

Synthesis, Characterization and Copolymerizations of N-Methacryloxy Phthalimide with Styrene for Removal of Cu(II) Ions From Aqueous Solutions

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Abstract

The monomer N-methacryloxyphthalimide (NMP) was prepared by the reaction of methacrylic acid (MA) with N-hydroxyphthalimide (NHP) in the presence of N,N-dicyclohexylcarbodiimide (DCCI). The copolymerization of NMP with Styrene (St) was carried out in dimethylformamid (DMF) using Benzoyl peroxide (BzO₂) as initiator at 70°C.

The monomer reactivity ratios for the copolymerization of NMP with St was found to be $r_1 = 0.6341$ and $r_2 = 0.573$ by the Kelen-Tudos methods. The adsorption of Cu (II) ions onto the copolymers was examined, and found that the (NMP/St) (0.5: 0.5) copolymer has the highest up take capacity. For these target, the batch adsorption experiments was conducted to explore the kinetics and isotherms of the removal process onto resin with pH-value, initial concentration, temperature, and contact time as the controlling parameters. The kinetic and isotherm data could be well elucidated with Lagergren-second-order equation and Langmuir model respectively. Thermodynamic parameters, involving ΔH° , ΔS° and ΔG° were also calculated from graphical interpretation of the experimental data. The standard heat of adsorption (ΔH°) was found to be endothermic and the entropy change value (ΔS°) was calculated to be positive for the adsorption of Cu(II), ions onto the tested adsorbent. Negative value of ΔG° indicated that adsorption process for tested metal ions onto resin was spontaneous.

Keywords: Synthesis; copolymerization; chelating resin; copper ions; adsorption isotherms; kinetics; thermodynamics.

1. Introduction

As the number of ecological and health problems associated with environmental contamination continues to rise, the determination of heavy metal ion at trace level in environmental samples is becoming great importance [1]. Increasing concentrations of these metals in water constitute a severe health hazard mainly due to their non-degradability and toxicity. Although heavy metals could be found naturally in soils, sediments, water and even in living organisms, anthropogenic releases can increase its concentration to unacceptable levels. Heavy metal contamination exists in aqueous waste-streams from many industries such as chemical, plating, mining, tanneries, painting, plumbing, as well as agricultural sources where fertilizer and fungicidal spray are intensively used [2,3]. The electroplating industries are examples of processes that may create serious problems, since their wastewaters may contain large number of heavy metals, including chromium, copper, nickel, zinc, manganese and lead. High intake of copper (over 1.0 mg/l in drinking water) gets accumulated in the liver of human beings and animals resulting in ailments like hemochromatosis and gastrointestinal problems [4]. A wide range of methods are available for the removal of metal ions from aqueous solutions. These include ion exchange, solvent extraction, reverse osmosis, precipitation, chemical oxidation and reduction, filtration, electrochemical treatment and adsorption. The adsorption process has been the most frequently applied method in the industries, and still is the most widely studied. the selective adsorption technology with chelating resins has received an

enormous attention and increasing application due to the remarkable simplicity, high efficiency and low cost during the following multi-adsorption interaction processes to heavy metal ions such as ion exchange, physical adsorption and chelation [5-7]. Particularly, chelating resins have received an enormous attention because of its remarkable selectivity and high efficiency [8].

To develop this promising technology, several researchers have obtained some series of chelating resins through the polymerization of conventional chelating monomers such as acrylic acid, methacrylic acid and vinylpyridine [9-11]. In another procedure to invent chelating resins with different matrix structures and functional groups, synthetic polymers are firstly pre-pared, and the manifold low-molecular weight ligands are then grafted in succession by functionalization reactions [12-14]. Chelating resins are applied in many industrial and laboratory separation processes. Wastewater treatment, pre-concentration of ionic species and catalysis are some examples of the variety of applications of these materials [15-17].

The work described herein involved the following studies: (I) Synthesizing of N-methacryloxyphthalimide (NMP) monomer; (II) Copolymerization of (NMP) (monomer-1) with (St) (monomer-2) to (NMP/St) copolymers at different molar ratios; (III) Characterization of all the above synthesized substances by FT-IR, ¹HNMR; (IV) Calculating for monomer reactivity ratios by the Kelen-Tudos and Finman-Ross methods (V) An examination of the adsorption of Cu(II) ions onto

(NMP/St) copolymers to choosing the copolymer of highest adsorption capacity; and (VI) A study of Langmuir and Freundlich adsorption isotherms also the adsorption kinetics and thermodynamic parameters of adsorption of Cu(II) ions onto resin with highest adsorption capacity.

2. Materials and methods

2.1 Materials

Methacrylic acid (MA), N-hydroxyphthalimide (NHP), N, N-dicyclohexylcarbodiimide (DCCI), styrene (St) and benzoyl peroxide BzO₂ were from (Aldrich).

Coppersulphatepentahydrate(CuSO₄.5H₂O), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were supplied by (Sigma). All the solvents were of reagent grade and were purified by distillation before use.

2.2 Methods

2.2.1 Synthesis of (NMP) monomer

NMP was prepared by the reaction of NHP with MA in the presence of DCCI. To a cold solution (0-5°C) of 3.26 g (0.02 mol) of NHP and 1.722 g (0.02 mol) of MA in methylene chloride (100 mL) was added 4.1 g (0.02 mol) of DCCI, with stirring. After stirring for 15 h at room temperature, the precipitated dicyclohexyl urea was removed by filtration and the filtrate was evaporated to dryness in vacuum the residue was washed several times by petroleum ether (40-60). The yield was 88% and m.p. was 101-102°C.

