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Article

Synthesis, Characterization and Anti-biological Activities of Colloidal Copper Nanoparticles Stabilized by Cationic Thiol Polyurethane Surfactants

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Abstract: Metal nanoparticles have attracted considerable interest particularly because of the size dependence of physical and chemical properties and its enormous technological potential. Among different metal nanoparticles, copper nanoparticles have attracted great attention because copper is one of the most key metals in new technology. Chemical methods are used to synthesize copper nanoparticles. In this paper, the new cationic Thiol polyurethane surfactants with different alkyl chain length were synthesized (PQ10, PQ14 and PQ18). The chemical structure of the synthesized surfactants was confirmed using infra-red spectroscopy (IR) and proton nuclear magnetic resonance spectroscopy (1H NMR). Copper nanoparticles colloidal solution of 40–80 nm diameters was prepared using sodium borohydride in aqueous solution at room temperature as reducing agent. The nanostructure of the synthesized surfactant with copper nanoparticles with diameters ranging from 31.5 to 10.3 nm was prepared and characterized using ultra violet spectrophotometer (UV), infra-red spectroscopy (IR) and transmission electron microscope (TEM). The results declare formation and stabilization of copper nanoparticle using synthesized cationic surfactants. Antimicrobial activity of the synthesized cationic surfactants and their nanostructure with copper nanoparticles were evaluated against pathogenic bacteria and fungi. The antimicrobial activity showed the enhancement in the antimicrobial activity of the

synthesized cationic surfactants in the nanostructures form.

Keywords: Polyurethane, Cationic surfactants, Copper nanoparticles, Antimicrobial activity, Transmission electron microscope.

1. Introduction

Copper nanoparticles have great interest due to their optical, catalytic, mechanical and electrical properties. Copper is a good alternative material for noble metals such as Au and Ag as it is highly conductive and much more economical than them [1, 2]. Copper plays an important role in electronic circuits because of its excellent electrical conductivity. Copper nanoparticles are inexpensive and their properties can be controlled depending on the synthesis method. Also in catalyst, the nanoparticles have a higher efficiency than particles [3, 4, and 5]. Copper nanoparticles are synthesized through different techniques. The most important methods for the synthesis of copper nanoparticles are chemical methods such as chemical reduction, electrochemical techniques, photochemical reduction and thermal decomposition. Copper nanoparticles can easily oxidize to form copper oxide. To avoid oxidation, these methods were usually performed in non-aqueous media, at low precursor concentration, and under an inert atmosphere (argon, nitrogen) [6-10]. In the present study stable copper nanoparticles with narrow size and homogenous distribution were synthesized via surfactant assisted wet chemical reduction method using sodium borohydride as a reducing agent, cationic Thiol polyurethane surfactants as a capping agent. Even today, the exact mechanism of antimicrobial action of the CuNPs remains unknown. The general view seems to be a combination of several factors: releasing Cu^{+2} ions, their penetration and disruption cell membrane and biochemical pathway by chelating cellular enzymes and DNA damage [11-13].

Previously reported antibacterial activity of copper nano particle, it was found that it has significant potency to act as bacteriocidal agent than gold, silver, zinc nano particles. Combination of different Nano particles such as Silver & Copper may show more significant effect on bacterial growth. Gram-positive bacteria have a thick cell wall containing multiple layers of peptidoglycan, while gram-negative bacteria have a relatively thin cell wall consisting of a single layer of peptidoglycan. Surfaces of copper nano particles interact directly with the bacterial cell wall & outer membrane, leads to rupture of cell wall & killing bacteria [14-16]. Mechanism of action of copper nano particle may be:

(1). Accumulation of nano particles in membrane alters permeability leads to release of lipopolysaccharides, integral proteins & intracellular fluid.

(2). Oxidative damage to cell structure due to formation of Reactive Oxygen Species.

(3). Bacterial cells generally take up whole metallic ions inside which deplete affect ATP production & DNA replication[17].

Regardless of chemical & physical properties of copper nano particle it has extremely high surface area to volume ratio. Specifically copper nano particles having a potential to kill pathogenic bacteria [18, 19].

