Preparation of poly hydroxamic acid from poly (styrene –methyl methacrylate) and study of the kinetics of nickel ion sorption by the prepared acid

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ABSTRACT

In this paper, the copolymer (styrene-methyl methacrylate) was prepared by using free radical polymerization for the copolymerization between methyl methacrylate and styrene in an equal molar mixing ratio and using benzoyl peroxide as a starter at a temperature of 70 °C. Then the prepared copolymer was converted to poly hydroxamic acid, and this was done by reacting the copolymer with hydroxylamine hydrochloride at a base medium of = 13 using sodium hydroxide with heat escalation for a period of 70 °C. The nickel ion sorption capacity of the resultant product was evaluated using poly hydroxamic acid and spectroscopic FT-IR. As well as studying the effect of time, temperature, and acidity function on the sorption capacity by chelating poly hydroxamic acid. Where it was shown that the capacity of adsorption increases with increasing time and decreases with increase in temperature mediated by poly hydroxamic acid. The equations of Arrhenius and Vant Hof were used, and from the enthalpy values, it was shown that the reaction was exothermic, and from the negative compression energy values, it was found that the reaction is spontaneous and the type of physical detention is mediated by poly hydroxamic acid.

1- INTRODUCTION

Hydroxamic acid copolymers are one of the most important chemicals utilized in the production of stable chelating agents. It is also one of the chelated polymers with a ring structure that is used to remove ions of toxic heavy elements from aqueous solutions, such as iron, vanadium, copper, and other toxic heavy metal ions. It has a wide range of applications in analytical chemistry because it has the ability to bind to a metal through more than one donor atom. In addition, the hydroxamic acid units in the polymer chain are spaced appropriately, allowing the hydroxamic acid to coordinate with the metal ion to form an octahedral complex with a 1:3 ratio and good stability [1,2].

Organic substances hydroxamic acid and substituted nitrogen derivatives are known for their ability to preferentially adsorb heavy metal ions and hydroxamic acid polymers that are known for this property[3].

Hydroxamic acid molecules have one negative charge and include the ligands O,O Di denate [4]. Hydroxamic acid is also a derivative of hydrogen connected to nitrogen in hydroxylamine molecules, with the following general chemical formula [5,6].

Where R is an alkyl group, either saturated or unsaturated, a substituted aryl group, or a polymer:

Furthermore, despite their important properties, hydroxamic acids are one of the least well-studied compounds, and it is difficult to determine the correct...
structure of hydroxamic acids due to the fact that they exist in three chemical forms (Tautomeric Forms), as shown by the structural formulas below (a, b, c) [7].

Fig. 1: The aromatic formula of poly hydroxamic acid

The capacity of hydroxamic acids to form a stable chelate with heavy metal ions is one of their most well-known characteristics [8]. Hydroxamic acid is a widely distributed chemical with structural features found in a variety of naturally induced compounds. It plays an essential role in medical and biological aspects, and was first discovered by Loosen in 1869 [9].

In addition, recent research and studies of hydroxamic acid have shown a way to separate the natural compounds found in fungi and algae, which are antibiotics against the factors of division and growth of malignant tumor cells. Also, the compositions and materials manufactured for hydroxamic acid were shown to have anti-malarial, anti-fungal, and anti-bacterial activities. It is an alternative to the manufacture of HCA as stable chelating reagents with high selectivity with some heavy metal ions such as iron.[10,11].

The ability of hydroxamic acids to chelate heavy metals has long been known. With ions such as Fe3+, Mo6+, V5+, Ti+4, Hg2+, UO2+, and Cu2+, it has been proven to be effective chelating ligands [12].

The coordination between nickel ion and poly(styrene-like methacrylate) hydroxamic acid is illustrated in Figure (2)[7].

Fig. 2: shows the bonding of nickel to hydroxamic acid

2. EXPERIMENTAL
2-1. Materials
Methyl methacrylate (99 percent HIMEDIA), Styrene (98 percent SIGMA), hydroxyl amine hydrochloride (98 percent ), sodium hydroxide, potassium hydroxide, GPR, initiator benzoyl peroxide (B.P), solvent gasoline (99 percent), ethanol (99.9% ), Manganese (II) chloride, and nitrogen gas were employed.[10].

