

Thiophene-Modified CMC/Chitosan Hybrid Polymers for the Removal Metal Ions from Wastewater

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Received: 28.09.2020; Revised: 19.10.2020; Accepted: 21.10.2020; Published: 25.10.2020

Abstract: 5-Acetyl-4-amino-N-(4-chlorophenyl)-2-(phenylamino)thiophene-3-carboxamide was synthesized and used in CMC and Chitosan modifications to improve their efficiency in removing heavy metal ions from wastewater. The modified polymeric membranes were characterized, and their efficiency was investigated compared to the unmodified membranes in removing the heavy metal ions from their aqueous solutions. The effect of contact time was investigated, and monitoring of the change in pH during treatment was carried out. For heavy metal ions, the copper (II) ion was selected as a representative example, and its concentration was determined by ICP spectrometry.

Keywords: polymers modification; chitosan; carboxymethyl cellulose; thiophene; Cu(II); wastewater.

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1. Introduction

Toxic metals are one of the most polluting substances to water resources causing water pollution. It is one of the most important environmental problems in the world. These pollution types from industrial and domestic activities are not regularly monitored and recorded as a problem [1,2]. Heavy metals are dangerous to humans and the environment, and thus both surface and underground environments have been contaminated [3]. The most dangerous heavy metals in the environment are heavy metals, including zinc, copper, lead, arsenic, mercury, cadmium, and chromium [4]. In this study, copper was chosen because it was one of the first minerals extracted and used on a large scale by humans for various purposes [5]. Copper plays a vital role in the biochemical processes of many organisms, including humans. However, high levels of copper ions can cause adverse effects on human health, such as gastrointestinal symptoms, liver toxicity, osteoporosis, and Wilson's disease [6,7]. Water treatment removes or reduces the concentration of pollutants and unwanted components. Thus the water becomes suitable for the desired end-use such as drinking and irrigation [8,9]. Traditional techniques such as chemical precipitation, ion exchange, reverse osmosis, ultrafiltration, and chemical oxidation/reduction to remove heavy metal ions from their aqueous solutions have inherent disadvantages, including lower efficiency, high cost, and the generation of more toxic sludge or other waste [10]. The search for cheaper, more efficient, and environmentally friendly technologies has attracted the attention of scientists. The adsorption method has emerged as a better alternative to traditional techniques [11,12]. Bio-adsorbents derived from natural polymers such as starch [13], cellulose [14], chitin/chitosan [15,16], and agricultural waste [17,18] are particularly important because they are renewable, cost-effective, biodegradable, non-toxic, hydrophilic, environmentally friendly and reusable [17,19]. The efficiency of

polymeric adsorbents in removing water contaminants has been recognized [20]. The functional groups in the polymeric skeleton enhance adsorption efficiency and increase the chance of removing any contamination [21,22]. The current study includes the preparation of CMC and CS composite membranes modified with different thiophene derivative content and their application for the removal of Cu(II) ions in wastewater treatment.

2. Materials and Methods

Carboxymethyl cellulose (CMC, MW 41 kDa), Chitosan (Viscosity 3275 cps, 82.4% deacetylated), and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (98.5-101%) was purchased from Alpha Chemika, India. Acetic acid glacial (99%) was purchased from Fisons, England. IR spectra were recorded on a Thermo Scientific Nicolet is10 FT-IR spectrometer. ^1H NMR spectrum was run on JOEL-ECA 500 MHz in $\text{DMSO}-d_6$. Chemical shifts (δ) are given in ppm. Cu(II) ion concentration was estimated using ICP-OES Perkin Elmer/Optima 7000 DV.

2.1. Synthesis of 5-acetyl-4-amino-N-(4-chlorophenyl)-2-(phenylamino)thiophene-3-carboxamide (3).

A solution of thiocarbamoyl derivative 2 (0.66 g, 0.002 mol) in 20 mL ethanol containing triethylamine (0.5 mL), chloroacetone (0.18 mL, 0.002 mol) was added. The reaction mixture was heated under reflux for 2 hours. The solid product that formed was filtered off, dried, and recrystallized from ethanol to give the targeted functionalized thiophene 3. The chemical structure of 3 was revealed by its IR and ^1H NMR spectra.

Yellow crystals in 64% yield; m.p. = 250-252 °C; IR (KBr): 3420, 3318, 3268 (NH and NH_2), 1642 (C=O), 1597 (C=O), 1561 cm^{-1} (C=C). ^1H NMR ($\text{DMSO}-d_6$): δ /ppm 2.09 (s, 3H, CH_3), 7.10 (t, $J = 7.00$ Hz, 1H, Ar-H), 7.35-7.39 (m, 6H, Ar-H), 7.47 (s, 2H, NH_2), 7.65 (d, $J = 8.50$ Hz, 2H, Ar-H), 9.76 (s, 1H, NH), 9.96 (s, 1H, NH). ^{13}C NMR ($\text{DMSO}-d_6$): δ /ppm 28.04, 105.70, 120.31 (2C), 121.89 (2C), 124.01, 126.97, 128.29 (2C), 129.39 (3C), 137.90, 140.85, 154.36, 157.51, 162.46, 186.67. Analysis calculated for $\text{C}_{19}\text{H}_{16}\text{ClN}_3\text{O}_2\text{S}$ (385.87): C, 59.14; H, 4.18; N, 10.89%. Found: C, 59.27; H, 4.12; N, 10.81%.