2. Materials and Methods

2.1. Materials

Fatty alcohols (octanol, dodecanol and hexadecanol) were purchased from Sigma, Germany. Toluene diisocyanate TDI (97 %) was purchased from DOW, USA. Mercapto acetic acid, Bromoacetic acid and Sodium borohydride were purchased from Aldrich, Germany. Copper Chloride dihydrate was purchased from BDH, British. Triethanol amine and solvents were obtained from ADWIC chemicals company, Egypt.

2.2. Instrumentation

- Elemental analysis: VARIO Elemental Analyzer
- FTIR spectroscopy: Perkin Elmer Genesis Fourier Transformer FTIR measured at 4000-400 (cm^{-1}) applying potassium bromide compressed thin pellet technique.
- The nuclear magnetic resonance spectra were measured by Varian NMR-300, Mercury 300 MHz spectrometers using $CDCl_3$ as solvent and trimethyl silane (TMS) as a reference to determine the different chemical shifts δ(ppm); GPC measurements were performed using GPC-7890A instrument equipped with DB-23 column, 60 mm x 0.25 mm, i.d. of 0.25 μm.
- TEM images were performed using TEM-JEOL JEM-2000, Germany.

2.3. Synthesis

2.3.1. Preparation of triethanol amine mono mercaptoacetate

Triethanol amine (0.1 mole) and mercaptoacetic acid (0.1 mole) were charged in 250 mL round flask in presence of xylene (75 mL) as a solvent and *p*-toluene sulfonic acid (0.1 g) as a dehydrating agent. The completion of the reaction was monitored by obtaining 0.1 mole of H_2O (1.8 mL) [20]. At the end of the reaction, the solvent was removed by evaporated by the effect of evacuation, while *p*-toluene sulfonic acid was eliminated from the reaction medium by take out the obtained esters by dissolving in ether (diethyl ether). The evaporated solvent was recovered and purified to reuse. The unreacted and

excess reactants were eliminated from the products by successive sanitization of the crude products to afford triethanol amine mono mercaptoacetate in a yield of 96%.

2.3.2. Preparation of thiol polyurethane (P)

Thiol polyurethane polymerization reaction was carried out in a suitable flat bottom glass reactor (500 mL) connected to a mechanical rotor, dropping funnel, thermometer and condenser. Inside the reaction vessel, a mixture of toluene diisocyanate (TDI, 0.1 mole) dissolved in methyl ethyl ketone (50 mL), triethanol amine mercaptoacetate (0.2 mole) and five drops of triethylene diamine dropped during 20 min was mixed [21]. The reaction medium was continuously mixed at 30 ºC for 30 min to obtain the pre-polymer. The ratio of isocyanates (NCO) to reactive hydroxyl group (OH) was reserved at 1:2 in polyurethane reaction polymerization. The prepared polymer was washed twice using appropriate amounts of methyl ethyl ketone and finally dried (yield 92%).

2.3.3. Preparation of fatty esters bromoacetate (Q10, Q14 and Q18)

Fatty esters bromoacetate (Q10, Q14 and Q18) were prepared throughout reacting different fatty alcohols (0.1 mole) namely: decanol, tetradecanol and octadecanol and Bromoacetic acid (0.1 mole) in the presence of xylene (100 mL) as a solvent and *p*-toluene sulphonic acid (0.01 wt.%) as dehydrating agent under heating and stirring conditions until the expected amount of water (1.8 mL) is produced. At the end of the reaction, xylene was stripped off using reduced pressure; *p*-toluene sulphonic acid was eliminated by extracting the product from diethyl ether and the solvent was removed [22] to afford the different fatty esters bromoacetate (yield 95-98%).