2.2.2 Copolymerization of (NMP) with (St) monomers

The copolymerization was deaerated by flushing with pure, dry nitrogen gas and then sealed. The conversions of the polymerization were controlled to be less than 10%. After the polymerization, the copolymers were precipitated by adding fresh methanol. The precipitated polymers were filtered off and washed repeatedly with methanol. The copolymers obtained were purified twice by dissolving in DMF and reprecipitating with methanol. The polymers were dried in vacuum for 24 hours.

2.2.3 Adsorption experiments

The adsorption experiments have been studied by batch technique. First the adsorption of all synthesized copolymers was tested with 0.76 mmol/L copper solution, 0.05 g of copolymer and 25 ml of copper solution at pH 4.5, 30 °C. The batch adsorption experiments were conducted to explore the kinetics and isotherms of the removal process

onto resin. 0.05 g of the resin and 25 ml of labeled 0.76 mmol/L copper solution of different pH was stirred with uniform speed using a magnetic stirrer for 1.5h. The pH of the adsorptive solutions was adjusted with the suitable quantity of NaOH and HCl, monitored with a digital pH meter. All experiments were carried out at 30°C except for the temperature dependence studies where temperature varied from 30-60°C. Before adding the adsorbent, an aliquot of the bulk solution was withdrawn for the measurement of initial concentration. For the evaluations of capacity (q_e) as a function of contact time, from 1 to 7 hrs time intervals were applied at 0.8595 mmol/L of copper solution for the resin at pH 5.33. At the end of each time interval, the solution was filtered for phase separation and the concentration of supernatant solutions was measured, then (q_e) for adsorbed copper ions onto the resin was determined from the following equation:

$$q_e = (C_o - C_e)(V/m) \quad (1)$$

Where C_o and C_e are the initial and equilibrium Cu(II) ion concentration in the aliquots, respectively. V (L) is the solution volume and m (g) is the mass of sorbent.

The sorption isotherm experiments were conducted at a temperature of 30 °C and pH 5.33 by batch sorption procedure.

2.3 Analyses

2.3.1 FT-IR spectroscopy

The IR spectrum of all synthesized substances was measured as KBr pellets using FT/IR-BRUKER, Vector 22 (Germany) Spectrophotometer.

2.3.2 ¹H-NMR spectroscopy

The proton magnetic resonance spectrum of all synthesized substances in DMSO-H as a solvent and using TMS as a zero reference were recorded on a Varian Gemini 200 MHz spectrophotometer, Cairo University.

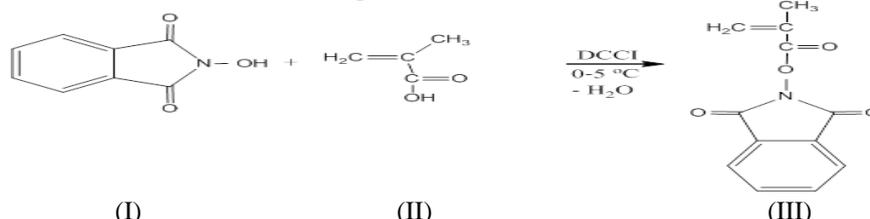
2.3.3 Determination of the metal ions concentration

Metal ions concentration was determined by using Hitachi atomic absorption Z-6100 polarized Zeeman spectrometer.

3. Results and discussion

3.1 Synthesis of NMP monomers

In the present investigation, NMP (III) was prepared by the reaction of NHP (I) with MA (II) in the presence of DCCI, according to the following scheme (Scheme 1). The monomer was crystalline solid.



Sch (1) The structure of the monomer was confirmed by IR and ¹HNMR spectra Table (1)

Table (1) IR and ¹HNMR Spectra of the Monomer (III).

Compound	IR spectra			segment	¹ HNMR Chemical shift (ppm)
	$\nu_{C=O}$ (ester) cm ⁻¹	$\nu_{C=O}$ (cyclicimide) cm ⁻¹	$\nu_{C=C}$ (vinylidene) cm ⁻¹		
III	1740	1797, 1840	1625	-CH ₃ CH ₂ =C- C ₆ H ₄ -	1.85 6.1-6.49 7.98

3.2 Copolymerization of NMP with st monomer

Copolymers of NMP and St with different feed compositions were prepared by using BzO₂ initiator in DMF (Scheme 2). Copolymerization was restricted to give less than 10% conversion. The ¹HNMR and IR spectra of the copolymer, poly(NMP/St) (0.5:0.5) is shown in able (2) .

The copolymer composition was determined from ¹HNMR spectral analysis of the copolymer. The assignment of the resonance peaks in the ¹HNMR spectrum allows the accurate evaluation of the content of each kind of monomer incorporated into the copolymer chain.

3.2.1 Reactivity ratios

The reactivity ratios r_1 and r_2 of copolymerization of NMP (monomer-1) with (St) (monomer-2) has been determined using Fineman-Ross [18] and Kelen-Tudos [19] methods. The mathematical details of these procedures are given in Tables (3, 4). The plots are show in Fig (1, 2) for Fineman-Ross and Kelen-tudos respectively. The results of the reactivity ratios are given in Table(5).

The results of the reactivity ratios are given in Table (5) show that NMP is generally more reactive than St; $r_1 > r_2$, hence the copolymers contain a higher proportion of NMP units. The product of r_1 and r_2 is less than the unity (0.3633), which indicates random distribution.

3.2.2 Copolymer compositions

With these values of r_1 and r_2 , the variation of the instantaneous mole fraction f_1 of NMP in the initial feed may be calculated using the following copolymer composition (Equation 2).

$$F = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2) \quad (2)$$

Where $F = F_1/F_2$, r_1 =reactivity ratio of NMP, r_2 =reactivity ratio of St, f_1 =mole fraction of NMP in the feed, f_2 =mole fraction of St in the feed. Fig (3), show the copolymer composition curves of NMP/St system.