2.2. Preparation of CMC/thiophene (CMC/3) composite membranes.

An amount of 0.25 g sodium carboxymethylcellulose (CMC) was dissolved in 15 mL of distilled water by stirring at room temperature until complete dissolution. An amount of thiophene derivative 3 corresponding to 25% w/w CMC was dissolved in 5 mL acetone with heating and shaking, and then this amount was added to the previous mixture dropwise during stirring for 3 hours. After that, the solution was poured into a glass petri dish of 60 mm diameter and left to dry at 60 ± 2 °C for 2 days. The dried film assigned as CMC1 was taken off and stored at room temperature. Two similar samples assigned as CMC2 and CMC3 were prepared using amounts of thiophene 3 corresponding to 50% and 100% w/w of CMC, respectively. A blank sample of CMC membrane was also prepared without adding thiophene 3 for comparison.

2.3. Preparation of CS/thiophene (CS/3) composite membranes.

An amount of 0.25g Chitosan (CS) was mixed under stirring at room temperature for 2 h with 2 mL of glacial acetic acid and diluted while stirring with 5 mL of 1% v/v aq. acetic acid solution. After that, further 10 mL of distilled water was added, and the mixture was stirred

until complete dissolution. An amount of thiophene 3 corresponding to 25% w/w CS was dissolved in 5 mL acetone with heating and shaking, then this amount was added to the previous mixture dropwise during stirring for 3 hours. Thereafter, the solution was poured into a glass petri dish of 60 mm diameter and dried at 60 ± 2 °C for 2 days. The dried film assigned as CS1 was taken off and stored at room temperature. Two similar samples assigned as CS2 and CS3 were prepared using amounts of 3 correspondings to 50 % and 100% w/w of CS, respectively. A blank CS membrane was also prepared without adding 3 for comparison.

2.4. The adsorption of copper(II) ions by the adsorbents.

A stock solution of 100 ppm Cu(II) ions was prepared by adding about 100 mL distilled water to accurately weighed 0.392 g of CuSO₄.5H₂O in a 250 mL beaker under stirring at room temperature until complete dissolution. The solution was quantitatively transferred into 1L measuring flask, and distilled water was added to the mark. The obtained solution was kept to be used in the adsorption experiments. The adsorption of Cu(II) ions by different adsorbents was performed by the batch method under different contact times. In all experiments, 0.1 g of the investigated adsorbent was added in 100 ml of the previously prepared stock solution, and the concentration of the adsorbed Cu(II) ions was back determined by ICP spectrometer. The adsorption percent removal of Cu(II) ions on the studied adsorbents were determined by Eq. (1) [23]. The adsorbents used in this investigation are CMC, CMC1-CMC3 and CS, CS1-CS3 as examples for CMC- and CS-based adsorbents, respectively.

$$\% \text{ Removal} = (C_i - C_f / C_i) \times 100 \quad \text{Eq. (1)}$$

The parameters C_i and C_f (mg/L) represent the initial and final concentrations of copper (II) ions.

2.4.1. Effect of contact time.

An amount of 0.1 g of the adsorbent was added to 100 mL of 100 ppm Cu(II) solution. After different time intervals over 24 h, about 1 mL of the solution was taken, and the concentration of the adsorbed Cu(II) ions was back-determined by ICP spectrometry. In Table 1, the results are shown.

2.4.2. Effect of adsorption process on pH.

The adsorption process was carried out with the monitoring of the change in pH using 0.1 g adsorbent and 100 ppm initial adsorbate concentration over contact time of 24 h. The results are given in Table 1.

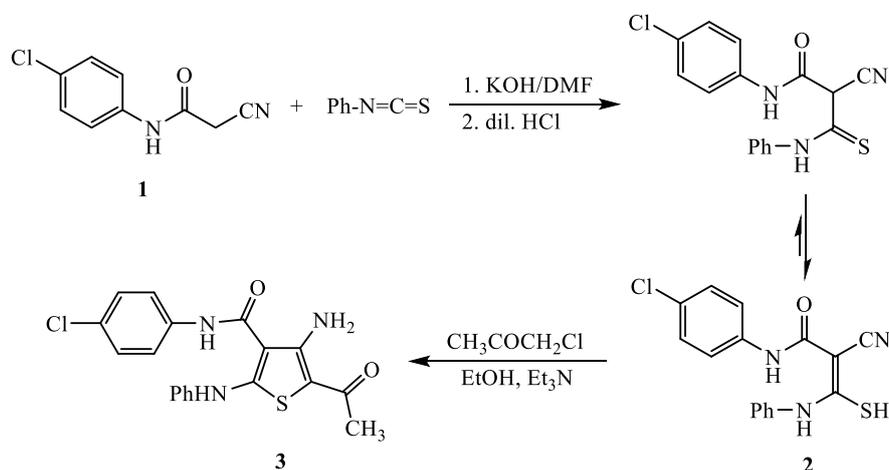
Table 1. Dependence of pH and Adsorption Capacity of Cu(II) ions on the contact time for CMC- and CS-based blends with thiophene derivative 3.