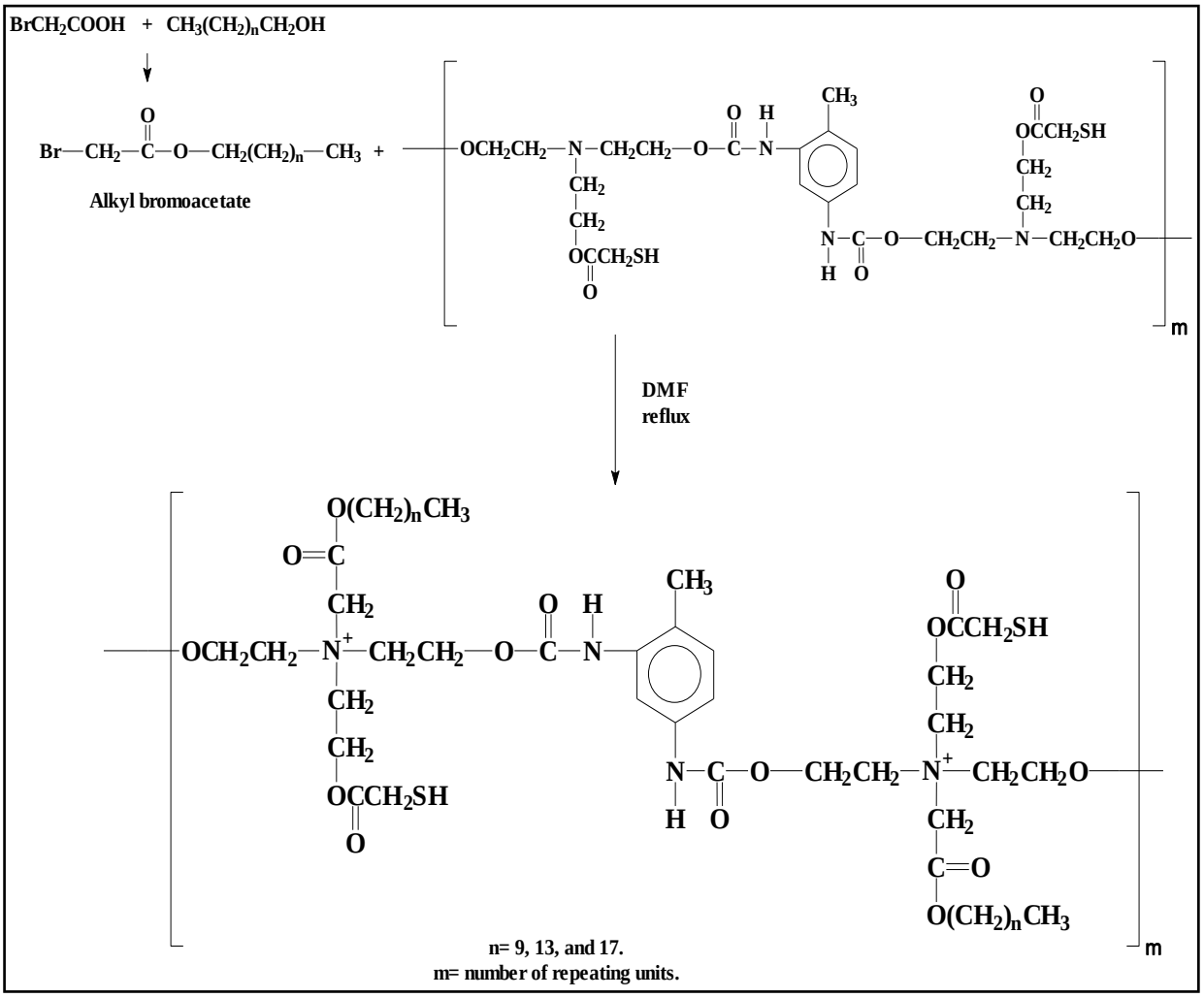
2.3.4. Preparation of cationic Thiol polyurethane surfactants (PQ10, PQ14 and PQ18)

Cationic Thiol polyurethane surfactants were prepared by refluxing equimolar amounts of Thiol polyurethane (**P**) and decyl, tetradecyl, octadecyl esters (Q10, Q14 and Q18) individually in a suitable amount of dimethyl formamide (DMF) for 20 h. The produced compounds were filtered off, washed by excess DMF, and dried under reduced pressure at 50 ºC to afford yellow to brown viscous liquids designated as: PQ10, PQ14 and PQ18 (yield 82-89%) [23, 24] **(Scheme 1)**.

