









Synthesis of Multifunctional Polymers Based on Tert-Butyl Acrylamide/Octyl Acrylate as Lubricant Additives and Adsorbents for Copper Ion from Aqueous Solution

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Abstract

Two homopolymeric and three copolymeric additives for base oil were synthesized using octyl acrylate (OA) and tert-butyl acrylamide (TBA) monomers. The two additives named P1 and P2 are the homopolymers of TBA and OA, respectively, whereas copolymeric additives named Co1, Co2, and Co3 were synthesized by varying the ratios of TBA:OA as 1:3, 3:1 and 1:1, respectively. The prepared polymers were characterized by Fourier Transform Infrared (FTIR). Based on the solubility of synthesized polymers in base oil and reactivity ratios of TBA/OA copolymer (0.222, 0.434) calculated by Fineman-Ross method, P2, Co1, Co2 and Co3 were selected to evaluate their performance as pour point depressant (PPD), viscosity improver (VII), and anticorrosion additives in base oil. Additives P2 and Co1 showed the best performance as (PPD) and (VII) whereas Co2 and Co3 revealed the best performance as anticorrosion additives. The flash point of base oil increased as a concentration of polymeric additives increased in the base oil. In addition to study the performance of synthesized polymers as lubricant additives, the capability of polymers for removing CuII from synthetic wastewater was also investigated. Different parameters such as pH of solution, contact time, and CuII concentration were changed in order to study their effect on adsorption capacity of polymers. Generally, polymers with high TBA content such as P1, Co2, and Co3 showed good performance in removing CuII.

Keywords: Heavy metals removal, Octyl acrylate, Pour point depressants, Reactivity ratios, Tert-butyl acrylamide, Viscosity improvers.

Introduction

To minimize the problems caused by the use of lubricating oils in addition to improve their performance, several techniques have been employed. Polymers are considered attractive materials for this purpose. The applications of polymeric additives derived from acrylate have attracted considerable interest compared to other conventional additives due to their storage stability and high oil solubility^{1,2}. Corrosion inhibitors, antioxidants, pour point depressants (PPDs),

antiwear, antifrication, detergents, viscosity index improvers (VIIs), and dispersants additives are among the essential types of these additives^{3,4}. The applicability of a lubricant formulation in low and high temperature operational circumstances with effective and efficient performance is determined by the fluidity and viscosity change with temperature; hence PPDs and VIIs are used as additives in large quantities. Different types of additives have been used to improve the properties of lubricating oils.

For example, polymeric additives are the most important materials used as base oil additives⁵⁻⁸. In this field, there are many types of research have been achieved so far. Ghosh and his coworkers have shown the application of poly dodecyl methacrylate and dodecyl methacrylate/vinyl acetate copolymers as pour point depressant and viscosity index improver additives for base oil⁹. Singh and his team have mentioned the application of poly alkyl acrylate, poly *N,N*-dimethylacrylamide and their copolymers with different ratios as pour point depressants, corrosion inhibitors, antioxidants, viscosity index improvers, and dispersants additives in lubricating oil¹⁰. Jung has synthesized copolymers and terpolymers of methyl methacrylate with four methacrylate monomers which have been synthesized firstly in the same research¹¹. In this study, poly (dodecyl methacrylate-co-methyl methacrylate-co-hexadecyl methacrylate), at a molar ratio of 3.5: 3 : 3.5, showed the best pour point depressant. The prepared terpolymer decreased the base oil's pour point by up to 23 °C. In the field of using polymers for heavy metals removal, the polymers synthesized from hydrophilic monomers such as acrylamide derivatives, vinyl pyrrolidone, acrylic acid and hydroxyl ethyl acrylate can be used for removing heavy metals ions from wastewater¹²⁻¹⁵. The presence of some atoms having high electron density such as Nitrogen and

Oxygen plays the main role in the adsorption of heavy metals because such atoms can easily form strong coordinate bonds with metal ions¹⁶. On the other hand, many studies have been reported on using different types of natural polymers for heavy metals removal. Sodium alginate, dextran based hydrogel, starch/acrylic acid, and granular alginate have all shown good performance in removing Zn²⁺, Mn²⁺, Pb²⁺, Cd²⁺, and Cu⁺² from wastewater¹⁷⁻¹⁹.

To determine the validity of using copolymers for biomedical and industrial applications, the reactivity relationships of the copolymer should be determined and studied. The properties of any synthesized copolymer are directly affected by the reactivity ratio values. Different methods can be employed to determine reactivity ratios including linear and nonlinear procedures²⁰⁻²².