Fig (3), show the copolymer composition curves of NMP/St system, which shows azotropic composition. The azotropic feed composition $f_1(az.)$ is given by:

$f_1(az) = (1-r_1) / (2-r_1-r_2)$, $f_1(az)$ = azotropic feed composition. A plot of copolymer composition

against the composition of the feed is shown by a solid line in Figure (3). The dashed line represents the ideal random copolymerization.

3.3 Adsorption studies

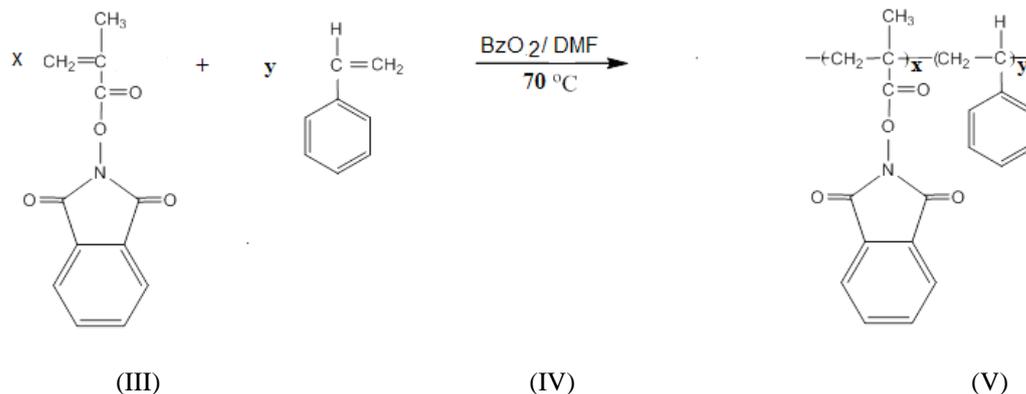
3.3.1 Examination of the adsorption of Cu (II) ions onto (NMP/St) copolymers

Figure (4) shows the uptake capacities of (NMP/St) copolymers of different molar ratios towards Cu (II) ions as a function of the adsorbate composition at fixed pH, adsorbent weight, stirring time and adsorbate concentration at 30°C. It is clear from the fig that the (NMP/St) (0.5/0.5) copolymer, has the highest uptake capacity.

3.3.2 Factors affecting the adsorption of Cu (II) ions onto (0.5:0.5) (NMP/St) resin

3.3.2.1 Effect of pH

Figure (5) shows the adsorption capacity of resin towards Cu (II) ions as a function of pH of the adsorbate at fixed adsorbent weight, fixed stirring time and fixed adsorbate concentration at 30°C. It is clear from the fig that the adsorption capacity of the resin towards Cu (II) ions increased as the pH value of the solution increased from 2.31 to 5.33 and then decreased with increase in pH. The adsorption capacity of the resin towards Cu (II) ions was minimum under highly acidic conditions (pH=2.31). This was because the binding sites for metal ions onto the adsorbent were mainly occupied by H₃O⁺ ions which restricted the approach of Cu (II) cations as a result repulsive forces [20-22], the amide groups become protonated and therefore the coordination with the metal ion is hindered giving lower uptake values. However, as the pH value of the solution increased, a number of associated H₃O⁺ ions diminished, exposing an increasing in negatively charged adsorbent surface and thereby allowing an increasing number of positively charged Cu (II) ions to be adsorbed. This higher uptake may be attributed to the presence of free lone pair of electrons on the nitrogen atom suitable for coordination with the metal ion to give the corresponding resin metal complex. The adsorption capacity of towards Cu(II) ions at pH values above 5.33, no further adsorption occurred due to the precipitation of Cu (II) ions as Cu(OH)₂ [23].



Sch (2)

Table (2) IR and ¹HNMR Spectra of copolymer RV; poly (NMP/St) (0.5: 0.5).

Compound	IR spectra			¹ HNMR	
	$\nu_{\text{C=O}}$ (ester) cm ⁻¹	$\nu_{\text{C=O}}$ (cyclicimide) cm ⁻¹	$\nu_{\text{C=C}}$ (vinylidene) cm ⁻¹	segment	Chemical shift (ppm)
V (NMP/St) (0.5: 0.5)	1739.69	1780.4, 1809	-----	-CH ₃ -CH- -CH ₂ -C- -C ₆ H ₄ -C ₆ H ₅	1.843 3.57 2.004 7.834 7.125

Table (3) Copolymerization of NMP with St (Fineman-Ross method).

M ₁ (NMP)	M ₂ (St)	a	m ₁ (NMP)	m ₂ (St)	b	a/b	a-a/b	a ² /b
0.3	0.7	0.42856	0.337	0.6629	0.50837	0.8430	-0.414	0.3612
0.4	0.6	0.66667	0.44	0.56	0.78571	0.8484	-0.1817	0.562
0.5	0.5	1	0.516	0.48	1.075	0.9302	0.0698	0.930
0.6	0.4	1.5	0.601	0.398	1.5075	0.9950	0.505	1.5
0.7	0.3	2.33333	0.65	0.35	1.85714	1.2564	1.07693	2.92

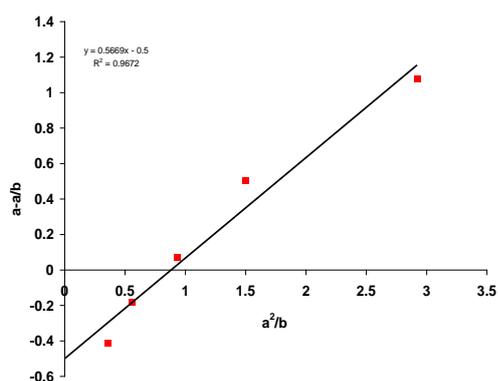

Fig (1) Fineman-Ross plots for the copolymerization of NMP with St.