2.3.5. Synthesis of colloidal copper nanoparticles self-assembled and stabilized by cationic Thiol polyurethane surfactants PQ-Cu NPs

Colloidal Cu nanoparticles were prepared by the reduction of copper chloride dihydrate in presence of cationic Thiol polyurethane surfactants as stabilizer and capping agent using sodium borohydride $NaBH_4$ as reducing agent. [25, 26] (0.03 mole) of the synthesized cationic Thiol polyurethane surfactants (**PQ10, PQ14 and PQ18**) dissolved separately in 100 ml ethanol and then, an

ethanoic solution (30 ml) of copper chloride dihydrate (0.01 mole) was added dropwise under intense stirring. The resulting mixture was added to ascorbic acid (0.1 mole) (as antioxidant of colloidal copper) and mixed for 15 min. in magnetic stirring at room temperature. After then a freshly prepared aqueous solution (50 ml) of sodium borohydride (0.1 mole) was added dropwise under continuous strong stirring for about 30 min. The initial light green color of the reaction mixture turned blue and eventually dark blue indicating the formation of colloidal copper nanoparticles self-assembled by cationic Thiol polyurethane surfactants. The copper nanoparticles capped by the synthesized cationic surfactant were separated and washed with deionized water by centrifugation, while using acetone as a non-solvent in order to remove excess cationic surfactant. The resulting precipitates were dried under vacuum oven at 60 ^{o}C for 2 hours.



Scheme 1: Preparation of cationic Thiol polyurethane surfactants

2.4. Biological Activity

The antimicrobial activity of synthesized cationic Thiol polyurethane surfactants and their

nanostructures with copper nanoparticles were measured against a wide range of test-organisms comprising: (bacteria and fungi)

2.4.1. The media

The following media used in the antimicrobial activity of synthesized products, the bacterial species grow on nutrient agar, while fungi mold grow on Czapek's dox agar. (a) Nutrient agar: Nutrient agar consists of Beef extract (3.0 g/l); peptone (5.0 g/l), sodium chloride (3.0 g/l) and agar (20.0 g/l), then, completes the volume to 1 l, heated the mixture until the boiling and sterilizes the media by autoclave. (b) Czapek's Dox agar: Czapek's Dox agar consists of sucrose (20.0 g/l), sodium nitrate (2.0 g/l), magnesium sulfate (0.5 g/l), potassium chloride (0.5 g/l), ferrous sulfate (0.01 g/l) and agar (20.0 g/l), then, complete the volume to 1 l, heated the mixture until the boiling, and sterilize the media by autoclave.

Table 1: Elemental analysis of the synthesized cationic Thiol polyurethane surfactants

compound	M.wt*	Formula	C%		H%		N%		S%		Br%	
	g/mole		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
PQ10	21400	$(C_{49}H_{86}O_{14}N_4S_2Br_2)_n$	48.54	48.50	7.05	7.06	5.27	5.25	6.02	5.98	15.05	15.01
PQ14	23200	$(C_{57}H_{102}O_{14}N_4S_2Br_2)_n$	52.04	52.00	7.74	7.76	4.76	4.73	5.44	5.41	13.60	13.56
PQ18	25000	$(C_{65}H_{118}O_{14}N_4S_2Br_2)_n$	54.97	54.93	8.31	8.29	4.35	4.32	4.97	4.95	12.44	12.39

***** Obtained molecular weight from GPC measurements, n≈18

2.4.2. Microorganisms

The different species of tested organisms were obtained from the unit of Operation Development Center, Egyptian Petroleum Research Institute. The used microorganisms were Gram-positive bacteria (Bacillus subtilis and Staphylococcus aureus), Gram-negative bacteria (Salmonella typhimurium and Escherichia coli), Yeast and Fungi (Candida albicans and Aspergillus niger). An assay is made to determine the ability of an antibiotic to kill or inhibit the growth of living microorganisms, the technique which used is: filter-paper disk-agar diffusion (Kirby-Bauer) are as the following [27]:

1) Inoculate flask of melted agar medium with the organism to be tested.

2) Pour this inoculated medium into a Petri dish.

3) After the agar has solidified, a multilobed disk that impregnated with different antibiotics laid on top of agar.

4) The antibiotic in each lobe of disk diffuses into medium and if the organism is sensitive to a particular antibiotic, no growth occur in a large zone surrounding that lobe (clear zone).

5) The diameters of inhibition zones were measured after 24–48 h at 35–37 C (for bacteria) and 3–4 days

at 25–27 C (for yeast and fungi) of incubation at 28 ºC

6) Measure each clear zone and compare between them to determine the antibiotic which is more inhibitor.

3. Results and Discussion

3.1. Chemical Structure

Scheme 1 represents the preparation of polyurethane cationic surfactants. The elemental analysis of the prepared cationic polyurethane surfactants **(Table 1)** showed the comparable values of the predicted and obtained ratios of the different elements in their chemical structure. The chemical structures of the prepared cationic polyurethane surfactants were confirmed using molecular weight measurements, elemental analysis, FTIR spectroscopy and ^{1}H-NMR spectroscopy.