In keeping with our ongoing studies on the synthesis of multifunctional polymers, the hydrophilic monomer tert-butyl acrylamide and hydrophobic monomer octyl acrylate, were selected to prepare their homopolymers and copolymers, and then used as additives for base oil and adsorbents for Cu⁺² from synthetic wastewater. In addition, the molar ratios of copolymer were varied as 1:3, 3:1 and 1:1 to study their effect on the performance of prepared polymers as base oil improvers and heavy metals adsorbents.

Materials and Methods

Materials

All chemicals were purchased from Sigma-Aldrich chemical Co. Tert-butyl acrylamide was purified by recrystallization from methanol. Octyl acrylate was purified by passing through a column of aluminum oxide; the inhibitor hydroquinone was eliminated by washing with 10% sodium hydroxide solution. Potassium persulfate and benzoyl peroxide were recrystallized from methanol and chloroform, respectively. The base oil was collected from Total oil corporation ltd., Baghdad. Copper chloride hydrate, sodium hydroxide, hydrochloric acid, and solvents were used as received.

Synthesis of Tert-butyl acrylamide/octyl acrylate Copolymers at Low and High Conversion

The copolymerization of tert-butyl acrylamide and octyl acrylate was carried out in dimethylsulfoxide (DMSO) as a solvent. Tables 1 and 2 show the synthesis conditions of copolymerization at high

and low conversion, respectively. The two procedures are quite similar, however the conversion percentage is different, it can be controlled by changing the polymerization time, 10-20 min for low conversion polymerization and 2-4 hr for high conversion polymerization. By adding benzoyl peroxide while continuously stirring, polymerization was initiated. The reaction solution becomes more viscous after the completion of polymerization, and the polymer is subsequently precipitated in ethanol. In order to precipitate a copolymer free of monomers, 25 ml of the reaction mixture was added to 55 ml of ethanol with stirring. The final product was then washed with ethanol and dried in a vacuum oven at 40 °C. Poly TBA and poly OA were synthesized, for comparison purposes, by following the same procedure with using potassium persulfate for TBA and benzoyl peroxide for OA as initiators. The successful synthesis of copolymers and homopolymers was

confirmed by FTIR. The reaction conditions are shown in Table 4. The chemical structures of synthesized poly tert-butyl acrylamide, poly octyl

acrylate, and tert-butyl acrylamide/octyl acrylate copolymer are shown below.

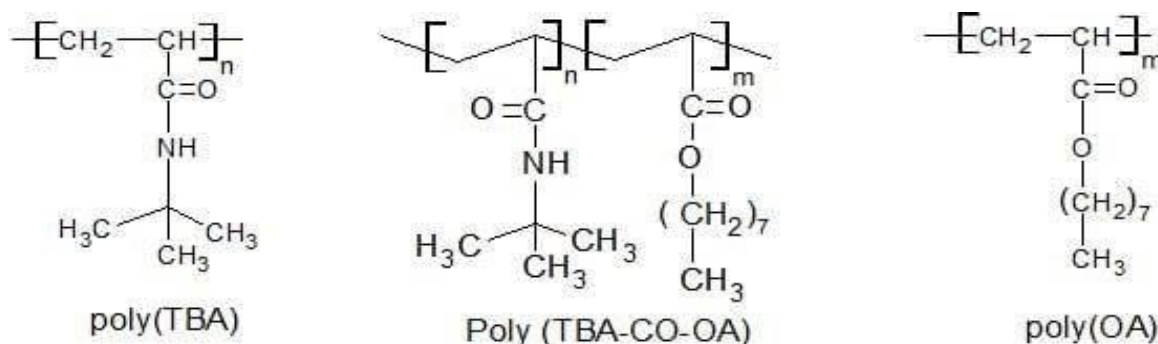


Figure 1. The chemical structures of synthesized polymers

Table 1. Reaction conditions of synthesis homo and copolymers at high conversion

Compound	TBA:OA mole ratio	Time (hr)	Temperature (°C)	Yield %
Poly TBA, P1	TBA only	2	70	65
Poly OA, P2	OA only	3	80	68
TBA/OA, Co1	1:3	4	80	75
TBA/OA, Co2	3:1	4	80	72
TBA/OA, Co3	1:1	4	80	66

Characterization

The functional groups in poly TBA, poly OA, and TBA-co-OA were determined with the help of Perken Elmer-1650 spectrophotometer using a KBr disk method at a wavenumber range of 400 to 4000 cm^{-1} . Elemental Analyzer CHNS-932 instrument was employed to determine Nitrogen % in the copolymers. The concentration of Cu^{+2} in the solutions, before and after adsorption by polymers, was determined by using Shimadzu-3600 UV according to the standard procedure.