2-2. Instruments
The following devices were utilized to complete the study: a centrifuge, a delicate balance, a water bath with a cooling and heat pump for liquid recycling, a pH meter, a thermometer, an infrared, ultraviolet, and visible radiation device type GBC, Absorption Atomic Device (AAS) Model Berkin, Atomic Absorption Spectroscopy.

2-3. Preparation of Poly (styrene -co-methyl metha acrylate):
The monomers were purified by two steps and then polymerized by taking equal volumes of monomers and placing them in a water bath at a temperature of (70-80) after oxygen was expelled from it by passing nitrogen gas over it and adding the initiator Benzyl Peroxide. After increasing the viscosity of the mixture, benzene was added to dissolve the polymer, then the contents were poured into a beaker containing ethanol for the purpose of precipitation, then it was raised on a bottle for an hour and left to dry. Finally, it was diagnosed using FT-IR spectrum as shown by the following equation.[13]

Fig. 3: Shows the copolymerization equation between styrene and methyl methacrylate

Poly (Styrene)
A certain weight of the previously prepared copolymer was taken and the appropriate solvent was added to it, as well as a certain weight of (Hydroxyl amine hydrochloride). After taking the necessary steps and the appropriate conditions, the filtrate was taken with a basic medium pH = 12-13 and thermal escalation was conducted for (83) hours with magnetic stirring at a temperature (70-80 ºc). The precipitate was collected which is poly hydroxamic acid, purified, and carried out FT-IR spectroscopy [13,14,15].

2-4. Studying of Applications of poly (St- Co – MMA) hydroxamic acid
2-4-1. Determined of Sorption Capacity of nickel (II) ion by Poly (St- co –MMA) hydroxamic acid
The adsorption capacity (Sorption Capacities) of poly(styrene-like methacrylate) hydroxamic acid was determined for the nickel ion and this was done by determining the remaining concentration (Ce) of the metal ion
in the filtrate after treatment with hydroxamic acid, which in turn represents the equilibrium concentration. The residual concentration of metal ions was determined using atomic absorption device and UV-Vis spectrophotometer, where the equilibrium concentration (C_e) and adsorption capacity (Q) of the nickel ion Ni^{2+} from the following equation:[14,15]
\[
Q_e = \left( C_o - C_e \right) \frac{V}{M} \hspace{1cm} (1)
\]

Where Qe (mg.g\(^{-1}\)) represents the quantity of dissolved metal ion, (C, Ce) represents the initial and equilibrium metal ion concentration in solution (mg/L), V (L) represents the volume of the solution, and M (g) represents the weight of the sorbent poly (St-Co-MMA) hydroxamic acid. Poly (St-Co-MMAHA) was also used to assess the sorption capacity of Iron ion, Zinc ion, and Manganese (II).[16]

2-5. Study of adsorption of Poly (St- Co –methyl methacrylate) hydroxamic acid:

2-5-1. Study of the Effect of Temperature on sorption Capacity of Nickel (II) ions Poly (St- Co-MMA) HA:

The effect of temperature on the adsorption capacity of poly hydroxamic acid (Styrene - such as methacrylate) for the studied Ni^{2+} ions was studied by determining the initial concentrations, equilibrium concentrations and adsorption capacity, at temperatures 20 °C, 40 °C and 60 °C, 80 °C as well as for ions Mn^{2+}, Fe^{2+}, and Zn^{2+} [14,17,18].

3. Results and Discussion

3-1. Characterization of (Styrene –Co- methyl methacrylate) :

Poly (styrene-Co- methyl methacrylate) produced was diagnosed by using infrared spectrometer FT-IR where the absorption bands matched the structural formula of the compound, as the infrared spectrum showed an absorption band in the region (1785) \( \text{cm}^{-1} \) is due to the absorption of the carbonyl group (C=O), the absorption band in the region (2991)\( \text{cm}^{-1} \) is due to the absorption of the (CH) group, and the absorption band in the region (1291)\( \text{cm}^{-1} \) is due to the absorption of the group (C-O) , and the absorption band in the region (1440) \( \text{cm}^{-1} \) is due to the absorption of the (C=C) alkene group[19].