3.1.1. FTIR spectroscopic analysis

The chemical structures of the prepared cationic surfactants and their intermediates were confirmed using FTIR spectroscopic analysis.

FTIR spectra of Triethanol amine mercaptoacetate showed the following absorption bands: broad absorption band centered at 3435 cm^{-1} corresponds to -OH stretching; weak absorption band at 2550 cm^{-1} corresponds to stretching of S-H group; absorption band at 2932 cm^{-1} attributed to symmetric stretching of C-H group; 1018 cm^{-1} corresponds to C-N stretching group of aliphatic amine and absorption band at 1732 cm^{-1} corresponds to C=O ester group**.**

Thiol polyurethane compound (**P**) showed the following absorption bands: 1663 cm^{-1} corresponds to C=O of urethane group; 1458 and 1462 cm^{-1} corresponds to N-H of urethane group; 1508-1510 cm^{-1} described for the double bonds in the phenyl moiety (C=C) in toluene diisocyanate moiety (TDI).

FTIR spectra of alkyl bromoacetate esters (**Q10, Q14 and Q18**) represented the disappearance of the broad band at 3400 cm-1 of alcoholic hydroxyl groups of the reacted fatty alcohols, the appearance of new absorption bands at: 1736-1738 cm-1 corresponds to carbonyl ester indicates the ester (Q10, Q14 and Q18) formation; 1275-1277 cm-1 corresponds to ether linkages C-O-C; 2920-2922 cm-1 and 2849-2850 cm1 corresponded to symmetric and asymmetric stretching of C-H groups. The characteristic absorption band of C-Br bond was appeared in the range of 663-667 cm-1.

FTIR spectra of the prepared cationic polyurethane surfactants showed similar absorption bands to the absorption bands of triethanol amine mercaptoacetate, thiol polyurethane and alkyl bromoacetate esters. Furthermore, IR spectra recorded a disappearance of the absorption band at 660 cm-1 and the appearance of a new absorption band at 3040 cm-1 corresponded to C-N+ group (**Figure 1**).

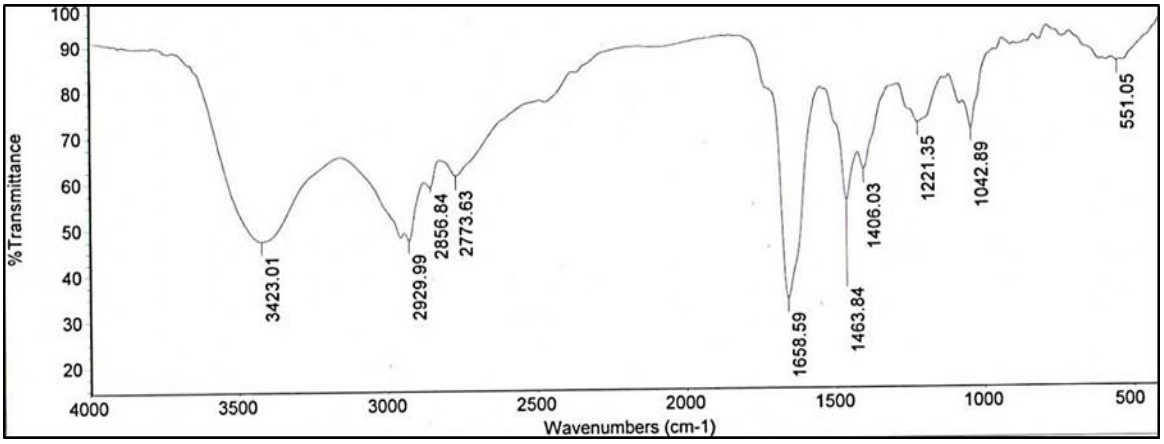


Figure 1: FTIR spectra of cationic polyurethane surfactants (PQ10).