Table (4) Copolymerization of NMP with St (Kelen-Tù dđ s method).

a	b	a ²	a(b-1)	ab+a ²	η	ξ
0.42856	0.50837	0.18367	-0.210698	0.7068	-0.2981	0.25986
0.66667	0.78571	0.44444	-0.142857	1.253	-0.1140	0.3547
1	1.075	1	0.075	2.10628	0.03560	0.47477
1.5	1.5075	2.25	0.7613	3.8014	0.20027	0.59188
2.33333	1.85714	5.44444	2	7.3556	0.27190	0.74017

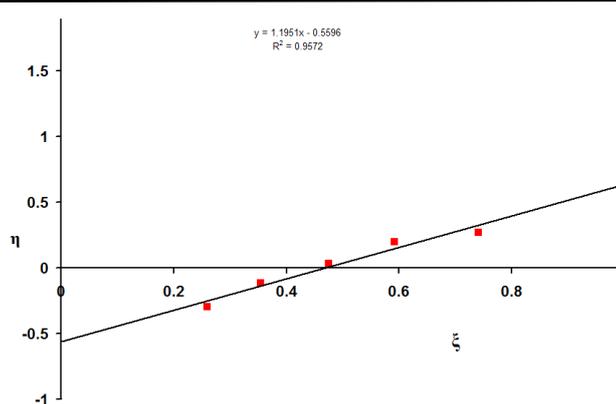


Fig (2) Kelen-Tudos plots for the copolymerization of NMP with St.

Table (5) Monomer Reactivity Ratios for the Copolymerization of NMP with St

M1-M2	Fineman-Ross		Kelen-tudos			
	r_1	r_2	r_1	r_2	$r_1 r_2$	α
NMP-St	0.5668±0.060	0.5025±0.0930	0.6341±0.0783	0.573±0.0776	0.3633	1.029

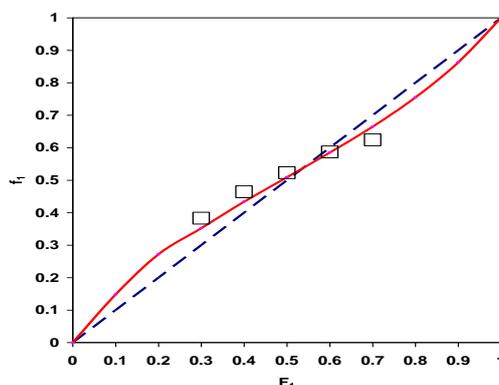


Fig (3) Copolymer composition diagram of poly (NMP-St) system.

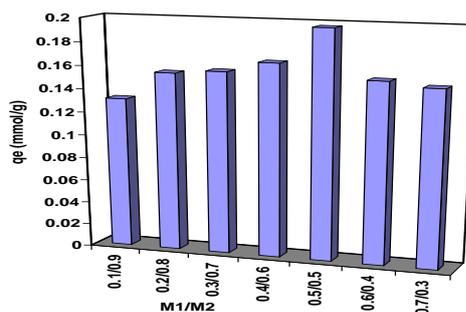


Fig (4) Examination of the adsorption of Cu (II) ions onto (NMP/St) copolymers.

3.3.2.2 Effect of initial ion concentration of Cu(II) ions on adsorption process

The dependence of the adsorption capacity of resin towards Cu(II) ions on the initial concentration of Cu(II) ions was studied by varying the latter over the range 0.2 to 1.2 mmol/L at 30°C, at fixed stirring time, and pH Fig (6). It clear that the sorption amount of Cu²⁺ ions on the resin gradually increases with increasing the initial ion concentration to reach an equilibrium value at

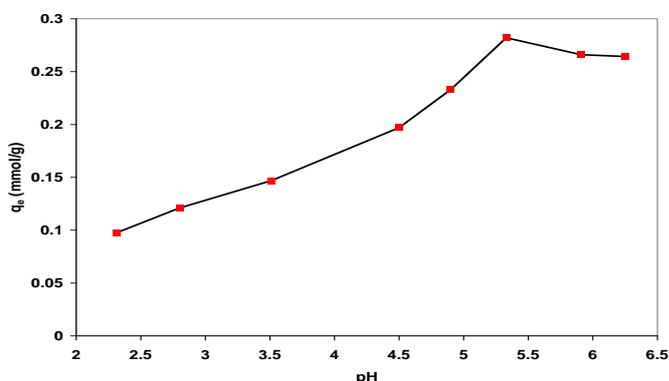
approximately 0.8595 mmol/L for resin, at which occupation for all sites on the adsorbent was achieved, and thus all sorption experiments in the present study were carried out at initial ion concentration 0.8595 mmol/L.

3.3.2.3 Effect of contact time on adsorption process

In order to determine the influence of contact time between resin and aqueous solution on copper

adsorption, at fixed pH, concentration and 30°C, variations of adsorption capacity (q_e) versus time (1-7h) were plotted, as it can be seen in Fig (7). It was observed that the adsorption of Cu^{2+} ions from aqueous solution using the adsorbent is

continuously increased with time increase until reaching equilibrium between two phases after 6h. Therefore, this obtained equilibrium time was selected for the next adsorption experiment .



Fig(5) Effect of pH on The adsorption capacity of resin towards Cu(II) ions from aqueous solution at 30°C.

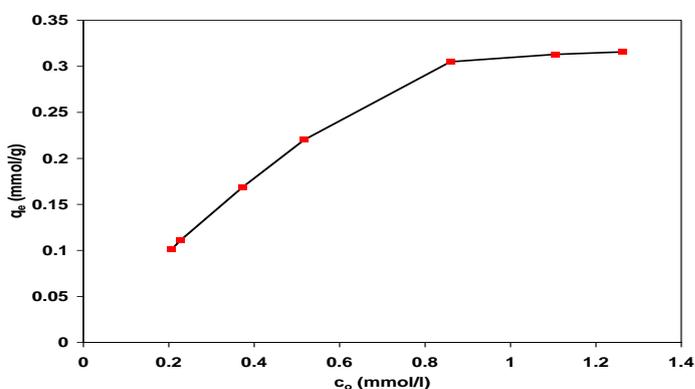


Fig (6) Effect of initial concentration on the adsorption capacity of resin towards Cu(II) ions at 30°C.