The polymer (styrene-like methacyrlate) was also diagnosed by magnetic resonance spectroscopy (NMR), where the results showed the following:

The nuclear magnetic resonance (NMR) spectrum of the Poly(St-co-MMA) proton showed a sharp single signal at chemical displacement = 1.25 (\( \delta \)) belonging to the protons of the methyl group (CH3) attached to the carbon atom (1beta-C-C). Also, the nuclear magnetic resonance (NMR) spectrum showed a sharp single signal at chemical displacement = 3.64 (\( \delta \)) belonging to the methyl group (CH3) ester protons. It also showed a binary sign at chemical displacement = 2.03 belonging to the protons of the ethylene group (-C-C-). It also showed multiple signs at chemical displacements = 7.22 -7.42 due to aromatic protons. It also showed a multiple sign at chemical displacements = 2.55 due to the proton of the carbon atom attached to the aromatic ring.

Fig. 5: NMR spectra of poly (Sty-co-MMA)

3-2. Characterization of Poly (Sty –C- MMA ) hydroxamic acid:

Hydroxamic acid was formed from a copolymer (styrene-like methacrylate) using the free radical mechanism of copolymerization using the initiator benzoyl peroxide, with a conversion ratio of 10 percent. As illustrated by the following equation:

Fig. 6: Equation for the formation of poly hydroxamic acid from a copolymer.

The ester group of the poly (Styrene-Co-methyl methacrylate) was converted into hydroxamic acid to produce poly hydroxamic acid. Treatment of poly (St-Co-MMA) with
potassium hydroxide (KOH) or sodium hydroxide (NaOH) in alkaline medium at pH =13 resulted in hydroxyl amine hydrochloride. The general technologies previously used to manufacture poly hydroxamic acid were used [15,20].

Using FT-IR spectroscopy, the resulting compound was diagnosed, as the spectrum showed an absorption band in the (3200) region that belongs to the absorption of the O-H group, and an absorption band in the region (3444) that belongs to the absorption of the N-H group, and an absorption band in the (930) region that belongs to the absorption of the group (N-O). The absorption band in the region (1724) belongs to the C=O group, and the absorption band in the region (1440) belongs to the absorption of the C=C group. (FTIR) spectra Figure 6:

3-3. Sorption of Ni²⁺ by poly (St-Co-MMA ) HA:

After treatment with poly (Styrene-Co-methyl methacrylate) hydroxamic acid, Table (1) shows the initial and equilibrium metal ion concentrations (Co, Ce), as well as the adsorption capacity (q) of Ni²⁺. (Co, Ce) and q were measured at 100 mg/ L, 69 mg/liter, and 1610 mg/g, respectively [14].

Table. 1: The values of C₀, Cₑ and adsorption Capacity (q) of Ni²⁺ by poly (Styrene-Co-Methyl metha acrylate)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>C₀ (ppm)</th>
<th>Cₑ (ppm)</th>
<th>Ce mg/L *10²</th>
<th>Cₑ mg/ L *10²</th>
<th>Qₑ (mg/ g) *10²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni²⁺</td>
<td>100</td>
<td>82</td>
<td>1</td>
<td>0.82</td>
<td>18</td>
</tr>
</tbody>
</table>

3-4. Effect of Time on Ni²⁺ sequestration capacity:

The effect of time on the adsorption capacity of poly(styrene - methyl methacrylate) for nickel metal ion Ni²⁺ was studied after we established the other factors of acidity, temperature and concentrations. The maximum adsorption capacity (the highest adsorption capacity of poly hydroxamic acid) was also calculated as shown in Figure 7 [10,19].