Time, min	Adsorption Capacity of Cu(II) ions, mg/g polymer								pH							
	CMC-Based Samples				CS-Based Samples				CMC-Based Samples				CS-Based Samples			
	CMC	CMC1	CMC2	CMC3	CS	CS1	CS2	CS3	CMC	CMC1	CMC2	CMC3	CS	CS1	CS2	CS3
0	0	0	0	0	0	0	0	0	5	5	5	5	5	5	5	5
10	0.6	27.58	33.67	37	27.33	1.83	2.43	0.88	5.1	5.8	6	6.1	5.6	5.1	5.2	5.1
30	6.2	31.8	47.56	44.84	23.91	3.05	3.16	2.3	6.5	5.9	6.3	6.3	5.7	5.2	5.3	5.3
165	4	41.17	33.39	36.67	37.24	3.11	27.99	3.55	6.9	6.1	6.5	6.5	6.1	5.2	5.4	5.4
300	8	50.75	40.76	40.22	34.08	7.48	44.81	4.09	7.6	6.3	6.6	6.6	6.2	5.4	5.6	5.5
510	7.6	47.72	35.7	37.68	32.06	26.38	52.26	12.78	7.8	6.4	6.7	6.6	6.3	5.7	5.8	6.2
720	10.8	43.68	39.51	34.68	39.83	30.68	61.69	9.2	8	6.5	6.8	6.7	6.5	6	6.2	6.4
1440	12.6	35.49	35.68	30.97	43.97	37.58	66.63	26.33	8	6.7	6.8	6.8	6.5	6.2	6.3	6.4

3. Results and Discussion

3.1. Synthesis and characterization of 5-acetyl-4-amino-*N*-(4-chlorophenyl)-2-(phenylamino)-thiophene-3-carboxamide (3).

The precursor, *N*-(4-chlorophenyl)-2-cyano-3-mercapto-3-phenylamino-acrylamide (2) was prepared by the reaction of 2-cyanoacetamide derivative 1 [24] with phenyl isothiocyanate. The mechanism of the reaction involves nucleophilic addition of the active methylene group from cyanoacetamide derivative 1 to phenyl isothiocyanate to form the corresponding non-isolated sulfide salt as an intermediate, which is then treated with dilute hydrochloric acid to furnish the most predominant tautomer *N*-(4-chloro-phenyl)-2-cyano-3-mercapto-3-phenylamino-acrylamide (2) (Scheme 1). Heterocyclization of the thiocarbamoyl precursor 2 with chloroacetone to furnish the corresponding functionalized thiophene compound 3 was achieved by heating in ethanol containing a catalytic amount of triethylamine. The suggested mechanism involves nucleophilic displacement of chlorine atom from chloroacetone by the sulfur nucleophile of thiocarbamoyl derivative 2 to constitute the sulfide intermediate, which undergoes intramolecular addition of methylene function to the nitrile group. IR, ¹H NMR, and ¹³C NMR spectra revealed the chemical structure of thiophene derivative 3. The IR spectrum of 3 displayed absorptions at 3420, 3318, and 3268 cm⁻¹ indicating the stretching vibrations of NH and NH₂ groups, in addition to absorptions at 1642 and 1597 cm⁻¹ for two carbonyl groups (C=O). The ¹H NMR spectrum showed a singlet at δ 2.09 ppm for three protons (CH₃). The aromatic protons resonate as a triplet at δ 7.10 ppm, multiplet at δ 7.35-7.39 ppm, and a doublet at δ 7.65 ppm for the aromatic protons. The two protons of amino-function resonate as a singlet at δ 7.47 ppm. The singlet signals at δ 9.76 and 9.96 ppm were assigned for the protons of two NH groups.



Scheme 1. Synthesis of 5-acetyl-4-amino-*N*-(4-chlorophenyl)-2-(phenylamino)thiophene-3-carboxamide (3).

3.2. Characterization of CMC membranes.

IR spectroscopy of CMC film showed the broadband at 3432 cm⁻¹ that can be related to the stretching of –OH groups that lead to inter- and intra-molecular hydrogen bonding. The absorption bands appeared at 2854 cm⁻¹, 2924 cm⁻¹ for C–H stretching groups, and at 1427 cm⁻¹ and 1607 cm⁻¹ were attributed to symmetrical and asymmetrical stretching vibrations of the carboxylate groups, respectively. Also, the absorption bands observed in the 1117–1314 cm⁻¹ region were assigned to –C–O– stretching in the polysaccharide skeleton.

