Sorption of Chromium (VI) from an Aqueous Solution by a New Polymeric Resin Prepared by Gamma Radiation

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ABSTRACT

A new polymeric resin poly(maleic acid –acrylamide )-Cesium P(MA-AM)-Cs was prepared by gamma radiation-induced co-polymerization of maleic acid ( MA) with acrylamide (AM) in the presence of cesium chloride CsCl as a metal salt in aqueous solution route at 25 K Gy to be used as a sorbent. The polymeric resin was characterized using Fourier transform infra-red spectroscopy (FTIR), simultaneous thermogravimetry TGA, DTA differential gravimetric analysis and Scanning Electron Microscope (SEM). The data showed that the polymeric resin was thermally stable up to 481°C. The sorption of Cr (VI) onto the prepared polymeric resin was investigated using batch equilibrium technique in relation to the pH, adsorbent weigh, initial concentration, contact time and temperature. The results showed that the adsorption capacity was highly pH-dependent and the maximum adsorption was attained from a solution as concentration of about 100 ppm at pH 2 with an adsorbent dosage of 0.05 g l⁻¹ and contact time 30 minute at room temperature (25°C). The adsorption capacity was found to be 74.6 mg/g at these specific conditions. Different models were tried to scan the surface of the exchanger. The sorption equilibrium data was fitted with Langmuir, Freundlish isotherm. The results indicated that the isotherm successfully fit the Langmuir adsorption isotherm. Lagergren-first –order and pseudo-second-order model were tested kinetically to describe the possible mechanism of the sorption process reaction. The experimental data fitted well with the pseudo-second-order kinetic model and the ion exchange mechanisms with controlled diffusion are predominates. In addition, thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the sorption were calculated. These parameters showed that the sorption of Cr (VI) onto the present polymeric material was spontaneous and endothermic in nature.

Key Words: preparation, characterization, sorption, Cr (VI), thermodynamic parameters, kinetic and isotherm model.

1. INTRODUCTION

Heavy metals are potentially hazardous to human health even in minute quantities[1]. Chromium becomes one of the most hazardous heavy metal pollutants in industrial waste water due to improper disposal of wastes and accidental releases[2]. Chromium is a typical heavy metal which is used extensively in industries such as electroplating, tanning, textiles and thus is widely present in the effluents of these industries. Chromium is commonly found in two oxidation states; hexavalent (Cr (VI)) and trivalent (Cr (III)).

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The trivalent form is an essential nutrient (1). Trivalent chromium is widely used in tanning industries and electro deposition processes that generate high volumes of effluents at high chromium concentrations (3). Although trivalent chromium is not particularly toxic, its disposal as liquid effluents in natural waters or as sludge in soils has to be avoided and controlled, as it may be oxidized, especially in soils, to the hexavalent form, which is highly toxic, carcinogenic and mutagenic in nature (4). It is highly mobile in soil and aquatic systems and also is a strong oxidant capable of being absorbed by the skin (5).

The hexavalent form is 50 times more toxic than the trivalent form (6). Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage (7). The tanning process is one of the largest sources of chromium pollution at the global scale. In the chromium tanning process, the leather takes up only 60 – 80% of applied chromium, and the rest is usually discharged into the wastewaters causing serious environmental impact. The maximum permitted limit for trivalent chromium in wastewater is 5mg/L and for hexavalent chromium is 0.05 mg/L (8).

High concentrations of Cr (VI) in natural waters can pose a major water quality and health problem for human beings. Human toxicity includes lung cancer, as well as kidney, liver and gastric damage (9, 10). The permitted limit of Cr (VI) for the discharge into inland surface water is 0.1 mg/L, however the guidelines for drinking water prescribed by the WHO for Cr (VI) is 0.05 mg/L. Thus, Cr (VI) removal is a recent research area attracting a great interest (11).