3-5. Effect of pH on Ni²⁺ sequestration capacity:

The effect of the acid function on the adsorption capacity of poly(styrene – Co- methacrylate) hydroxamic acid for the metal ion was studied by determining the initial concentrations (C₀) and equilibrium concentrations (Cₑ) as well as the adsorption capacity (Q), where we found that the values of the adsorption capacity (Q) are greater at the values of (pH=6), and the values of the adsorption capacity (Q) are lower or higher as the values of (pH) are lower than (pH=6). as shown in Figure(8).[17]

3-6. Effect of Temperature on Ni²⁺ adsorption capacity ::

Figure 9 shows the effect of temperature on the adsorption capacity of poly hydroxamic acid (styrene - such as methacrylate) for the metal ion that was studied by determining the initial concentrations, equilibrium concentrations and adsorption capacity[10]. Since the values of (Q) at °C (20) are as high as possible.[18]
3.7. Study of the kinetics of sorption of metal ion Ni^{2+} by poly(styrene-Co methacrylate) hydroxamic acid:

The kinetic of metal ion retention was studied by means of poly(styrene-like methacrylate) hydroxamic acid at different temperatures 20 °C, 40 °C, 60 °C, 80 °C, where the second-order equation was used to calculate the retention velocity constant, which is called the world equation (HO and McKay 1998). Which is represented by the following Equation: [13,14,21]

\[
\frac{t}{q_t} = \left( \frac{1}{k_2 q_e^2} \right) + \frac{t}{q_e} \quad \text{..................(2)}
\]

where \(q_t = (\text{mg g}^{-1})\) and \(q_e=(\text{mg.g}^{-1})\), respectively, are the quantities of adsorption at time (min) and equilibrium, and \(k_2\) (g.mg^{-1} min^{-1}) is the second-order rate constant, fig. 11:a-b: A straight line was obtained by plotting ( \(t/q_t\) ) against time (min), and the slope and intercept of the plot were used to calculate the values of \(q_e\) and \(k_2\). The \(k_2\) values were found to be, (1.17*10^{-3}, 1.26*10^{-3}, 1.40*10^{-3}, 1.57*10^{-3} (g/mg. min)), \(q_e\) = (81, 75, 69, 63 (mg/g)) at (20, 40, 60, 80,) °C, respectively.

Table. 2: shows the kinetic values of nickel ion retention Ni^{2+} mediated by poly (styrene - co- methacrylate) hydroxamic acid at temperatures 20°C, 40°C, 60°C, 80°C

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Q(t mg/g)*10^{-2} of Mn^{2+}</th>
<th>60(min)</th>
<th>120(min)</th>
<th>180(min)</th>
<th>240(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>4.6</td>
<td>5.1</td>
<td>5.9</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>3.7</td>
<td>4.1</td>
<td>5.0</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>2.6</td>
<td>3.2</td>
<td>3.9</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>1.0</td>
<td>1.7</td>
<td>2.1</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

3.8. Thermodynamics of the adsorption process:

Activation energy:

The effect of thermodynamic functions on the ion adsorption process mediated by poly hydroxamic acid was studied at different temperatures (293, 313, 333, 353 K) and the obtained results were recorded that show the thermodynamic values of nickel ion adsorption mediated by poly hydroxamic acid.

The activation energy is assumed to be the rate constant in the Arrhenius equation, as shown below [8,14],

\[
\ln k_3 = \ln A – \frac{E_a}{RT} \quad \text{..................(3)}
\]

The Arrhenius factor is A, while the sorption activation energy is \(E_a\) (kJ.mol^{-1}). The slope of a straight line was used to calculate the value of activation energy, which was found to be (9.9768) in the plot \(T \ln k_3\) as a function of \((T K_3)\) shown in Figure (11). (kJ.mol^{-1}) kJ.mol-1 kJ .mol^{-1} kJ. Because the rate is controlled by the intra-particle diffusion mechanism when the activation energy is low, it can be deduced that the process is guided by physical nature interaction.
3.9. Parameters of Thermodynamics:

At 293, 313,333, and 353 °K, the amount of Ni\(^{2+}\) sequestration at equilibrium was observed. The constant \(K_d\) for the equilibrium section is computed as follows: [15]
\[
K_d = \frac{q_d}{C_e} \quad \text{..........................(5)}
\]

At 20 °C, 40 °C, 60 °C, and 80 °C, the values of \(K_d\) for sorption of Ni\(^{2+}\) by poly (Styrene- Co- methyl metha acrylate) HA were 3.88, 3.46, 3.19, and 2.96 ml.g\(^{-1}\), respectively.