3.1.2. ^{1}H-NMR Spectroscopic analysis

The H^{1}NMR spectra of the synthesized cationic surfactants (**Figures 2, 3** for PQ10 and PQ14 as representative for the prepared surfactants) showed the appearance of signals at: δ = 0.85 ppm (t, 3H, C$\underline{H}_3$) assigned to terminal methyl group; 1.25 ppm (m, nH, C$\underline{H}_2$) attributed to the methylene groups of the fatty chains; 2.5 ppm (t, 3H, C$\underline{H}_3$Ph) assigned to methyl group of toluene diisocyanate moiety; 7.8 ppm, 8.0 ppm and 8.2 ppm (m, 4H, phenyl group).

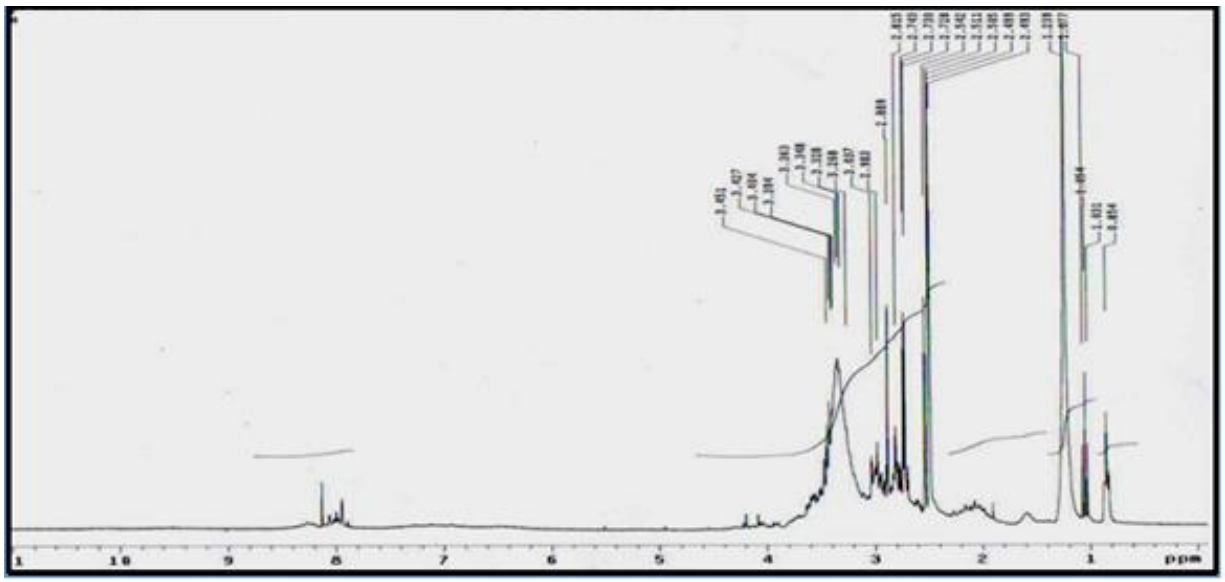


Figure 2: ^{1}H-NMR spectra of PQ10 surfactant

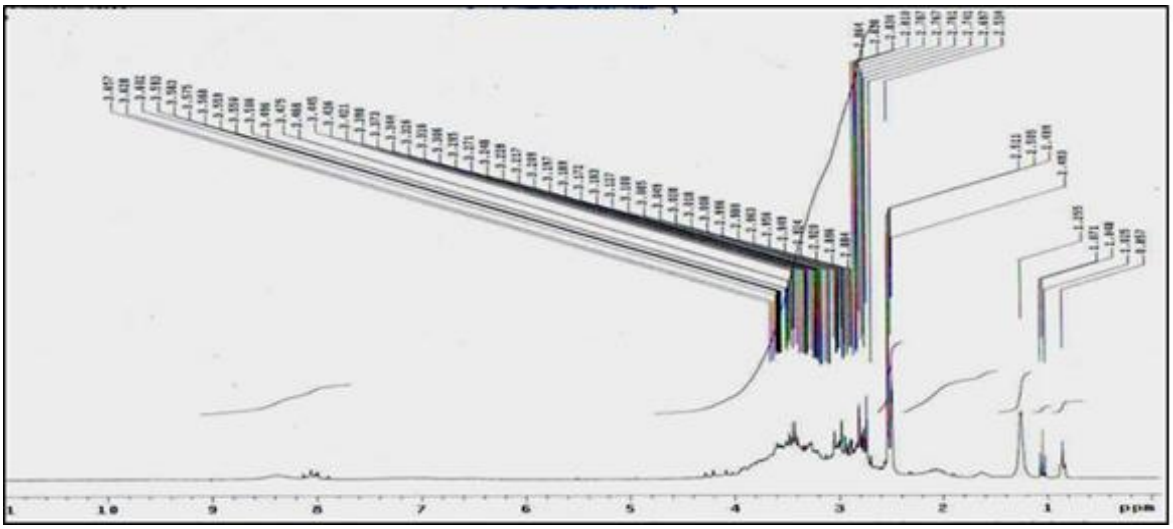


Figure 3: [1]H-NMR spectra of PQ14 surfactant

3.1.3. Molecular weight measurements

The molecular weights of the prepared cationic surfactants were determined using GPC chromatographic measurements according to the methodology of our colleague [28]. The results showed that the surfactant molecules contain an average of 18 repeated units (exactly 17.8 units). The obtained values of the molecular weights of the different surfactants were listed in **Table 1.**

3.1.4. UV-Vis Spectroscopy