Thus, most of the methods for removal or abatement of Cr(VI) from environmental samples are based on the reduction of Cr (VI) to Cr (III) followed by precipitation and removal of Cr (III). Cr (VI) is present in the form of anionic species in the aqueous solutions. To remove these toxic metal ions from water, the adsorbent must have the anion exchange properties. Treatment technologies applied for removing Cr (VI) from wastewater include adsorption, biosorption, co-precipitation, electrodialysis, chemical precipitation, electrochemical precipitation, membrane filtration, solvent extraction, reverse osmosis and ion exchange (12-18).

Adsorption is widely used to remove heavy metals from industrial waste waters. Detailed heavy metal adsorption studies involving equilibrium and kinetic data as well as the effects of pH, temperature, surface area, and other relevant conditions over the adsorption process have been undertaken (19, 20).

In the present paper, a new polymeric resin [poly (maleic acid –acrylamide)-Cs is prepared by gamma radiation for sorption of Cr(VI) from aqueous solution. Several adsorption parameters such as pH, initial chromium concentration, contact time, adsorbate weight, isotherm and kinetic aspects were investigated. In addition, the equilibrium parameters of Cr(VI) at pH = 4 were investigated at 35, 40, 50 and 60°C.

2. EXPERIMENTAL

2.1. Chemicals and Reagents:

All chemicals used in this work were of analytical grade type. The main chemicals and reagents used in the present study are listed as follows:

Maleic acid (HOOCH=C=CHCOOH) was obtained from Laboratory Rasayan, S. D. Fine Chem. Ltd. (India). Acrylamide monomer (H2C=CHCONH2) was obtained from BDH (UK), and was used without purification. Acetone was obtained from Aldrich products (Germany), Potassium dichromate (K2Cr2O7) and chromium oxide Cr2O3 was purchased from Beijing Chemical Factory. All these chemicals were used without further purifications.
2.2. Instruments:

Synchronized thermal analysis, DTA, and thermogravimetric procedure, TG was carried out in order to study the thermolysis of the hybrid materials using a Shimadzu simultaneous DTA-TG50 analyzer, Shimadzu, Japan. The phase evolution at various stages of synthesis was analyzed using a Shimadzu X-ray diffractometer, Model XD 490, Japan) with Cu-Ka radiation and Bragg–Brentano focusing geometry was employed. Fourier transforms infrared (FTIR), spectrophotometer BOMEM FT-IR Model 157, Canada was used 400–4000 cm\(^{-1}\) for studying the spectra of the prepared hybrid materials. A gamma counter containing a NaI-Tl scintillation counter of the type Nucleus- Model 500 and scalar rate amplifier model 2010 was used for measuring the gamma radioactivity level throughout this work.

2.3. Radioactive Cr-51 production:

For preliminary radiochemical investigations, radioactive \(^{51}\)Cr was produced through the irradiation of chromium oxide \(\text{Cr}_2\text{O}_3\) at the Egyptian Second Research Reactor, ETRR-2. Accurate amounts of caesium carbonate and europium oxide samples (about 10 mg) were wrapped in thin aluminium foils that were previously cleaned with acetone, and finally placed in thick aluminium irradiation capsules. They were transferred to an aluminium irradiation box of length of 670mm then irradiated in ETRR-2 core at a thermal neutron flux of \(10^{14}\) n cm\(^{-2}\) s\(^{-1}\) for about 4 h.

2.4. Polymeric resin preparation:

For determination of the optimum condition for the preparation of new polymeric resin \(\text{P(MA-AM)-Cs}\) using gamma radiation in the presence of cesium chloride (CsCl) as a metal salt was studied by a free radical mechanism. It will study the effect of CsCl on the capacity toward \(\text{Cu}^{2+}\) for poly(maleic acid – acrylamide) resin \(\text{P(MA-AM)-Cs}\).