3.3. Characterization of CMC/ thiophene (CMC/3) composite membranes.

The modification of CMC with 3 occurs by physical mixing of the components dissolved in suitable solvents at room temperature. IR spectrum of the obtained film of CMC with 3 showed an obvious shift and increased in the intensity of the absorption bands corresponding to the carboxylate group of CMC and the carbonyl groups of 3 at 1607 cm^{-1} and 1642 cm^{-1} , respectively, to lower values at 1600 cm^{-1} and 1641 cm^{-1} . In addition, the broad bands related to the stretching of OH group in CMC and NH groups in 3 suffer a weak shift of the absorption bands at 3432 cm^{-1} to 3422 cm^{-1} for OH groups and at 3420 cm^{-1} to 3272 cm^{-1} for NH group and at $3318, 3268\text{ cm}^{-1}$ to 2919 for NH_2 group. The absorption band at 1562 cm^{-1} is also related to the secondary amine group (NH group). This shift occurs due to the increased dipoles effect and formation of strong electrostatic interactions facilitating the intermolecular hydrogen bonding.

3.4. Characterization of CS membranes.

IR spectrum of CS film showed the characterizing bands of CS. The broad absorption band at 3448 cm^{-1} is corresponding to H-bonded NH, NH_2 , and OH (stretching) that lead to inter- and intra-molecular hydrogen interactions. The band at 2924 cm^{-1} corresponds to aliphatic CH stretching. The band at 1629 cm^{-1} is corresponding to C=O group of HN-C=O , while the bands at 1157 cm^{-1} and 1032 cm^{-1} are attributed to C-O-C stretching vibrations. The stretching vibrations of methylene C-H appeared at 2855 cm^{-1} , while the band at 1419 cm^{-1} is attributed to NH of HN-CO functionality, and the bands at 1000 cm^{-1} - 1100 cm^{-1} are assigned to C-O and C-N stretching and C-C-N bending vibrations.

3.5. Characterization of CS/ thiophene (CS/3) composite membranes.

The modification of CS with 3 occurs by physical mixing of the components dissolved in suitable solvents at room temperature. The incorporation of 3 withing CS matrix affected the absorption of the obtained film in the IR range. IR spectrum of CS/3 film showed an obvious shift of the absorption band corresponding to C=O groups from 1629 cm^{-1} in CS and 1642 cm^{-1} in 3 to 1637 and 1652 cm^{-1} , respectively, with an increase in the intensity. Also, the broad bands related to the stretching of OH and NH_2 groups of CS and NH groups of 3 suffered an obvious shift from 3448 cm^{-1} to 3450 cm^{-1} for NH, NH_2 , and OH in CS and from $3420, 3318,$ and 3268 cm^{-1} to 3450 cm^{-1} for NH and NH_2 groups in 3, hence, the absorption band at 3450 cm^{-1} increases in intensity. This shift occurs due to the increased dipoles and the formation of strong electrostatic interactions that allow intermolecular hydrogen interactions. The band appeared at $2924,$ and 2856 cm^{-1} are related to the C-H groups.

3.6. Dependence of adsorption capacity on contact time for CMC-based samples.

Figure 1 showed that the adsorption rate of copper ions was significantly high at the start of the process for all blended CMC samples with 3 during the first 10 minutes compared to the slight elevation of the unblended CMC sample, and this rise continued up to 30 minutes. After that, the behavior of the CMC blends was different from the blank CMC sample. The maximum removal percent of copper ions by CMC1, CMC2, and CMC3 was 50.75, 47.56, and 44.84%, respectively. The adsorption capacity of copper (II) ions increased by CMC1, CMC2, and CMC3 to a maximum of 50.75, 47.56, and 44.84 mg/g, respectively, then gradually

decreased to the equilibrium value. Although CMC1 had the highest adsorption efficiency for copper ions at 300 min, it showed a greater decrease in reaching the equilibrium value after that time compared to the rest of the membranes blended with 3, while sample blank (CMC) exhibited a slow increasing behavior of adsorption capacity of Cu(II) ions until equilibrium value of 12.6 mg/g as well as the maximum percentage of its removal for copper ions was 12.6% in the period from 720 to 1440 minutes.