Pour Point Evaluation

By using the standard method ASTM D-97²³, pour point temperatures of base oil, without and with different concentrations of polymeric additives were calculated. By averaging three experimental results conducted under identical conditions, the experimental data were recorded. The pour point of the base oil composition is reduced to a larger scale by a good pour point depressant.

Viscosity Index Evaluation

The kinematic viscosity of base oil, without and with different concentrations of polymeric additives, at 40 and 100 °C were measured according to ASTM D445

procedure. In addition, ASTM 2270-93 method was employed to calculate the viscosity index²⁴.

Anti-Corrosion Test

By using the standard corrosion testing method, the anticorrosion activity of the potential polymeric additions was examined^{25,26}. The steel metal was initially cut and machined into small pieces that measured 30mm×20mm×4mm (area: 2.4 square inches). By using carborundum emery paper grade number C 201 AH, the metal pieces were hand polished after being machined and milled. The metal pieces were then cleaned using xylene-isopropanol solution (1:1). The steel pieces were weighed prior to being exposed to the formulated base oil. The tests were performed in an air oven for 14 days (336 hours) at a temperature of 95 °C. Using derusting solution composed of 36 % HCl containing 5 % Sb_2O_3 + 4 % SnCl_2 , the metal pieces were derusted after the test period, and they were then weighed again.

Flash Point Test

Flash points of base oil, with and without polymeric additives, were performed by using Pensky-Martens closed cup tester. The test was done according to the standard method ASTM D93.

Heavy Metals Removal Studies

CuCl₂.6H₂O salt was used to prepare different concentrations of the stock solutions of Cu²⁺. pH value of adsorption solution (2, 5, 7, and 9), contact time (1-24 hr) of metals ions with adsorption solution, and Cu²⁺ concentration (100, 1000, 2000 and 3000 ppm), were changed to study their effect on the adsorption efficiency of hydrogels. pH of solutions was adjusted by sodium hydroxide and hydrochloric acid. All experiments were conducted at 30 °C.

50 mg of prepared polymer was placed into 50 ml of aqueous solution of Cu²⁺. UV spectrophotometer was used to determine the residual of Cu²⁺ by using their standard curves. The following equation was then used to calculate the amount of adsorbed Cu²⁺ (mg) per (g) of polymer ²⁷⁻²⁹:

$$Aa \text{ (mg/g)} = \frac{(C_1 - C_2) \times V}{m}$$

Where C₁ and C₂ are concentrations of Cu²⁺ in its aqueous solution before and after adsorption, respectively. m is the mass of the dry polymer, and V is the aqueous solution volume of Cu²⁺.

Results and discussion

Characterization

The structures of poly TBA, poly OA, and TBA/OA copolymer are confirmed by FTIR as shown in Fig. 2 The absorption bands which appear in the FTIR spectra of TBA/OA copolymer belong to the stretching vibration in different functional groups of their corresponding homopolymers, poly TBA and poly OA, and as follow: the band at 1745 corresponding to (ester C=O), 3290 cm⁻¹ (amide N-

H), , 2860 (alkane C-H), 1645 cm⁻¹ (secondary amide C=O), and 1200 cm⁻¹ (amide C-N). The multiple peaks between 1050 and 1150 belong to (ester C-O-C). The complete homopolymerization and copolymerization processes are confirmed by the absence of a monomeric band at 1610 corresponding to (alkene C=C).