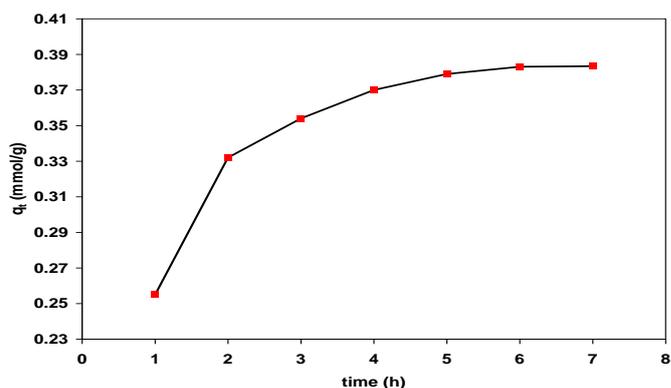


Fig (7) Effect of contact time on the adsorption capacity of resin towards Cu(II) ions at 30°C.

3.3.2.4 Effect of temperature

The influence of solution temperature on the adsorption capacity was examined, while other effective parameters were kept constant. The results observed is shown by Fig (8), which indicates that the capacity is considerably increased by enhancing the solution temperature from 30°C to 60°C in steps of 10°C. Generally as the temperature increases the

uptake value increases. This behavior may be attributed to: (I) The increase of active site number due to the more flexible resin framework on increasing the temperature; (II) the less dehydration of the active sites as well as the copper ions at elevated temperatures facilitating better interaction [24]. This enhancing of adsorption also can be attributed to

the fact at higher temperatures, cations move faster. This could be due to the fact that the specific or electrostatic interactions become weaker and the ions become smaller, since solvation is reduced

[25]. Based on this explanation, it is obvious that the adsorption of Cu^{+2} ions on the adsorbent is an endothermic process.

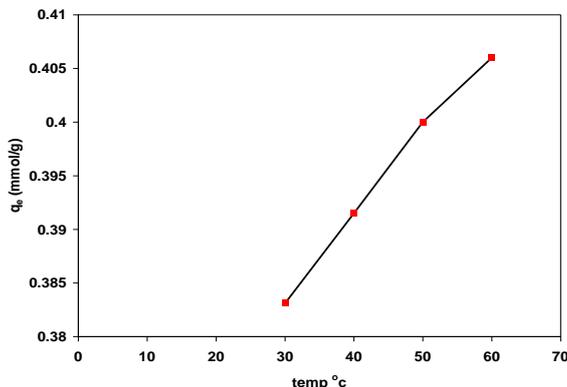


Fig (8) Effect of temperature on the adsorption capacity of resin towards Cu(II) ions at 30°C

3.3.3 Application of isotherm equations to the equilibrium adsorption data

In order to optimize the design of an adsorption system to remove heavy metal ions from effluents, it is important to establish the most appropriate correlation for the equilibration curve. Many theories have been tested in this study, viz. those of Langmuir and Freundlich.

3.3.3.1 Langmuir isotherm equation

The Langmuir adsorption model assumes that molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule and no trans-migration of adsorbate in plane of the surface. These sites are also assumed to be energetically equivalent and distant to each other, so that there are no interactions between molecules adsorbed to adjacent sites. The linear form of the Langmuir isotherm is represented by the following equation [26]:

$$C_e/q_e = C_e/Q^0 + 1/Q^0k \quad (3)$$

Where q_e is the amount of metal ion sorbed per unit weight of adsorbent (mmol/g), C_e the equilibrium concentration of the metal ion in the equilibrium solution (mmol/L), Q^0 (mmol/g) the monolayer adsorption capacity and K (L/mmol) is Langmuir constant that related to the heat of adsorption,

which is a measure of the energy of adsorption. With the slope and intercept of the linearized plot of C_e/q_e versus C_e (Figure.9). Q^0 and b can be calculated. The amounts of these parameters are presented in (Table6).

3.3.3.2 Freundlich isotherm

Freundlich isotherm is an empirical equation that encompasses the heterogeneity of sites and the exponential distribution of sites and their energies. The sorption data have been analyzed using the logarithmic form of the Freundlich isotherm as shown below [27]:

$$\log q_e = N \log C_e + \log K_F \quad (4)$$

Where K_F (mmol/ L) and N are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When $\log q_e$ is plotted against $\log C_e$, a straight line with slope N and intercept $\log K_F$ is obtained fig (10). The value of term N in the Freundlich isotherm model show the nature of isotherm to be unfavorable ($N > 1$), favorable ($0 < N < 1$) or irreversible ($N = 0$). The Freundlich constants (N value) shown in (Table 6) were smaller than 1.0 for Cu^{+2} ion indicating the facile adsorption process on the employed ion exchanger. The values of N and K_F are calculated and presented in (Table 6).

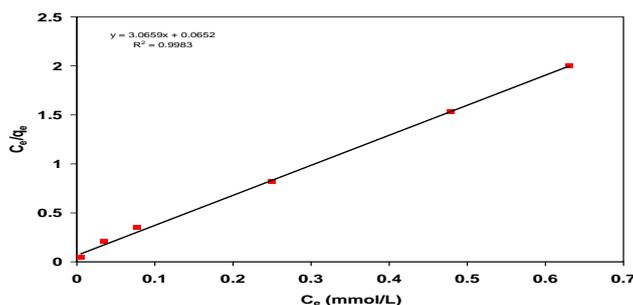


Fig (9) Langmuir adsorption isotherm of Cu(II) ions on resin at 30°C.