2.5. Batch experimental procedures:

2.5.1. Sorption equilibrium:

Adsorption equilibrium experiments were carried out in a temperature controlled thermostatic shaker operated at 180 rpm. All the Cr (VI) solutions required for experiments were freshly prepared by diluting the stock solution. The effect of pH on Cr (VI) adsorption by \(\text{P(MA-AAm)-Cs}\) was evaluated. The pH of the Cr (VI) solution was adjusted either by using \(10^{-1}\) (M) HCl or \(10^{-1}\) (M) NaOH. The volume of Cr (VI) solution was 50 mL with initial concentration 100 mg/L traced by \(\text{Cr}^{51}\) radioactive and the amount of adsorbent was 0.05 g. After 24 h of contact the adsorbent was separated from solution by filtration and the filtrate was analyzed for residual Cr (VI). Thereafter, 2 mL of the shaken solution was withdrawn for radiometric assay using NaI-Tl Scintillation detector connected to Nucleus Counting System, Enterprise, USA. The Cr (VI) removal efficiency was determined using Eq.(1).

\[
\%\text{ removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)
\]

Where, \(C_o\) and \(C_e\) are the initial and equilibrium concentrations (mg/L) of Cr(VI) respectively. At optimum pH, the effect of adsorbent dose on the removal of Cr (VI) was studied with 50 mL of 100 mg/L solution at 25 °C. The mass of adsorbent was varied from 10 mg to 150 mg.
The distribution coefficient, \( k_d \) (mL·g\(^{-1}\)), could be also calculated as:

\[
K_d = \frac{C_o - C}{V} \frac{X}{M} \quad (2)
\]

Where \( M \) is the solution volume (L) and \( m \) is the weight of the solid composite absorber (g).

### 2.5.2. Kinetic experiments:

The rate of adsorption for a specific cation was determined using a bottle containing 50 mL with initial concentration 100 mg/L traced by Cr\(^{51}\) radioactive in which 0.05 g from prepared \( P(MA-AAm)\)-Cs was added. The bottles were kept in a thermostated shaker bath at 25 ± 1°C for various periods of time. Adsorption of Cr (VI) on \( P(MA-AAm)\)-Cs was recorded in 30 min. intervals for a duration of 24 h for different batches.

### 2.5.3. Adsorption isotherms:

Once the equilibrium time was known, the adsorption isotherm could be determined for Cr(VI) ions. For this purpose, 50 mL with initial concentration 100 mg/L traced by Cr\(^{51}\) radioactive was shaken at 100 rpm with 0.05 g of PAAc-AN-TV, for 24 h at 25±1 °C. After the predetermined sorption time, the solution was filtered and the metal ion concentrations were measured. Initial and equilibrium metal ion concentrations in the aqueous solutions were determined radiometrically. Initial pH of the solutions was adjusted by adding hydrochloric acid or liquid ammonia solutions to the medium to maintain a constant pH. A HANA 30X model pH meter was used to adjust a desired pH value. The pH of the solution was buffered only at 4, except for as stated elsewhere. Since sorption experiments were temperature controlled, temperature influence experiments were carried out between 25 ±1 °C and 60 ±1 °C at optimum pH values for metal ion. Experiments were repeated three times in each case. The amount of sorbed metal ion was calculated from the change in the metal concentration in the aqueous solution before and after equilibrium and the weight of the dry polymeric resin; the amount of metal ion adsorbed by \( P(MA-AAm)\)-Cs was calculated as:

\[
q_t = \frac{(C_0 - C_t) V}{m} \quad (3)
\]

Where \( C_t \) (mg/L) is the concentration of Cr(VI) at any time \( t \).

Thermodynamic parameters, free energy (\( \Delta G^0 \)), enthalpy (\( \Delta H^0 \)) and entropy (\( \Delta S^0 \)) were also evaluated from the equilibrium data.

### 3. RESULTS AND DISCUSSION

#### 3.1. Preparation of polymeric material:

The typical optimized preparation procedures of polymeric material are shown in Scheme 1. The optimum condition for the preparation of P(MA-AM) Cs as an exchanger was determine by copolymerization of acrylamide (AM) with maleic acid (MA) in the presence of CsCl as an inorganic salt using gamma radiation, these data are shown in Table1.
Scheme (1): Synthesis and the expected structure of P(MA-AAm)-Cs interpolymer complex (resin).

Table (1): Experimental data of the optimum conditions for prepared polymeric material P(MA-AM)CsCl.