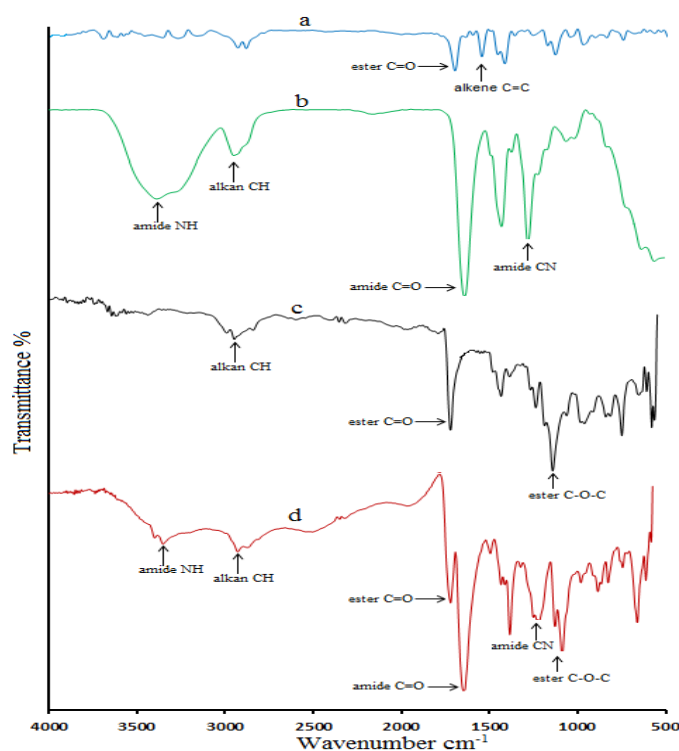


Figure 2. FT-IR of: a– OA monomer, b- poly TBA, c- poly OA, d- TBA/OA copolymer

Copolymer Composition

The mole fraction of TBA in the copolymer (F₁) can be determined by using Eq. 1 ^{30,31}:

$$\frac{N\% \text{ Copolymer}}{N\% M_1} = \frac{M. \text{ wt of } M_1}{M. \text{ wt of } M_1 + M. \text{ wt of } M_2 / F} \dots \dots 1$$

Where M_1 and M_2 are TBA and OA, respectively, $f=f_1/f_2$, and $F=F_1/F_2$. Fig. 3 shows the plot of the mole fraction of TBA in the copolymer (F_1) versus that of the mole fraction of TBA in the feed (f_1). The reactivity ratios were calculated by using Fineman-Ross method³² to be (0.222, 0.434), as shown in Fig. 4. Both r_1 and r_2 are between 0 and 1, moreover, the result of $r_1 \cdot r_2$ is less than unity (0.096). The obtained results could be explained in

terms of the stabilization of the corresponding macroradicals due to the presence of amide and carbonyl groups of each TBA and OA unit, respectively. TBA forms an alternative copolymer with OA with some blocks of TBA units distributed in the polymer chain. Similar behavior has been observed by Mohammed when phenyl acrylamide was copolymerized with methyl methacrylate³³.

Table 2. Feed and copolymer compositions, conversion, nitrogen analysis, and Fineman-Ross parameters of TBA/OA copolymers

Sample Code	f_1 (feed)	Conversion %	N %	$F_1 = F_1/F$ (copolymer)	G $f(F-1)/F$	X f^2/F
TBA/OA-1	0.10	13.16	1.01	0.127603	-0.6485	0.08440
TBA/OA-2	0.30	13.33	3.11	0.363018	-0.3234	0.32229
TBA/OA-3	0.50	15.01	4.21	0.47258	-0.1160	1.11604
TBA/OA-4	0.70	12.95	5.32	0.574942	0.6082	4.02510
TBA/OA-5	0.90	12.89	7.31	0.740565	5.8471	28.3759

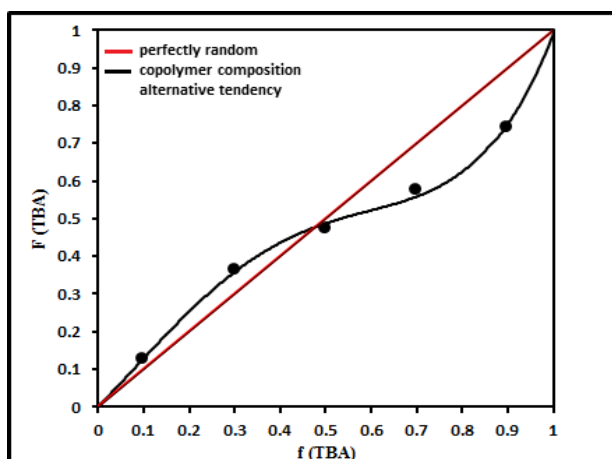


Figure 3. Variation of feed composition f_1 (TBA) with copolymer composition F_1 (TBA)