UV–Vis absorption spectra were used to determine the formation of colloidal copper nanoparticles stabilized by different cationic Thiol polyurethane surfactants. UV–Vis absorption spectra of the prepared colloidal copper nanoparticles stabilized by different cationic Thiol polyurethane surfactants were recorded in DMF as a solvent in order to monitor their formation and stability **(Figure 4)**. Cationic Thiol polyurethane surfactants with copper nanoparticles were confirmed by the appearance of new bands in UV spectra. UV–Vis spectroscopy is quite sensitive to the formation of copper nanoparticles due to surface Plasmon excitation.

UV spectrum of copper nanoparticles for characterizing the metallic nature whose broad peak corresponds to the Cu range from 500–600 nm [15, 16].

Figure 4 shows absorption spectra of Cu NPs capped by prepared cationic surfactants, which show absorption band listed in **table 2** which an indication on formation copper nanoparticles, due to surface Plasmon resonance of copper nanoparticles. Bands at λmax range from 208 to 224 nm characteristic for the used capping agents, which matches with the band, appeared for aqueous solution of the used capping agents alone. It is known that the amount and size of copper nanoparticles are positively related with the adsorption peak intensity and the λmax on the UV–Vis spectra respectively.

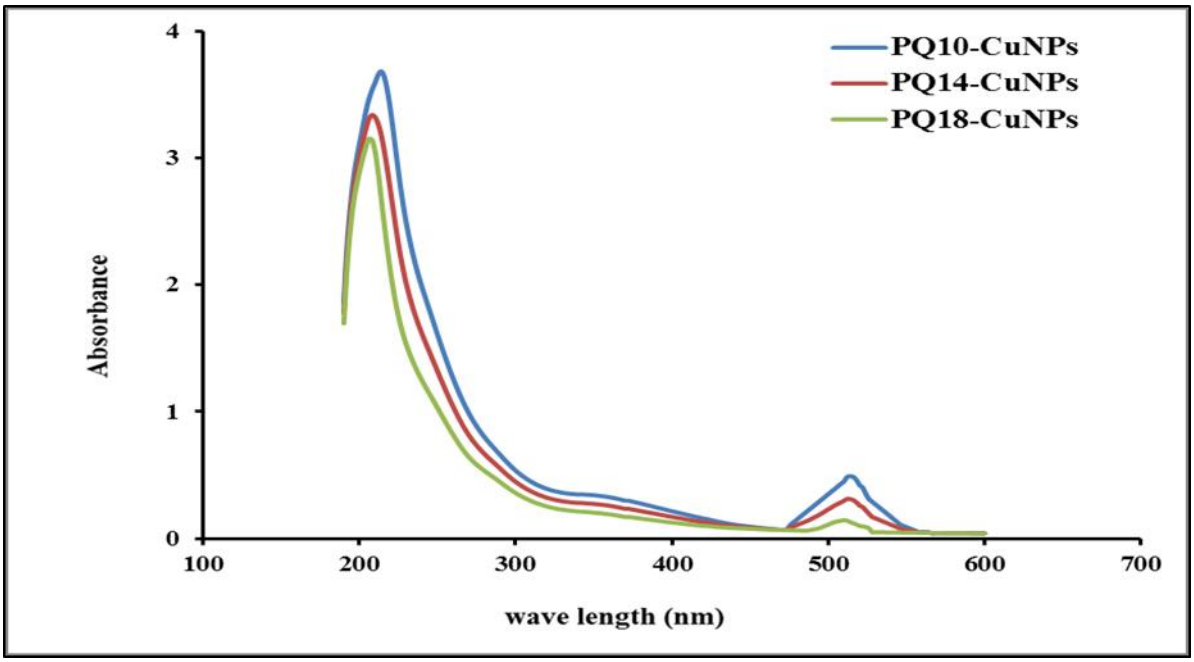


Figure 4: UV spectra of Cu NPs capped by prepared cationic Thiol polyurethane surfactants