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>Cs Cl (ppm)</th>
<th>Comonomer concentrations (MA-AM)</th>
<th>Comonomer compositions (MA-AM)</th>
<th>Dose KGy</th>
<th>q&lt;sub&gt;e&lt;/sub&gt; mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of CsCl concentration</td>
<td>100</td>
<td>10%</td>
<td>20:80</td>
<td>20</td>
<td>71.6</td>
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<td></td>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td>63.1</td>
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<tr>
<td></td>
<td>500</td>
<td></td>
<td></td>
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<td>55.6</td>
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<tr>
<td></td>
<td>700</td>
<td></td>
<td></td>
<td></td>
<td>42.7</td>
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<td>900</td>
<td></td>
<td></td>
<td></td>
<td>24.9</td>
</tr>
<tr>
<td>Effect of comonomer concentration</td>
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<td>10%</td>
<td></td>
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<td>53.9</td>
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<td></td>
<td>100</td>
<td>20%</td>
<td></td>
<td></td>
<td>48.1</td>
</tr>
<tr>
<td>Effect of comonomer composition (AM:IA)</td>
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<td>10%</td>
<td>20:80</td>
<td>20</td>
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<td></td>
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<tr>
<td>Effect of Dose</td>
<td>100</td>
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<td>10:90</td>
<td>20</td>
<td>35.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15%</td>
<td>20:80</td>
<td>10</td>
<td>35.2</td>
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<tr>
<td></td>
<td>100</td>
<td>15%</td>
<td>30:70</td>
<td>20</td>
<td>69.2</td>
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<tr>
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<td>100</td>
<td>15%</td>
<td>40:60</td>
<td>30</td>
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</tr>
<tr>
<td></td>
<td>100</td>
<td>15%</td>
<td>10:90</td>
<td>40</td>
<td>52.8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15%</td>
<td>10:90</td>
<td>50</td>
<td>47.2</td>
</tr>
</tbody>
</table>

From the above experimental data shown in Table 1, it was found that the optimum conditions for preparing the polymeric material after studying the above parameters are 100 ppm as inorganic salt, a comonomer concentrations 15%, a comonomer composition (MA-AAm) (85:15), and a radiation dose was 25 KGy.
3.2. Characterization:

3.2.1. FTIR analysis:

FTIR Analysis of P(MA-AAm)-Cs and P(MA-AAm)-Cs/Cr(VI) complex is shown in Fig.1. The given bands at 3440, 3427 cm\(^{-1}\) in 1a and 1b respectively is assigned for Free >NH stretching vibration while the bands at 1621 cm\(^{-1}\) characterized to >C=O stretching vibration of amide groups in polymer material.

Weak and slightly broad bands in (1a, 1b) at about 2921, 2847 and 2925 cm\(^{-1}\) was observed, which due to the stretching vibration aliphatic of single -C–H group while the observed bands 1119 cm\(^{-1}\) may characterizes the CH bending of the aliphatic –CH\(_2\) groups.

The bands observed at 1413 cm\(^{-1}\) in (1b) can correspond to symmetric stretching vibrations of carboxy groups while the bands at 1315 cm\(^{-1}\) correspond to -COO bending group\(^{20}\). The peak in (1a) was observed low frequency region at 445 cm\(^{-1}\) which may be attributed to the combined interaction of this metal ion Cs to –OH carboxylic groups of maleic acid.

The observed band in (1b) at 939 cm\(^{-1}\) may be attributed to interaction of amide groups of acrylamide with Cr (VI).

![Fig. (1): FTIR spectra of (a) P(MA-AAm)-Cs (b), P(MA-AAm)-Cs /Cr(VI).](image)

3.2.2. X-ray diffraction:

X-ray diffraction data give a great deal of information about the qualitative aspects of disorder in crystal structure since disordering results in the broadening of the diffraction maxima. The X-ray diffraction pattern in Fig. 2 for P(MA-AAm)-Cs showed intensities thereby suggested that the resin is amorphous in nature.
3.2.3. Thermal analysis:

Thermogravimetric analysis (TGA) plays a vital role in studying the structure and the properties of any material. TGA has been widely used to investigate the decomposition characteristics of polymeric materials. The TGA is the measurement of the weight change of a material as a function of temperature and time. TGA data was used here to provide an alternative model of the kinetics of the prepared polymer degradation.

