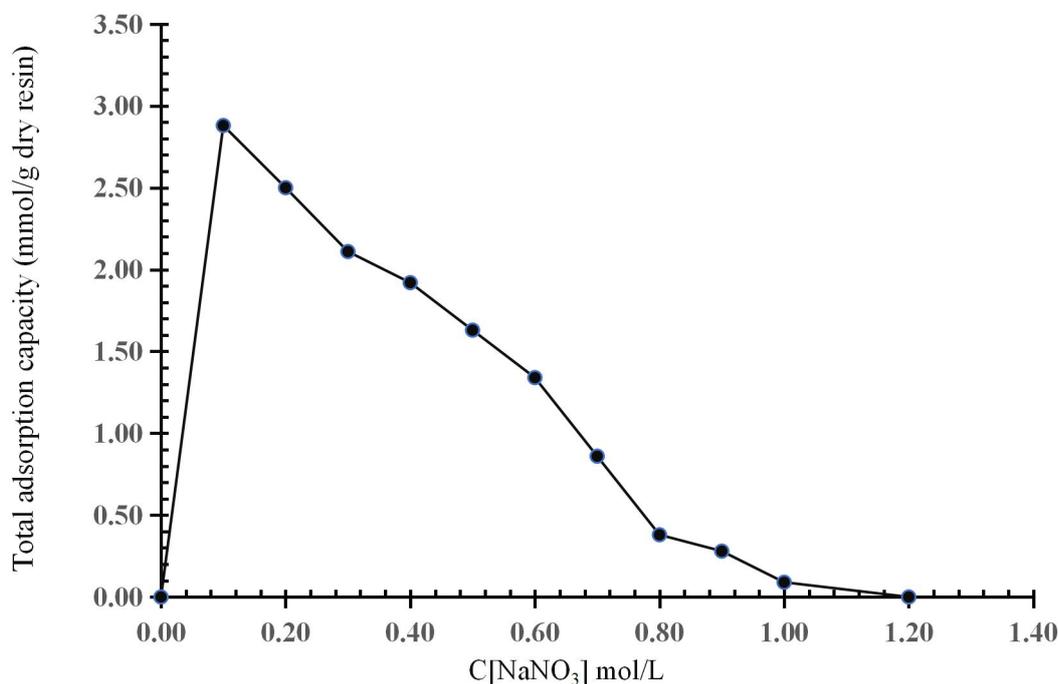


Fig. 6. The total adsorption capacity of chromium (III) ions as a function of NaNO₃ concentration by using XAD-4 and amine-N-polycarboxylate resin at 25 °C, pH= 6.5, adsorption time = 60 min)

Selective elution for separation of chromium (III) ions from various other metal ions was used. Table 1 reveals the obtained results. Only chromium (III) ions, Fe⁺² and traces of Zn⁺² are absorbent on the resin at pH 4.5, the passing of other metal ions through. Except of vanadium and palladium ions, more of the mineral ions are absorbent on the resin at pH 6.5. In both cases of pH, the chromium (III) ions are selectively eluted with 3M HCl. At pH 4.5, the total adsorption capacity of the resin for chromium (III) ions is low, very large quantities of chromium(III) ions cannot able to absorbent on the resin,

whilst at pH 6.5 the chromium (III) ions total adsorption capacity is high. However, at pH=5.9 remarkable quantities of most other mineral ions are also absorbed, which reduces the capacity of effective for chromium (III) ions. Later, if small quantities of chromium (III) ions are separation from big amounts of the additional metal ions and the favorite separation was at a lower pH. Otherwise, if great amounts of chromium (III) ions are to be separation from minor quantities of the other mineral ions, at big pH the separation was better.

Table 1. Separation of Cr⁺³ ions from, Mn⁺², Fe⁺³, Co⁺², Ni⁺², Cu⁺², Zn⁺², Cd⁺², Pd⁺², V⁺⁵

chromium (III) ions taken, mg	Strange mineral ion taken (each), mg	adsorption pH	chromium (III) ions found after desorption, mg
1.00	25.0	4.5	1.00
0.50	15.0	4.5	4.78
0.10	15.0	4.5	0.11
5.00	5.0	6.5	4.90
1.00	1.0	6.5	1.00
0.50	5.0	6.5	0.48
0.10	5.0	6.5	0.10

CONCLUSION

Chromium (III) Ions Uptake from Aqueous Solutions by Chelating Resin Containing Pendant Multidentate Ligand

The carboxylate form of the chelated polymer was re-prepared and indicated that ability to adsorption of chromium ion. Optimization conditions for chromium (III) adsorption were studied. The total capacity (T.C) of resin was showed at pH=6.5. The results show that, XAD-4 amine- N-polycarboxylate resin has a great possibility to remove chromium ions from contaminated wastewater. Furthermore, this work was given ability to remove and pre-concentration chromium ions from contaminated water and industrial waste

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