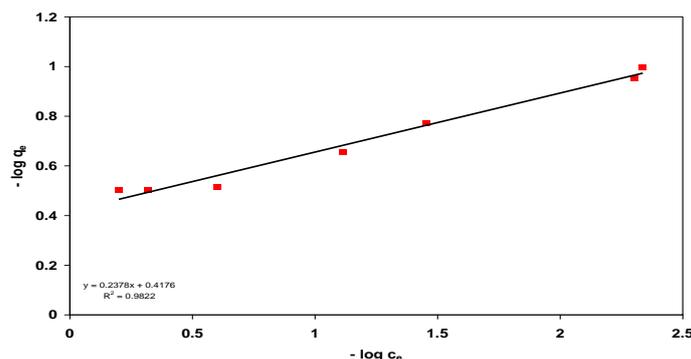


Fig (10) Freundlich adsorption isotherm of Cu(II) ions on to resin at 30°C.

Table (6) The parameters of Langmuir and Freundlich, isotherms for Resin at 30°C.

Isotherms	Parameters	Cu ⁺² /(Resin)
Langmuir	Q ⁰ (mmol/g)	0.3261
	K (L/mmol)	47.023
	R ²	0.998
Freundlich	K _F (mmol/L)	0.3822
	N	0.2378
	R ²	0.9822

As shown in (Table 6), the good fit experimental data with Langmuir and Freundlich, isotherm models and high correlation coefficient (R²) obtained for these plots (for Langmuir and Freundlich, models, respectively) indicates the validity of these models to the ion adsorption data.

3.3.4 Kinetic studies

The rate of uptake of Cu²⁺ by resin was studied by equilibrating the solid phase with a series of ion solutions for different time intervals. The data of the kinetics of Cu⁺² ions sorbet from aqueous solutions into the prepared ion exchanger

At different times were analyzed using Lagergren's pseudo first-order, pseudo second-order, and intraparticle diffusion model [28-30]. The conformity between experimental data and each model predicted values was expressed by correlation coefficient (R2). A relatively high R2 values indicates that the model successfully describes the kinetics of metal ion sorption removal.

3.3.4.1 Lagergren's Pseudo first-order model

The sorption kinetics of metal ions from liquid phase to solid is considered as a reversible reaction with an equilibrium state being established between two phases. A simple pseudo first-order model was used to correlate the rate of reaction and expressed as follows [28]:

$$dq_t / dt = K_1 (q_e - q_t) \tag{5}$$

Where q_e, and q_t (mmol/g) are the adsorption capacity of c ion at equilibrium and at time t, respectively. K₁ is the pseudo first-order rate constant (h⁻¹). After integration and applying boundary conditions t=0 to t=t and q_t=0 to q_t= q_t, the integrated form of (Equation 5) becomes [28]:

$$\log (q_e - q_t) = \log q_e - (K_1 / 2.303) t \tag{6}$$

Plots for (Equation. 6) were made for Cu²⁺ ions sorption at different times and shown in Fig (11). The mathematical linear form of the equations used and the plots made for analyzing the data have been given in (Table 7).

3.3.4.2 Pseudo second-order model

A pseudo second-order rate model is used also to describe the kinetics of the sorption of ions into adsorbent materials. The differential equation for chemisorptions kinetic rate reaction is expressed as [29]:

$$dq_t / dt = K_2 (q_e - q_t)^2 \tag{7}$$

Where K₂ is the pseudo second-order rate constant (g/ mmol h). For boundary conditions t=0 to t=t and q_t=0 to q_t= q_t, the integrated form of (Equation 7) becomes:

$$1 / (q_e - q_t) = 1/q_e + K_2 t \tag{8}$$

(Equation. 8) can be rearranged to obtain a linear form equation as:

$$(t/ q_t) = (1/ K_2 q_e^2) + (1/ q_e) t \tag{9}$$

If the initial sorption rate h (mmol/ g h) is:

$$h = K_2 q_e^2 \tag{10}$$

$$(t/ q_t) = (1/ h) + (1/ q_e) t \tag{11}$$

The kinetic plot of t/ q_t versus t for Cu²⁺ ions sorption is presented in Fig (12). The relationship is linear, and the value of the correlation coefficient (R²) as shown in (Table 7) suggest a strong relationship between the parameters and also explain that the process of sorption of copper ion follows pseudo second-order kinetic model.

3.3.4.3 Intraparticle diffusion model

Intraparticle diffusion model is explained with (Equation 12) given by Weber and Morris [30]:

$$q_t = K_{id} t^{0.5} \tag{12}$$

Where K_{id} is the intraparticle diffusion rate constant ($\text{mmol g}^{-1} \text{h}^{-0.5}$). K_{id} was determined from the plots of q_t against $t^{0.5}$ as shown in Fig (13) and (Table 7).

According to Weber and Morris, the adsorbate could be transferred from the aqueous phase over adsorbent in three different steps as: (a) rapid external surface adsorption; (b) intraparticle diffusion and (c) final equilibrium stage.

With respect to (Equation 12), if the plot gives a straight line, intraparticle diffusion can be accepted as the only rate-limiting step, but a multi-linearity is formed which indicates two or more stages involved in the adsorption of metal ions.

As can be seen from Fig (13), the adsorption process was controlled by three stages: (1) rapid transportation of metal ions from aqueous solution to adsorbent surface; (2) gradual adsorption stage where intraparticle diffusion is rate-limiting step Fig (14) and (3) final equilibrium step due to lower concentration of metal ions in aqueous phase, as

well as fewer number of adsorption sites are accessible. Based on these results, we can conclude that the intraparticle diffusion is not the only rate determining step. Therefore, the adsorption of metal ions onto adsorbent consists of both rapid surface adsorption and intraparticle diffusion. Thus, it is concluded that the adsorption of metal ions on resin may be controlled by external mass transfer followed by intraparticle diffusion.