The TGA curve illustrates a 3-stage process. The first stage is in the temperature range 78-380°C, which could indicate the removal of all surface and matrix-bound moisture from the polymeric resin. The weight loss occurs in this region is 33.4%. The second stage occurs from 350 to 481°C, the weight loss in this region is 37.8% due to imidation of amide groups with the release of ammonia gas and also due to water and CO₂ release as a result of dehydration of maleic acid and decarboxylation of maleic acid anhydride. Beyond 481°C there is a third stage of a very slow weight loss extending to 750°C. The weight loss in this region is 29.5% and may be related to chain scission and carbonization processes.

The DTA shows that an endothermic peak at (78°C) which is attributed to the removal of external water molecules and endothermic peak at (317°C) is due to the removal of interstitial water molecules removed by condensation of –OH groups. The two endothermic peaks at 407 and 499°C can be attributed to the release of ammonia gas and CO₂ release as a result of dehydration of maleic acid. There is also an exothermic peak at 603°C corresponding either to the condensation of –OH groups or to the formation of the metal oxides and the possibility of metal carbide formation²¹.

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**Fig. (2):** XRD spectrum of for P(MA-AAm)-Cs.

**Fig. (3):** TGA and DTA thermograph for P(MA-AAm)-Cs resin
3.2.4. Scanning electron microscopy (SEM) analysis:

The field emission scanning electron microscopy (FE-SEM, Supra 40 VP, Zeiss, Germany) was used to observe the surface morphology of P(MA-AAm)-Cs resin before and after loading with Cr(VI). The samples were gold coated to improve its conductivity to obtain good images. SEM micrographs of the synthesised materials are shown in Figs 4, 5. It can be seen that the synthesized material has a porous basic structure, which makes it a natural adsorbent. Figs. 4, 5 also show that there is a distinct change in surface morphology after adsorption of Cr (VI).

Fig. (4): SEM for the polymeric resin before loading with Cr(VI)

Fig. (5): SEM for the polymeric resin after loading with Cr(VI)

3.3. Batch Sorption Studies:

3.3.1. Effect of pH on adsorption:

The pH of the aqueous solution is an important parameter in the adsorption process. Hexavalent chromium removal by the P(MA-AAm)-Cs at 25±1 °C and an initial calculated Cr (VI) ion concentration of 50 mg/l was also found to be pH dependent. The effect of the initial solution's pH on the adsorption of Cr (VI) traced by radioactive 51Cr onto P(MA-AAm)-Cs was studied at a contact time, of 60 min and adsorbent dosage of 0.05 g at a pH range of 2.0–6.0 is shown in Fig. 6. The initial pH of the chromium solution was adjusted with 0.1M HCl and 0.1M NaOH solutions. It was found that the total amount of adsorption of Cr (VI) onto P(MA-AAm)-Cs decreases with increase of the pH from 2.0 to 6.0. The maximum adsorption of Cr (VI) onto P(MA-AAm)-Cs was found at pH 2.0. To explain the effect of pH, we need to clarify the type of interaction between Cr (VI) and P(MA-AAm)-Cs. It is widely believed that the mechanism for the adsorption of anions involves a surface complexation phenomenon in the adsorption process. Depending on the type of connection of an anion to an active surface site, the surface complexes formed are classified as inner and outer-sphere complexes. If the number of protonated surface groups is more than that of dissociated groups, the surface is positively charged and become suitable for anion adsorption. The pH effect was also attributed to the different complexes that Cr(VI) can form in aqueous solutions. The hexavalent Cr(VI) forms are Cr₂O₇²⁻ and HCrO₄⁻¹. The two forms are pH dependent. The predominant form of Cr(VI) below a pH of 2.0 is Cr₂O₇²⁻. Increasing the pH will shift the concentration from the Cr₂O₇²⁻ form to HCrO₄⁻¹. This could be explained as follows: Because of oxyanion forms such as HCrO₄⁻¹ and Cr₂O₇²⁻ of Cr (VI) in acidic medium, and the lowering of pH causes the surface of the adsorbent to be protonated to a greater extent, a strong attraction exists between these oxyanions of Cr(VI) and the positively charged surface of the adsorbent. In highly acidic media of pH 2–6, it can be stated that the adsorbent surfaces might be highly protonated and favor the uptake of Cr (VI). With further increase in the pH from 4 to 6, the degree of protonation of the surface decreases gradually and hence decreased adsorption is observed. The surfaces of P(MA-AAm)-Cs are covered with amine groups.
of which $pK_a$ are 10.6. Electrostatic interaction, ion-exchange, and surface complexation could be the major adsorption mechanisms which work individually or in combinations. Under acidic conditions, amine groups are easier to be protonated and the $\text{HCrO}_4^{-}$ anions attract protonated amine groups as shown in Scheme 2.