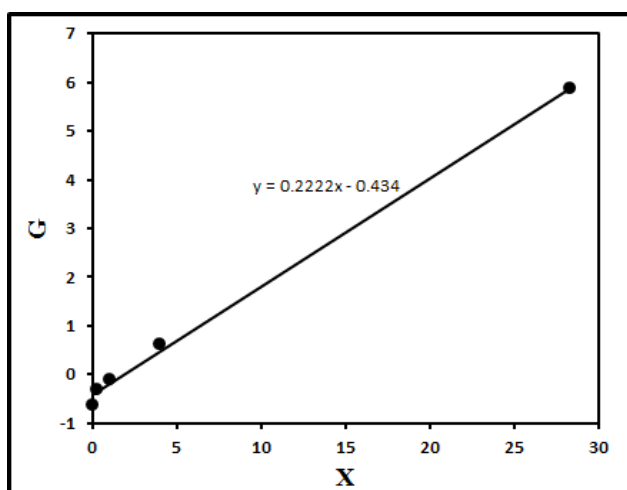


Figure 4. Fineman-Ross plot of TBA/OA copolymer

Formulation and Solubility of Additives in Base Oil

After determining the reactivity ratios of the copolymer, the base oil was used for the solubility investigations of the synthetic additives. According to the solubility results listed in Table 3, the prepared polymers are appropriate for this study since most of them have excellent solubility in base oil. Moreover, as a concentration of TBA increases in the feed composition of the copolymer, the solubility of copolymeric additive becomes more difficult in the base oil. Since OA is more reactive than TBA, ($r_{TBA} = 0.222$, $r_{HMA} = 0.434$), it reaches the copolymer faster than TBA. As a result, in the later stages of conversion, the substance has a structure that is very similar to TBA homopolymers. Thus, most of the copolymeric additives with high OA content, Co1 and Co2, are soluble in base oil whereas poly TBA (P1) remains insoluble in the base oils. However, all synthesized polymers were used as additives for base oil except P1 was set aside.

Table 3. Solubility of polymeric additives in base oil.

Polymeric additives	Solubility in base oil
Poly TBA, P1	---
Poly OA, P2	+++
1TBA/3OA, Co1	+++
3TBA/1OA, Co2	+
1TBA/1OA, Co3	++

Viscosity Study

The viscosity index of the base oil, without and with 2-6 g/l of polymeric additives, is shown in Fig. 5. The results revealed that all additives showed good viscosity index improver additive properties. It could be because of adding polymeric molecules with high molecular weight in the base oil. The values of the viscosity index indicated that better performance is obtained for poly OA (P2) and copolymers of TBA with OA of the molar ratios 1:3 (Co1) and 1:1 (Co3) than the copolymeric additive (Co2) prepared by using 3:1 as molar ratios. The best viscosity index improver performance was observed with the P2 in 4 g/l concentration. These results could be explained in terms of that increasing in the thermal kinetic energy of the molecules leads to a reduction in internal flow resistance³⁴.

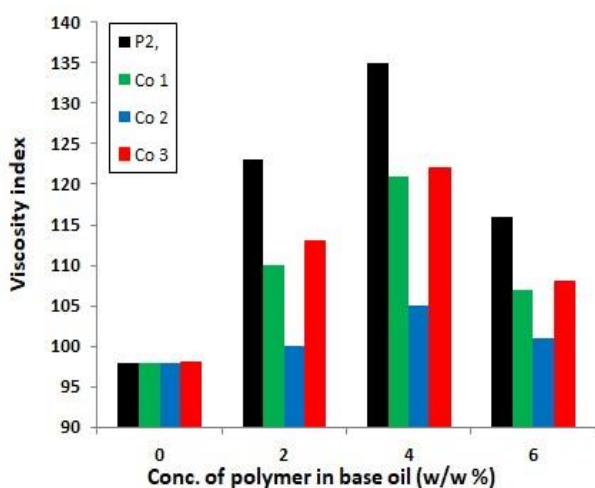


Figure 5. Effect of polymeric additives concentration on viscosity index of base oil

Pour Point Study

Pour points were determined and plotted versus polymeric additives amount in Fig. 6. From these results, most polymeric additives could be considered as pour point depressants. The behavior of additives such as pour point depressants and viscosity index improvers are slightly similar. Thus, poly OAA, 1TBA/3OA and 1TBA/1OA copolymers have better performance than 3TBA/1OA copolymer. Since the pour point of the base oil was listed as -11 °C, a remarkable lowering of the pour point was observed after the addition of polymers in the base oil. It is clearly observed that the efficiency of the pour point depressant gradually enhanced with the increase in the concentration of the

polymeric additives in the base oils. However, the enhancement in the pour points temperature values is because of the disruption of the rigid network of wax crystals in the base oils⁵.