Pseudo-first order, pseudo-second order and intra-particle diffusion parameters are given in (Table 7). Obviously, as it can be seen from the result represented in (Table 7), correlation coefficient of the second order kinetic is higher than the results obtained from the first-order kinetics. Therefore, the sorption behavior of Cu^{+2} onto adsorbent obeys the second-order kinetics. Moreover, the experiment capacity at equilibrium is closed to theoretical capacity obtained from the plot for second order.

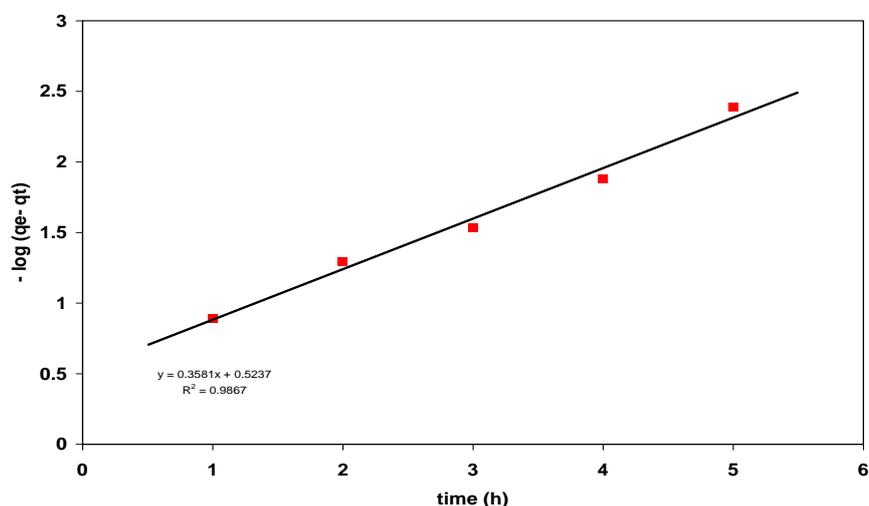


Fig (11) The first order kinetic plot of copper onto resin.

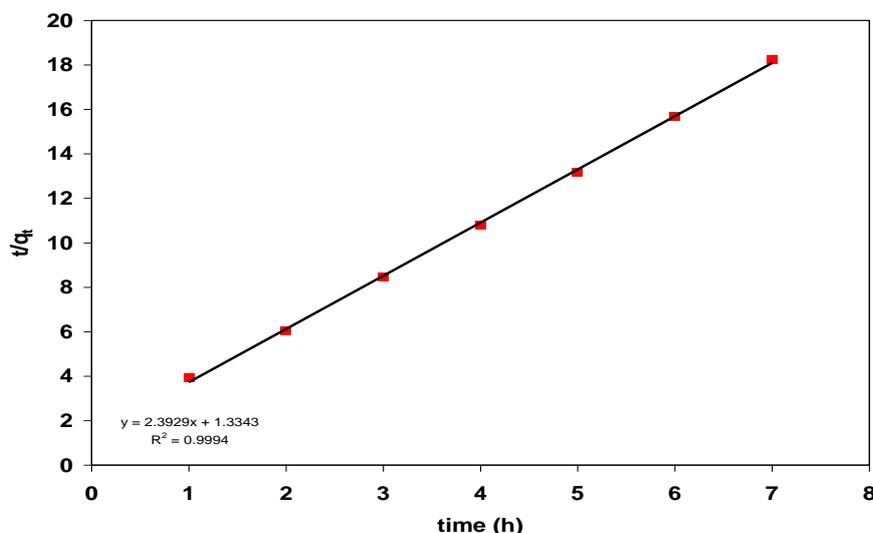


Fig (12) the second order kinetic plot of copper onto resin.

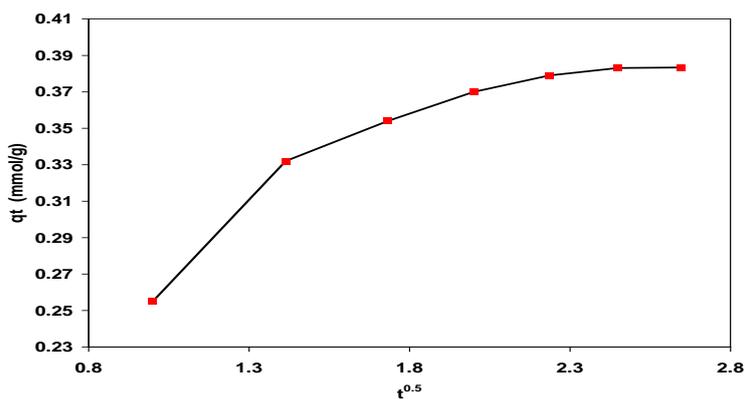


Fig (13) Plot of weber-morris intra particle diffusion model for the adsorption of Cu(II) onto resin.

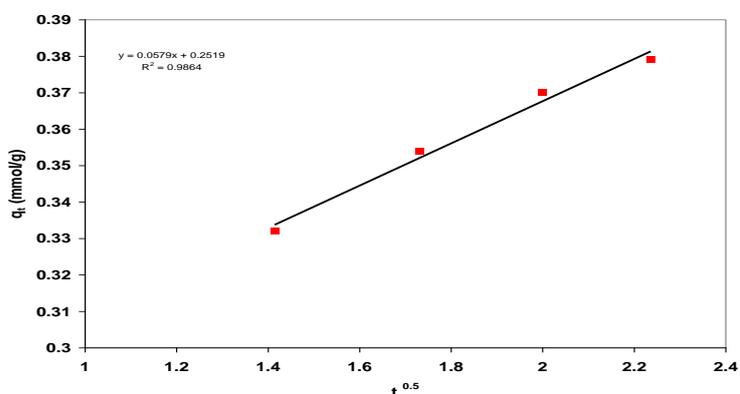


Fig (14) Test of the applicability of the intra-particle diffusion model for describing the adsorption of Cu(II) ions onto resin.