![Scheme 2](image)

**Scheme (2)**. Presumed mechanism of interaction between adsorbent P (MA-AAm)-Cs and adsorbate

Fig. (6): The effect of pH on adsorption of Cr (VI) onto P(MA-AAm)-Cs $C_r$ (10 mg/l), adsorbent dose (0.05g), shaking time 60 min and Temp. at 25±1 °C

3.3.2. The effect of initial concentration:

The effect of initial concentration of Cr(VI) traced by radioactive $^{51}$Cr on adsorption is illustrated in Fig. 7. The adsorption experiments were carried out at different initial Cr(VI) ion concentrations ranging from 10 to 100 mg/L. Initial concentration had a considerable effect on Cr(VI) removal. The extent of removal was suppressed by approximately 24 % when initial concentration was increased from 15 to 100 mg l$^{-1}$ for constant pH (4) and adsorbent dose (0.05g). At low initial Cr(VI) concentrations, the available sorption sites were easily occupied by $\text{HCrO}_4^{-}$ anions resulting in higher removal efficiencies. However, as the initial concentration of $\text{HCrO}_4^{-}$ anion increased, most of the available sorption sites became occupied, leading to a decrease in the removal efficiency.

![Fig.7](image)

**Fig.(7)**: The effect of initial concentration on adsorption of Cr (VI) onto P(MA-AAm)-Cs PH (2), adsorbent dose (0.05g), shaking time 60 min and Temp. at 25±1 °C
3.3.3. Effect of adsorbent dose:

Fig. 8 Shows the effect of adsorbent dose on the adsorbent capacity of Cr(VI) from the aqueous solution. It is observed that the uptake percentage increases from 38.9.12 to 96 % with an increase in the adsorbent dose from 10 mg to 50 mg. This is due to an increase in the surface area and availability of more active sites for sorption. Afterwards (from 50 mg), the removal efficiency remains unchanged with increase in adsorbent dose because the sorbate Cr (VI) becomes limiting in the system(24).

![Fig. 8](image)

**Fig. (8):** Effect of adsorbent dose on the removal of Cr(VI) by P(MA-AAm)-Cs resin.

3.4. Effect of contact time and kinetic parameters:

The contact time was also evaluated as one of the most important factors affecting the adsorption efficiency(25). In a batch-based study, samples were taken at different time periods varying between 5 and 240 min. As shown in Fig. 9, the concentration of residual chromium decreases with the increase of contact time. In other words, the removal of chromium from aqueous solutions increases with the increase of contact time. First, the adsorption equilibrium was reached very fast for Cr (VI) and took only 30 min. During the initial stage in the process a greater number of adsorption sites are available to the metal ions enabling them to interact readily with the adsorbent and hence leading to a high adsorption rate. In addition, the driving force for adsorption is the concentration gradient between the bulk solution and the solid-liquid interface. A higher adsorption rate is observed initially because gradient is higher during this time period. The slow adsorption rate observed during the later stage of the process may be attributed to the slower rate of diffusion of the solute into the interior of the adsorbent particles(26).