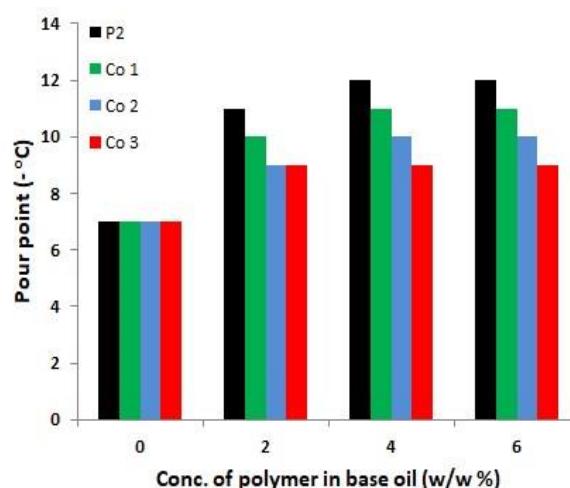


Figure 6. Effect of polymeric additives concentration on pour point of base oil

Anticorrosion and Flash Point Tests

Results of weight loss in the metal put in formulated oils are shown in Fig. 7. The obtained results reveal that both examined copolymers, 3TBA/1OA and 1TBA/1OA, have anticorrosive activity but 3TBA/1OA copolymer is comparatively more effective. At 4 g/l concentration of 3TBA/1OA, the values of weight loss decreased to 0.46 mg from the original values of 0.91 mg for the base oil. At 4 g/l concentration of 1TBA/1OA, the values of weight loss come out to be 0.50 mg. The higher activity of 3TBA/1OA copolymer is caused by the higher content of the TBA monomer due to their ability to interact with surfaces and form a protective coating on metallic surfaces. The polarity of TBA copolymers may also provide them with an anticorrosive characteristic. The results of flash points of formulated base oil showed that most additives have an effect in increasing the flash point temperature of base oil. The flash point of the original base oil is 210 °C, while with additives is about 215 °C. These results could be explained in terms of most polymers having high flash point temperatures compared to base oil.

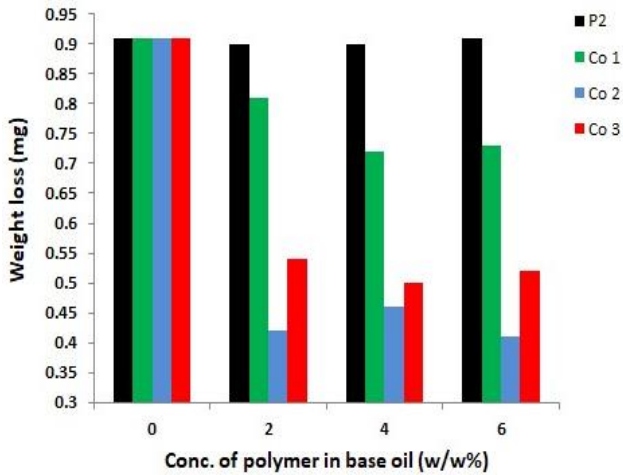


Figure 7. Effect of polymeric additives concentration on weight loss of metal

Results of Removing Cu^{+2} from Synthetic Wastewater

Fig. 8 shows the effect of pH solution on Cu^{+2} adsorption by polymers using 2000 ppm of Cu^{+2} solution for 15 hr. When the pH solution is increased from 3 to 5, a greater rise in the adsorption capacity of hydrogel for Cu^{+2} occurs. The amino groups of TBA undergo protonation at low pH values, which results in electrostatic repulsion with metal ions and reduce the metal's adsorption ability through the complexation process. At higher pH (9), Cu^{+2} forms insoluble $\text{Cu}(\text{OH})_2$, thus, the adsorption capacity decreases.

The influence of Cu^{+2} concentrations on the adsorption process at pH 7 for 15 hr was also investigated and shown in Fig. 9. As the initial Cu^{+2} concentration increases, the absorption of Cu^{+2} increases rapidly. The absorption then decreased after reaching the maximum at 2000 ppm. The maximum load capacity can be easily determined as 95 mg g^{-1} hydrogel. These findings demonstrated the potential industrial use of TBA/OA copolymers for the removal of Cu^{+2} from wastewater.

The experiments to study the effect of contact time were carried out using 2000 ppm of Cu^{+2} solution at pH 7. The highest binding of Cu^{+2} occurred within the first 15 hours and remained constant for the following 24 hours, as can be seen in Fig. 10.