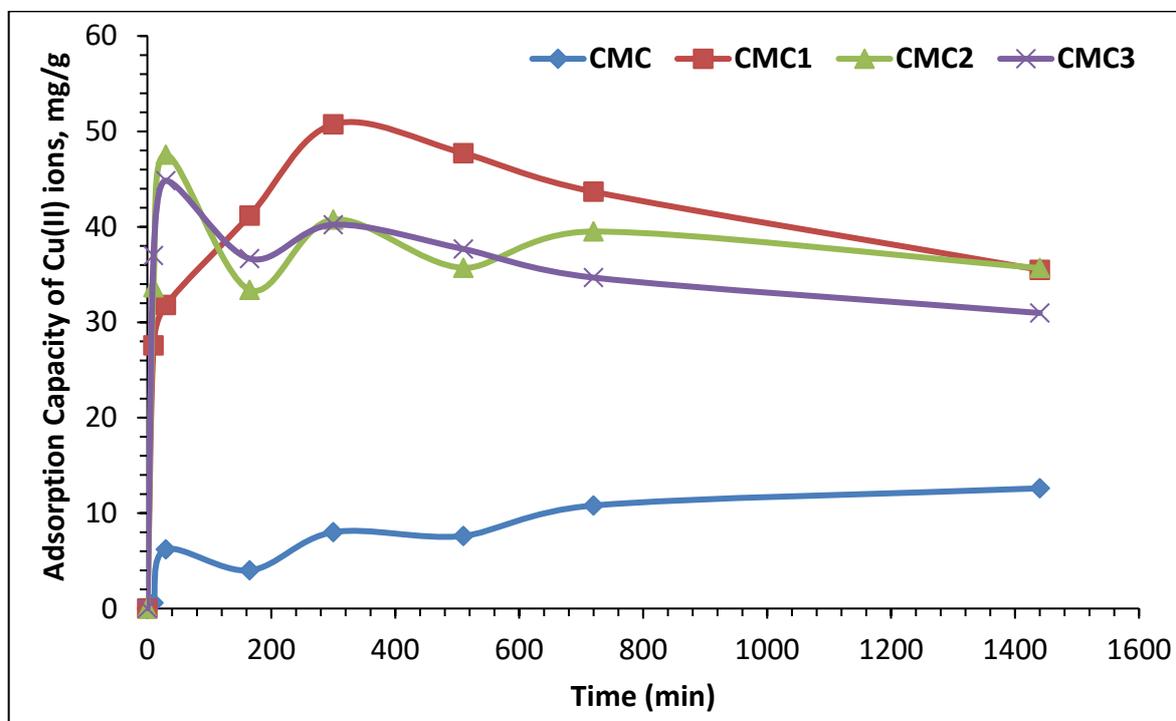


Figure 1. Dependence of adsorption capacity on the contact time for CMC-based samples.

The unexpected behavior of CMC1 can be attributed to the possible large site separation of thiophene 3 within the matrix due to the lower concentration of 3. It may cause a weak position of 3 within the CMC matrix, thus allowing the complex of 3 with Cu(II) ions to leach out the polymer matrix, while this behavior decreases in the rest of the membranes blended with 3 and this is due to the separation of the small site by 3 within the matrix. This means that the blended molecules of 3 are distributed close to each other within the CMC matrix. This may lead to further physical cross-linking of CMC with the help of two molecules and/or the possibility to coordinate Cu (II) ions with more than one molecule of 3 or inter-coordinate with two molecules of 3. This means that the CMC matrix blended with a higher concentration of 3 is more rigid. During the adsorption process, the polymer matrix is affected by two forces: hydration by water molecules trying to penetrate the matrix and the resistance of the polymer chains to create spaces between each other using the matrix. These two forces control the swelling of the matrix with water containing metal ions. Competition between the two forces may be a cause of the irregularity and fluctuation of the adsorption capacity of the CMC matrices in the Cu (II) ion solution. The increase in cross-linking by increasing the concentration of 3 in the CMC matrix led to a decrease in the efficiency of the functional groups in the CMC2 and CMC3 membrane to adsorb more copper ions, so their adsorption capacity was close to that of CMC1, and this is also due to reaching the saturation stage and the occurrence of stability. The adsorbed Cu(II) ions at equilibrium for CMC2 and CMC3 is still higher than the unblended CMC. Figure 2 shows the Images of blended CMC matrices with 3

along with the unblended CMC matrix as representative examples of CMC matrices before and after treatment with an aqueous solution of Cu(II) ions.

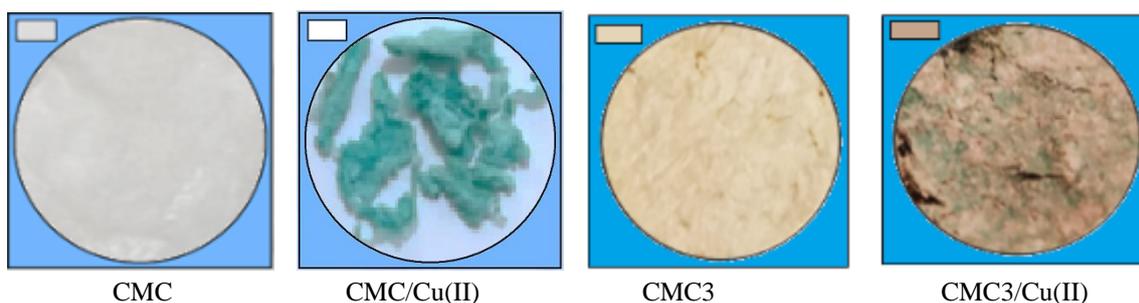


Figure 2. Images of representative examples for CMC matrices (unblended & blended) with 3 before and after treatment with aqueous solutions of Cu(II) ions.

3.7. Dependence of pH on contact time for CMC-based samples.

Figure 3 showed an increase in pH of the adsorption media overtime for all CMC samples, and it tended to be stable after about 12 h. Individually, the unblended CMC showed the highest increase in pH among the investigated matrices where it reached pH = 8, while the blended CMC samples showed an increase in pH in direct dependence with a concentration of 3 in the sample composition reaching 6.7, 6.8, and 6.8 for CMC1, CMC2, and CMC3, respectively. Thus, the increase in pH can be regulated by the order of CMC3 = CMC2 > CMC1.