The pseudo-first-order and pseudo-second-order kinetic models were selected to test the adsorption dynamics in this work because of their good applicability in most cases in comparison to the first and second-order models [27]. The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows;

\[
\log (q_e - q_t) = \log q_e - k_1 t \\
\]

Where \( q_e \) and \( q_t \) are the amounts of chromium ions adsorbed (mg g\(^{-1}\)) at equilibrium and at time \( t \) (min), respectively, and \( k_1 \) is the adsorption rate constant of pseudo first-order sorption (min\(^{-1}\)). In most cases, the first-order equation of Lagergren did not apply well throughout the whole range of contact times and is generally applicable over the initial 20–30 min of the sorption process. The plotting of \( \log (q_e - q_t) \) versus time deviated considerably from the theoretical data after a short period(28).
The pseudo-second order equation is based on the sorption capacity of the solid phase and is expressed as:

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  
……………………..(4)

where \( k_2 \) is the rate constant of second order sorption (mg g\(^{-1}\)), \( q_e \) the amount of metal ions adsorbed at equilibrium (mg g\(^{-1}\)) and \( q_t \) the amount of sorbate on the surface of the sorbent at any time (mg g\(^{-1}\)\(^{\text{19}}\)).

Similarly, Fig. 10 shows the application of the pseudo-second order model to the data as plot of \( t/q_t \) versus \( t \). Again the plot was linear, allowing the values of \( k_2 \) and \( q_e \) to be calculated from the slope and intercept. All kinetic parameters obtained employing the pseudo-first order and pseudo-second order models are listed in Table 2. It was found that the results from \( R^2 \) were fitted better to the pseudo-second order kinetic model. Furthermore, it can be concluded that \( q_e \text{calc.} \) is nearly to \( q_e \text{-exp.} \) in the pseudo-second order kinetic model.

**Table (2):** Experimental \( q_e \) values from pseudo-first-order and pseudo-second-order kinetics for adsorption of Cr(VI) ions onto P(MA-AAm)-Cs resin.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Cations</th>
<th>( q_e \text{(exp.)} ) (mg/g)</th>
<th>Pseudo-first order kinetics</th>
<th>Pseudo-second order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(MA-AAm)-Cs resin</td>
<td>Cr(VI)</td>
<td>74.6</td>
<td>-0.0634</td>
<td>0.9982</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>83.936</td>
<td>0.0056</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>76.05</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

3.5. Equilibrium adsorption studies:

The Langmuir and Freundlich adsorption isotherms were investigated. These are widely used to analyze sorption of data of Cr(VI) traced by \(^{51}\)Cr 10-100 mg/L on P(MA-AAm)-Cs polymeric resin.

The Langmuir isotherm equation (5) is valid for monolayer sorption onto a surface containing a finite number of identical sorption sites, and may be described in the linear form by the relationship\(^{27}\):

\[ \frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o} \]  
…………………………(5)
Where \( q_e \) (mg/g) and \( C_e \) (mg/L) are the amounts adsorbed and remaining in solution at equilibrium, respectively. \( Q^0 \) is the monolayer capacity and \( K_L \) is equilibrium constant which can be determined via the linearized Langmuir isotherm. The Langmuir model is depicted in Fig. 11, which shows that a plot of \( C_e/q_e \) versus \( C_e \) for the adsorption of Cr(VI) traced by \(^{51}\)Cr polymeric resin.

The Freundlich equation (6) is a purely empirical relationship based on sorption onto heterogeneous surface. Its linear form is commonly represented as:

\[
log q_e = logK_f + \frac{1}{n}logC_e 
\]  

Fig. 12 shows that the application of the Freundlich isotherm model in terms of a plot of log \( C_e \) versus log \( q_e \) for Cr(VI).

The equilibrium adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 2. Based on the adsorption experimental results, the Langmuir and Freundlich model parameters (\( Q^0 \), \( K_L \) and \( K_f \), \( n \)) were determined with linear regression.

As can be seen from Table 3, the values of \( R^2 \) and \( Q^0 \) demonstrated the agreement of the experimental data with the Langmuir model very well for the adsorption of Cr(VI) onto P(MA-AAm)-Cs resin. The theoretical \( q_e \) values were very close to the experimental \( q_e \) values as according to Langmuir isotherm curves in Fig.11. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites on P(MA-AAm)-Cs resin, since the Langmuir equation assumes that the surface is homogeneous \(^{29,30}\).