Table (7) Kinetic parameters for the Adsorption of Copper ions onto Resin.

Kinetic models	Parameters	Cu ²⁺ /(Resin)
Pseudo first order	K ₁ (h ⁻¹)	0.824
	R ²	0.9867
	q _e (theoretical) (mmol/g)	0.2994
Pseudo second order	K ₂ (g/ mmol h)	4.458
	R ²	0.9994
	q _e (theoretical)(mmol/g)	0.41
	q _e (exp) (mmol/g)	0.3831
Intraparticle diffusion model	K _{id} (mmol g ⁻¹ h ^{-0.5})	0.0579
	R ²	0.98

3.3.5 Adsorption thermodynamic parameters

In order to obtain the thermodynamic nature of the sorption process, several adsorption thermodynamic parameters including standard enthalpy (ΔH^0), standard entropy (ΔS^0), and standard Gibbs free energy (ΔG^0) were determined. The amounts of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the straight line obtained from plotting $\ln K_d$ values versus reciprocal temperature Fig (15), respectively, and using the following equations:

$$K_d = [(C_o - C_e)v] / [C_o m] \quad (\text{mL/g}) \quad (13)$$

$$\ln K_d = (\Delta S^0/R) - (\Delta H^0/RT) \quad (14)$$

Where K_d is distribution coefficient (mL/ g) of copper ions on resin C_o and C_e are the initial and final Cu(II) ion concentration in the aliquots, respectively. V (mL) is the solution volume and m (g) is the mass of sorbent. ΔH^0 , ΔS^0 and T are the standard enthalpy standard entropy and temperature in Kelvin, respectively, and R is the gas constant. The standard Gibbs free energy, ΔG^0 , of specific adsorption was calculated from the well-known equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (15)$$

The positives value of ΔH^0 and negative value ΔG^0 suggest that the sorption of copper on synthesized resin is an endothermic and a

spontaneous process (Table 8). Furthermore, the positive value of ΔS° demonstrates the increasing the randomness at the solid/solution interface during the adsorption process and thus the

decreasing value of ΔG° with increasing the temperature, indicate that copper adsorption on the adsorbent is more spontaneous at higher temperatures.

Table (8) Thermodynamic parameters for Copper Adsorption on the synthesized Resin.

ΔH° (kJ/mol)	ΔS° (kJ/K mol)	Temp. (K)			
		303	313	323	333
		$-\Delta G^{\circ}$ (kJ/mol)			
+16.21	+0.552	151.046	156.566	162.086	167.606

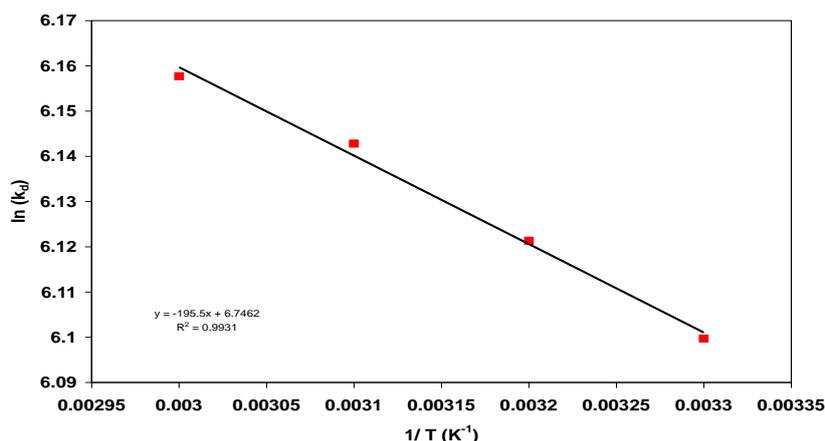


Fig (15) The effect of temperature on the distribution coefficient of copper ions on resin.

4. Conclusions

The NMP and poly (NMP-St) were synthesized and characterized by FT-IR and ^1H NMR spectra. The copolymer composition was determined from ^1H NMR spectral analysis of the copolymer. The monomer reactivity ratios have been calculated by the Kelen-Tudos and Finman-Ross graphical methods.

Utilization of the so-obtained copolymers for removal of Cu(II) ions from aqueous solution were examined. The results indicated that the (0.5/0.5)(NMP/St) copolymer has the highest adsorption capacity towards Cu(II) ions, so it was influenced by the pH of the aqueous solution, the initial concentration of the Cu(II) ions, the length of time for which the systems were stirred and the temperature.

The Langmuir and Freundlich adsorption models were used to provide a mathematical description of the adsorption equilibrium of Cu(II) ions onto resin. The results obtained showed that the adsorption equilibrium data were well fitted by the Langmuir and Freundlich models over the concentration range studied. Pseudo-first order, pseudo-second order and intra-particle diffusion parameters were calculated and showed that the sorption behavior of Cu(II) onto adsorbent obeys the second-order kinetics.

Application of standard thermodynamic equations allowed the values of ΔG° , ΔH° and ΔS° for the adsorption process to be determined. Negative values obtained for ΔG° indicated the

spontaneous nature of the adsorption process. Positive value obtained for ΔH° indicated that the adsorption process was endothermic. The positive values obtained for ΔS° demonstrated the increasing randomness at the solid/ solution interface during the adsorption of Cu(II) ions onto resin.

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