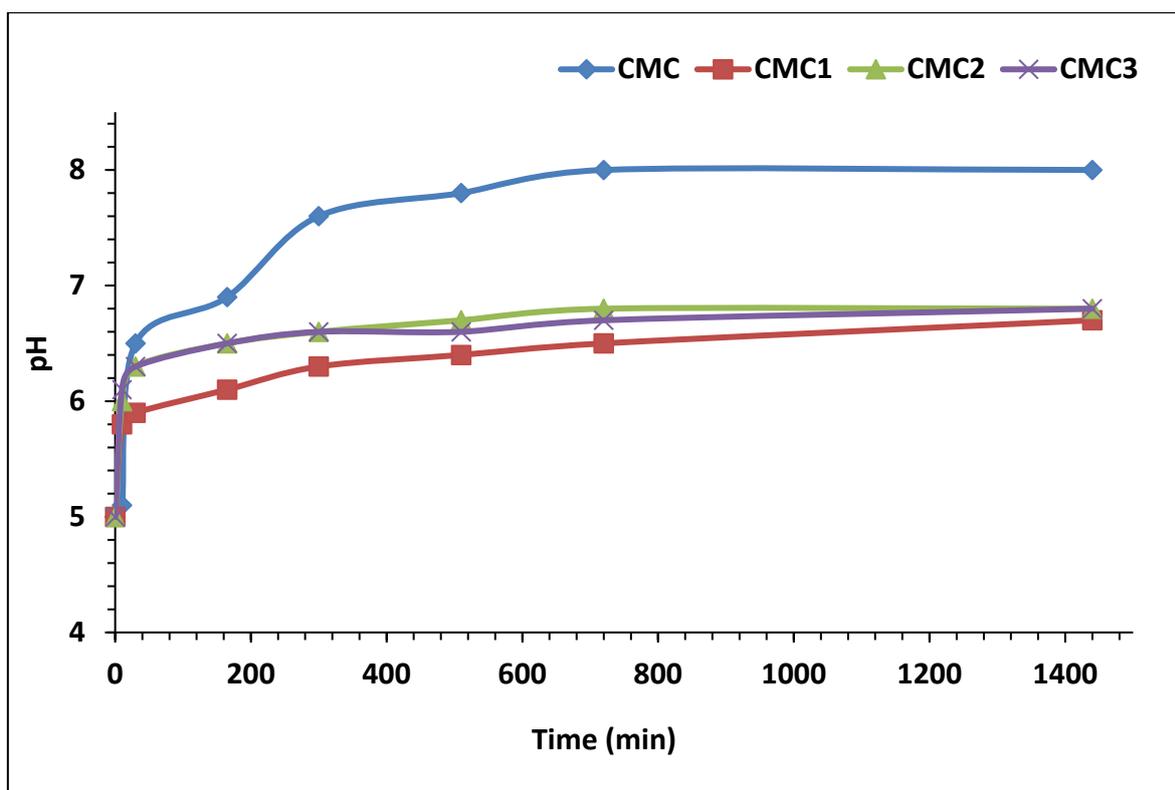


Figure 3. Dependence of pH on the contact time for CMC-based samples.

The change in pH during the adsorption process is one of the important consequences that basically tends to increase slowly over time until constant values reflecting the equilibrium state. This behavior may be attributed to several explanations, including the possible interaction between copper (II) ions and the chelating centers present in CMC matrices blended with 3 such as the carbonyl, amine, sulfur, chloride, carboxyl, and hydroxyl groups, and unblended

with 3 such as carboxyl and hydroxyl groups through ionic or coordinate bonding. The increased pH may also be attributed to the formation of insoluble $\text{Cu}(\text{OH})_2$ instead of adsorption onto CMC-based adsorbents [25]. On equilibrium, the accessible spaces of the adsorbent would be filled, and the pH remains constant. The stability occurring between CMC2 and CMC3 at $\text{pH} = 6.8$ within 1440 minutes despite the increase in the concentration of 3 may also be due to the increase in physical cross-linking, which reduced the effectiveness of the functional groups to adsorb more copper ions and reach the stage of equilibrium and saturation, which stabilized the pH of the solution.

3.8. Dependence of adsorption capacity on contact time for CS-based samples.

Fig. 4 showed that the adsorption capacity of copper (II) ions by unblended CS membrane with 3 were significantly increased compared to membranes of CS blended with 3 within 10 minutes. Subsequently, the CS mixtures behaved differently from the CS blank sample. As the unblended CS sample with 3 suffered fluctuations and an irregular increase in the adsorption capacity until it reached its maximum capacity at 1440 minutes. On the other hand, the adsorption capacity of membranes blended with 3 for copper ions regularly increased over time until they reached their maximum adsorption capacity at 1440 minutes as their adsorption capacity was 43.97, 37.58, 66.63, and 26.33 mg/g for CS, CS1, CS2, and CS3, respectively. The maximum removal of copper ions by CS, CS1, CS2, and CS3 was 43.97, 37.58, 66.63 and 26.33% for CS, CS1, CS2, and CS3, respectively.