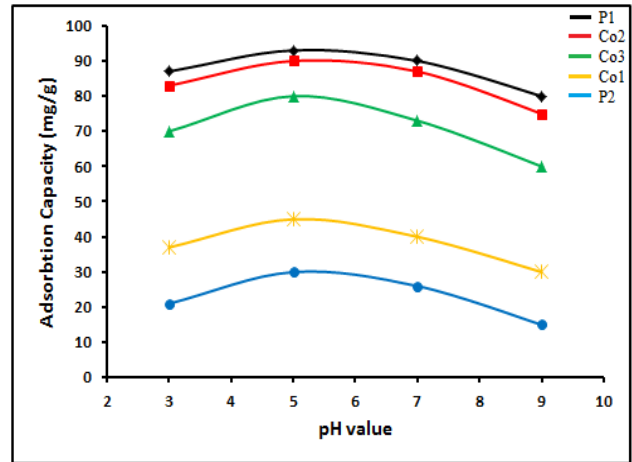


Figure 8. The effect of pH value on adsorption process using 2000 pm of Cu^{+2} solution for 15 hr

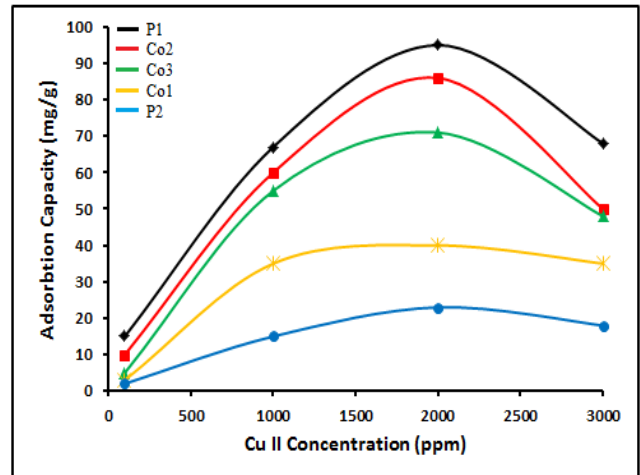


Figure 9. The effect of Cu^{+2} concentration on adsorption process at pH 7 for 15 hr

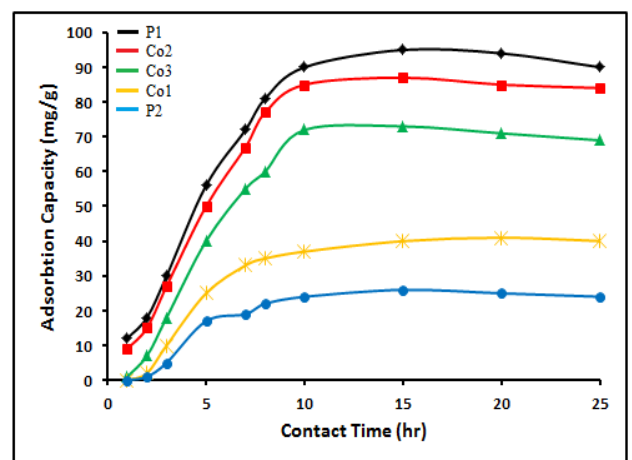


Figure 10. The effect of contact time on Cu^{+2} adsorption using 2000 ppm of Cu^{+2} solution at pH

In all cases, the adsorption capacity of TPA/OA copolymer toward Cu^{+2} increases as the concentration of TBA increases in the copolymerization feed. The results are quite common and could be explained in terms of TBA forming a coordination bond with Cu^{+2} more easily than OA does. This occurs due to the high electron density of the Nitrogen atom of the amino group in TBA. Fig. 11 shows the photograph of removing process of Cu^{+2} from its aqueous solution by TPA/OA copolymer while Fig. 12 shows the proposed mechanism of this process.



Figure 11. Photograph of right to left: Synthesized poly TBA/OA, Cu^{+2} solution, swollen polymer adsorbs Cu^{+2} , and purified water