When the temperature was increased from 20 to 80 °C, the values of \(K_d\) at the starting concentration of (100 mg/L) decreased, demonstrating that the adsorption is an exothermic process. The following equation was used to calculate the value of the enthalpy \(\Delta H\):
\[
\Delta H = E_a - RT \quad \text{..........................(6)}
\]

Where \(\Delta H\) is the standard enthalpy, \(T\) is the absolute temperature (K), \(R\) is the gas constant, and \(E_a\) is the activation energy. The values of \(\Delta H\) where (-586.09 , -626.09 , -666.09 , -706.09 kJ. Mol\(^{-1}\)) at (20 , 40 , 60 and 80 °C). The exothermic nature of the Ni\(^{2+}\) adsorption process by poly (Styrene- Co- methyl metha acrylate) Hydroxamic acid was confirmed by the negative value of the \(\Delta H\).

The following equations were used to determine the thermodynamic functions \(\Delta S\) and \(\Delta G\): [22]
\[
\Delta G = -RT \ln K_d \quad \text{.........................(7)}
\]
\[
\Delta G = \Delta H - T\Delta S \quad \text{.........................(8)}
\]
\[
\Delta S = (\Delta H - \Delta G) / T \quad \text{.........................(9)}
\]

Where \(\Delta S\) is the standard entropy and \(\Delta G\) is the standard Gibbs free energy. The values of \(\Delta G\) where (-791.11 , -776.42 , -772.56 , and -762.48 kJ.mol\(^{-1}\)), \(\Delta S\) where (0.699 , 0.479 , 0.319 , and 0.159 g.mol.K\(^{-1}\)) at (20 , 40 , 60 and 80 °C).

At an initial concentration of 100 mg/liter, the values of Go decreased with increasing temperature from 20 to 80 °C, indicating that adsorption occurred spontaneously at all temperatures.

4. CONCLUSION

Hydroxamic acid polymers with known properties Compounds having hydroxamic acid groups selectively chelate most ions of metallic metals such as nickel.

Polymers containing an ester, such as poly –acrylate, can be used to make hydroxamic acid polymers.

When pH=(6) and temperature is less than high, the capacity of Ni\(^{2+}\) sorption on poly (St-Co -MMA) Hydroxamic acid increases.

Ni\(^{2+}\) Sorption on Poly (St-Co -MMA) the second order kinetics of hydroxamic acid, as well as the exothermic sorption process and the decreasing negative order enthalpy, were followed.

The value of free energy (\(\Delta G\)) for Ni\(^{2+}\) sorption on poly (St-Co -MMA) Hydroxamic acid, indicating that the sorption is spontaneous.

5. REFERENCES


تحضير متعدد حامض هيدروكساميك من متعدد (ستايرين - مثيل ميثا أكريلات) ودراسة حركية احتجاز أيون النيكل بواسطة الحامض المحضر

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الخلاصة:

في هذا البحث، تم تحضير البوليمر المشترك (ستيرين- مثيل ميثا أكريلات) باستخدام بليسته المزروع الميزوري عند درجة حرارة 70 درجة مئوية. ثم تم تحويل البوليمر المشترك المحضر إلى متعدد حامض الهيدروكساميك. وتم ذلك عن طريق تفاعل البوليمر المشترك مع هيدروكسيل أمين هيدروكسيل في وسط قاعدي – 13 باستخدام هيدروكسيد الصوديوم مع إجراء تصبغ حراري بدرجة 70 درجة مئوية لمدة 83 ساعة. بعدها تم تعبين سعة احتجاز أيون النيكل باستخدام متعدد حامض الهيدروكساميك وكذلك طيف الأشعة تحت الحمراء FI-IR. بالإضافة إلى دراسة تأثير الزمن ودرجة الحرارة ودالة الحموضة على سعة احتجاز أيون النيكل عن طريق تخليل حامض الهيدروكساميك. حيث تبين أن سعة الاحتجاز تزداد بزيادة الزمن وتقل مع زيادة درجة الحرارة بوساطة متعدد حامض الهيدروكساميك. كما تم استخدام معادلات أرينوس وفانت هوف، ومن قيم المحتوى الحراري، تبين أن التفاعل كان طاردا للحرارة ومن قيم طاقة كبس السالبة، وجد أن التفاعل تلقائي، وأن نوع الاحتجاز هو فيزيائي، بوساطة متعدد حامض الهيدروكساميك.