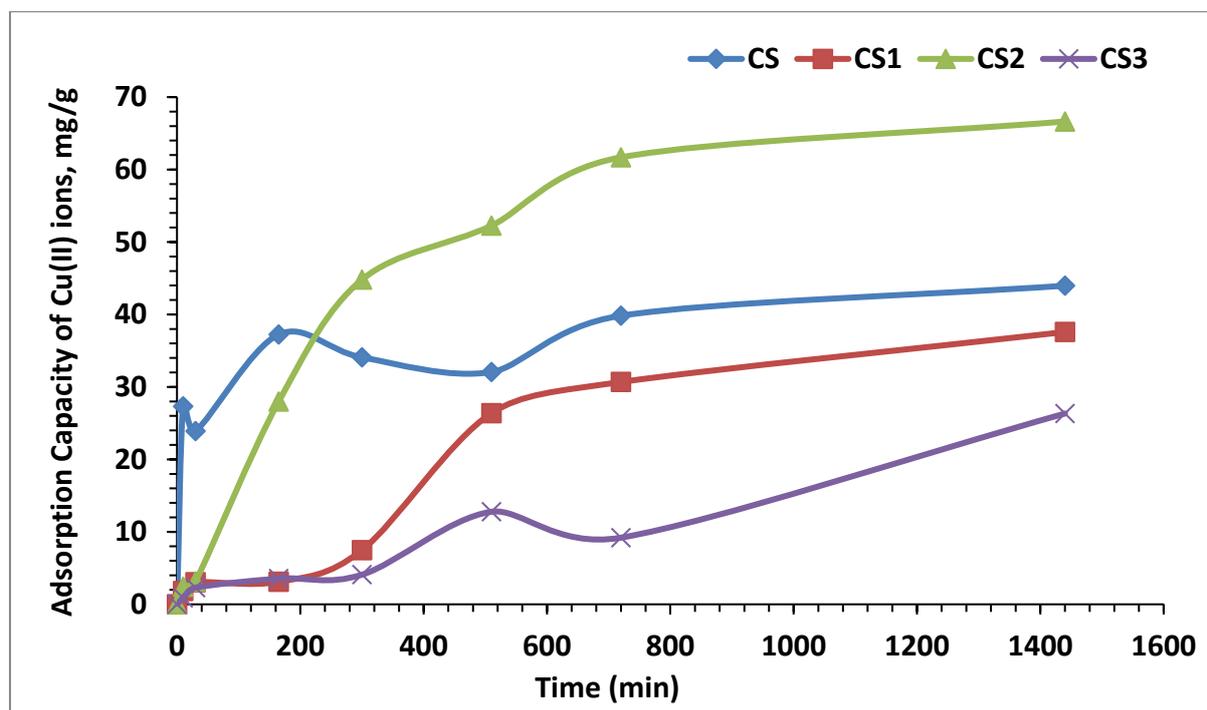


Figure 4. Dependence of adsorption capacity on the contact time for CS-based samples.

During the adsorption process, the polymer matrix is affected by two forces, which are the hydration by water molecules trying to penetrate inside the matrix and the resistance of the polymer chains to make spaces between each other within the matrix. Such two forces are controlling the swelling of the matrix with water containing the metal ions. The competition between the two forces may be the reason for the irregular and fluctuation of the adsorption capacity of CS matrices in $\text{Cu}(\text{II})$ ions solution. After a certain period, most of the chains

respond to the water pressure inside the polymer matrix, and more adsorption occurs until most of the available spaces are filled. In such a case, the adsorption capacity reaches its maximum, which depends on the content of the thiophene derivative (3) within the matrix. The adsorption capacity is dependent on the concentration of 3 within the matrix, which can be attributed to the potential physical cross-linking of the polymer matrix with the functional groups of 3. This cross-linking leads to an increase in the adsorption capacity, as happened with CS2. However, increasing the concentration of 3 within the matrix than 50% w/w of CS resulted in increased cross-linking, more rigidity, and decreased ability to absorb more water containing copper (II) ions, thus reducing its adsorption capacity. The membrane CS unblended with 3 had a higher adsorption capacity than CS1 and CS3. This is also due to the concentration of 3 within the CS matrix that controls the adsorption capacity. Figure 5 shows the Images of blended CS matrices with 3 along with the unblended CS matrix as representative examples of CS matrices before and after treatment with an aqueous solution of Cu(II) ions.