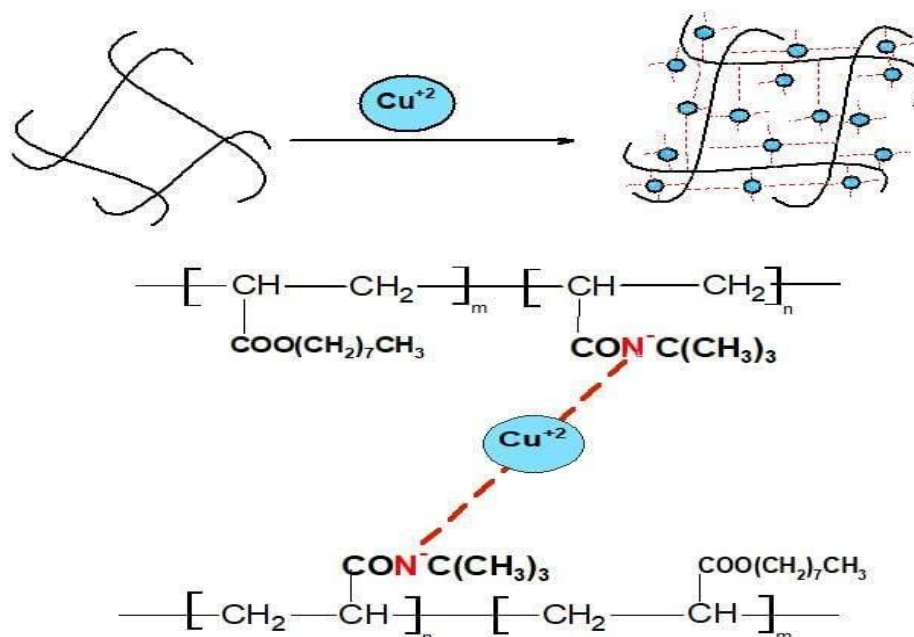


Figure 12. Mechanism of removing Cu^{+2} from wastewater by using TPA/OA copolymer

Conclusion

Poly TBA, poly OA, 3TBA-co-1OA, 1TBA-co-1OA and 1TBA-co-3OA were successfully synthesized and their structure was confirmed by FT-IR. Reactivity ratios of prepared TBA/OA copolymer (0.222, 0.434) calculated by the Fineman-Ross method had a direct effect on the solubility of prepared copolymeric in base oil. Thus, most of the prepared polymers were soluble in base oil with different degrees except poly TBA, which was insoluble. The performance of prepared polymers as anti-corrosion material, pour point

depressant and viscosity index improver in base oil was studied. Poly OA and 1TBA-co-3OA revealed the best performance as pour point depressants and viscosity index improvers, whereas 3TBA-co-1OA, 1TBA-co-1OA showed the best performance as anticorrosion materials. Thus, 1TBA-co-1OA could be considered as optimum additives for all studied properties. The prepared polymers were also examined as Cu^{+2} adsorbents with changing many parameters such as pH, contact time, and Cu^{+2} concentration. Most of the polymers, except poly

OA, showed good performance for removing Cu²⁺, especially poly TBA and 3TBA-co-1OA.

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Author's Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for

re-publication, which is attached to the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Author's Contribution Statement

A.M. and E.F. carried out the design, acquisition of data, analysis, interpretation, and participated in the drafting the manuscript. A.H.

helped in interpretation and analysis. M.A. contributed to manuscript conceptualization, and interpretation. All authors read and reviewed the final manuscript.

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تحضير بوليمرات متعددة الوظائف مشتقة من البيوتيل اكريلاميد والاوكتيل اكريلات كمضافات لزيوت التشحيم وممترات لايون النحاس من المحلول المائي

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الخلاصة

تم في هذا البحث تحضير بوليمرين متجانسين وثلاثة بوليمرات مشتركة بالاعتماد على البيوتيل اكريلاميد والاوكتيل اكريلات كمضافات لزيوت التشحيم. سميت البوليمرات المتجانسة P1 و P2 لكل من البيوتيل اكريلاميد والاوكتيل اكريلات اما البوليمرات المشتركة فتسمى Co1 و Co2 و Co3 فقد حضرت بتغيير نسب المونومرين البيوتيل اكريلاميد والاوكتيل اكريلات بشكل 1:3 و 1:1 و 3:1 تم تشخيص البوليمرات المحضرة بواسطة طيف الأشعة تحت الحمراء. بالاعتماد على ذوبانية البوليمرات المحضرة في زيوت التشحيم وقيم نسب الفعالية المحسوبة بطريقة فاينمان-روس فقد تم اختيار البوليمرات Co1, Co2, P2, و Co3 لتقييم اداءهم كمخفضات لدرجات حرارة الانسكاب ومحسنات للزوجة زيوت التشحيم ومضافات مضادة للتآكل. المضافات P2 و Co1 اظهرت كفاءة عالية كمخفضات لدرجات حرارة الانسكاب ومحسنات للزوجة اما Co2 و Co3 فقد اظهرت اداء جيدا كمضافات مضادة للتآكل كما تم دراسة فعالية البوليمرات المحضرة لازالة ايون النحاس من المياه الملوثة المحضرة تم استخدام قيم دالة حامضية مختلفة وزمن اتصال مختلف وتراكيز محاليل مختلفة لدراسة تأثيرها على عملية الازالة بصورة عامة فان البوليمرات ذات محتوى عالي من البيوتيل اكريلاميد قد اظهرت كفاءة عالية في عملية الازالة.

الكلمات المفتاحية: ازالة العناصر الثقيلة, الاوكتيل اكريلات, مخفضات درجات حرارة الانسكاب, نسب الفعالية, البيوتيل اكريلاميد, محسنات لزوجة زيوت التشحيم.