**Fig. (11):** Langmuir isotherm for adsorption of Cr(VI) ions onto P(MA-AAm)-Cs resin.

**Fig. (12):** Freundlich isotherm for adsorption of Cr(VI) ions onto P(MA-AAm)-Cs resin.

**Table (3):** Langmuir and Freundlich constants.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Experimental Loading ( q_{exp} ) mg/g</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q^0 ) (mg.g(^{-1}))</td>
<td>( k_L ) (L.mg(^{-1}))</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>74.4</td>
<td>76.45</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

**3.6. Effect of temperature and thermodynamic parameters:**

Evaluation of the thermodynamics, after attaining equilibrium in 30 min., was done at four test temperatures, namely, 298, 308, 313 and 323 °C. A 0.05 g mass of polymeric resin and 5 mL of 100 mg/l from each ion were equilibrated at their natural equilibrium pH of 4. The values for \( q_e \) have been plotted against the temperature, for the different temperatures tested in Fig. 13. The \( K_d \) values
increased with increase in temperature and showed the endothermic nature of the sorption. In addition to the electrostatic attraction plays an important role in the sorption process.

![Graph showing qe vs Temperature](image)

**Fig.(13):** Effect of temperature on adsorption of Cr (VI) ions onto P(MA-AAm)-Cs resin.

Values of thermodynamic parameters were calculated from the slope and intercept of a plot of the values of \( \log K_d \) against the reciprocal of temperature (1/T)

\[
\Delta G^0 = -RT\ln K_d \quad \ldots \ldots \ldots \ldots \ldots (7)
\]

\[
\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \ldots \ldots \ldots \ldots \ldots (8)
\]

Where \( K_d \) is distribution coefficient, \( \Delta G^0 \) is the free energy change, \( \Delta H^0 \) is the enthalpy change of the sorption process, \( \Delta S^0 \) is the entropy change, \( R \) is the universal gas constant, and \( T \) is the absolute temperature in kelvin. The plot of \( \ln K_d \) against 1/T for Cr(VI) ions is shown in Fig. 14 and summarized in Table 4.

The positive values of \( \Delta H^0 \) indicate that the sorption process was endothermic in nature, while the negative values of \( \Delta G^0 \) indicate the spontaneous nature of the sorption process. Similarly, the positive values of \( \Delta S^0 \) demonstrate the increased randomness at the solid/solution interface during the sorption process.

![Graph showing lnKd vs 1/T](image)

**Fig.(14):** Vant Hoff's plot (b) for adsorption of Cr (VI) ions onto P(MA-AAm)-Cs resin.

**Table (4):** Thermodynamic parameters for sorption of Cr (VI) ions on P(MA-AAm)-Cs resin.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>T, °K</th>
<th>( \Delta G^0 ) (KJ.mol(^{-1}))</th>
<th>( \Delta H^0 ) (KJ.mol(^{-1}))</th>
<th>( \Delta S^0 ) (J.mol(^{-1}).K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>298</td>
<td>-2.63</td>
<td>28.65</td>
<td>104.78</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-3.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-4.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-6.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. CONCLUSION

A new polymeric resin, namely P(MA-AAm)-Cs, was prepared and exhibits promising sorption characteristics for sorption of Cr(VI) ions. It can also be used as an alternative sorbent material in the treatment of radioactive liquid waste. The sorption equilibrium data was fitted with Langmuir, Freundlich isotherm model. The results indicated that the isotherm data successfully fit Langmuir model over the entire concentration range studied. Furthermore, the kinetics of metal ions was experimentally studied and the obtained rate data were analyzed using simple Lagergren-first–order and pseudo-second-order models. The results showed that the pseudo second-order sorption mechanism is predominant and the overall rate constant of sorption process appears to be controlled by chemical sorption process. The process is thermodynamically feasible as indicated by negative free energy change and positive entropy change which confirmed that the process is endothermic in nature.

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(21) S.S. Renat, Physical Chemistry of Inorganic Polymeric and Composite Material, 1992,Ch. 2, 44.