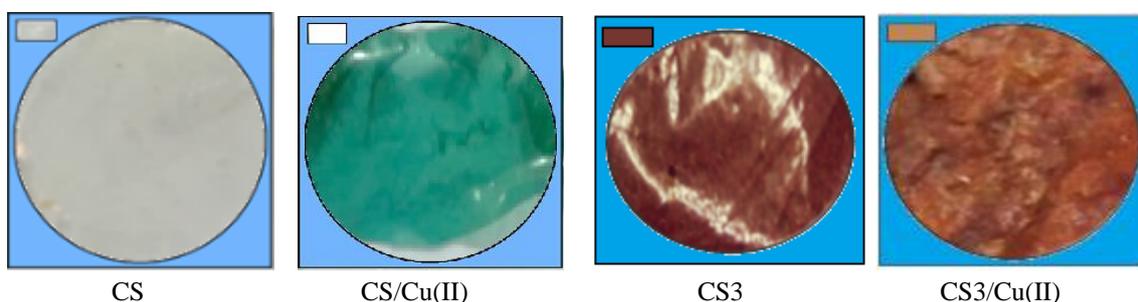


Figure 5. Images of representative examples for CS matrices (unblended & blended) with 3 before and after treatment with aqueous solutions of Cu(II) ions.

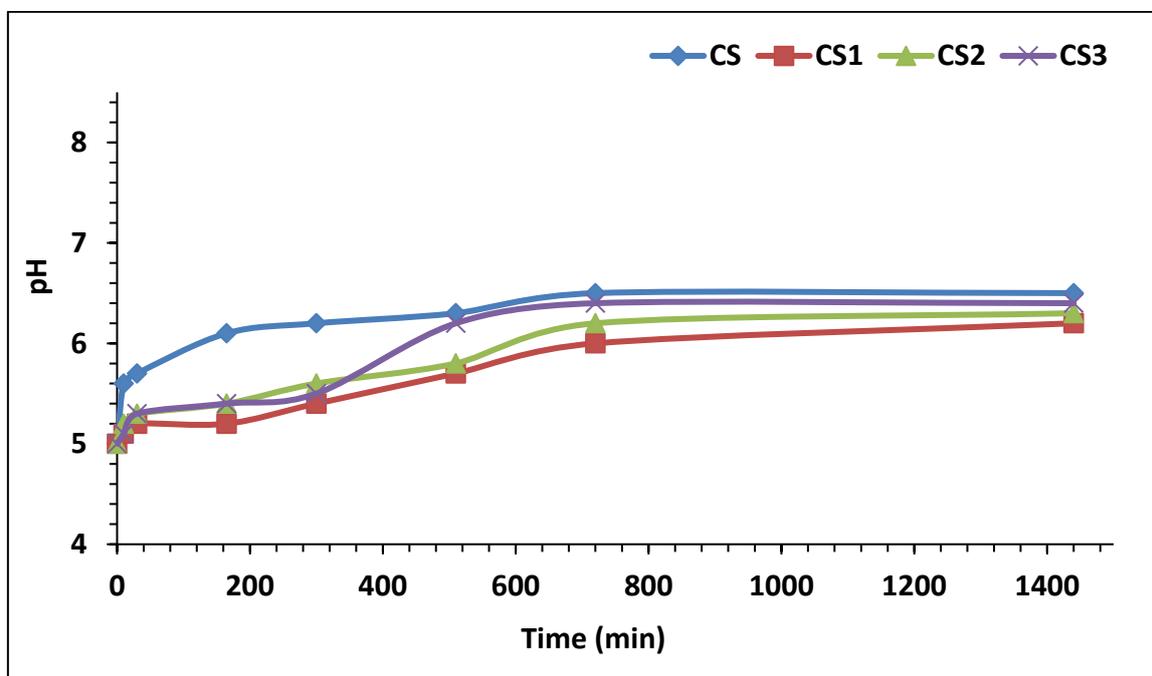


Figure 6. Dependence of pH on the contact time for CS-based samples.

3.9. Dependence of pH on contact time for CS-based samples.

In the case of CS-based adsorbents, the change in pH during the adsorption process is shown in Figure 6 and is similar to that of CMC-based adsorbents, reflecting the same attribution for such behavior. One of the important consequences is the change in pH during

the adsorption process, which tends mainly to increase slowly over time until constant values reflect a state of equilibrium. This behavior may be attributed to many explanations, including the possible interaction between Cu(II) ions and the chelating centers present in CMC matrices blended and unblended with 3 through either ionic or coordinate bonding. The increase of pH may also be attributed to the formation of the insoluble Cu(OH)₂ instead of adsorption onto CS-based adsorbents [25]. On equilibrium, the accessible spaces of the adsorbent would be filled, and pH remains constant.

4. Conclusions

The best adsorption capacity of Cu(II) ions from aqueous solution were 50.75 mg/g by CMC1 within 300 min, and its removal percent for copper ions was 50.75% in just 300 min, while it was 66.63 mg/g by CS2 within 1440 min and its removal rate for copper ions was also 66.63% at that time for CMC-based and CS-based adsorbents, respectively. The adsorption method was accompanied by a pH rise to a constant value in both blends. Therefore, both polymeric blends are able to extract from their aqueous solutions Cu(II) ions, and the adsorption process can be controlled within the matrix by the concentration of thiophene 3.

Funding

This research received no external funding.

Acknowledgments

This research has no acknowledgment.

Conflicts of Interest

The authors declare no conflict of interest.

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