Table 2: UV absorption maxima of Cationic Thiol polyurethane Nano compounds

Compounds	λ_{max} (nm)
PQ10-Cu NPs	**216, 514**
PQ14- Cu NPs	**212, 516**
PQ18- Cu NPs	**208, 518**

3.1.5. TEM spectroscopy

TEM spectroscopy determines the size and morphology of the formed nanoparticles. The size and morphology of the prepared colloidal copper nanoparticles stabilized by cationic Thiol polyurethane surfactants were investigated using transmission electron microscope (TEM), **Figures 5a-c**. It is clear from TEM images that the colloidal copper nanoparticles stabilized by cationic Thiol polyurethane surfactants are predominantly spherical in shape and polydispersed. The size of CuNPs is ranged between 10.3-31.5 nm according to the TEM image. That was in consistent with the published data for the synthesis of copper nanoparticles by the chemical reduction method [26]. The TEM image showed the self-assembling of the prepared surfactant on the copper nanoparticles which causes the stabilization of the nano size of these nanoparticles due to the formation of nano shells with the used surfactant.

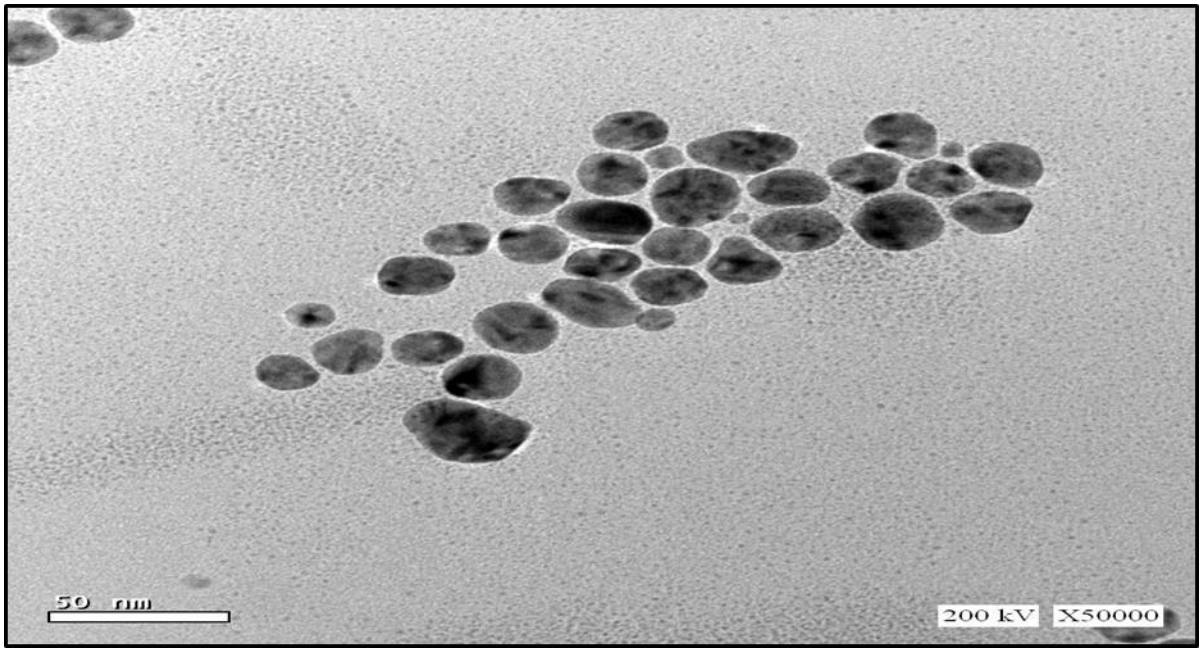


Figure 5a: TEM Image of CuNPs capped by PQ10 surfactant

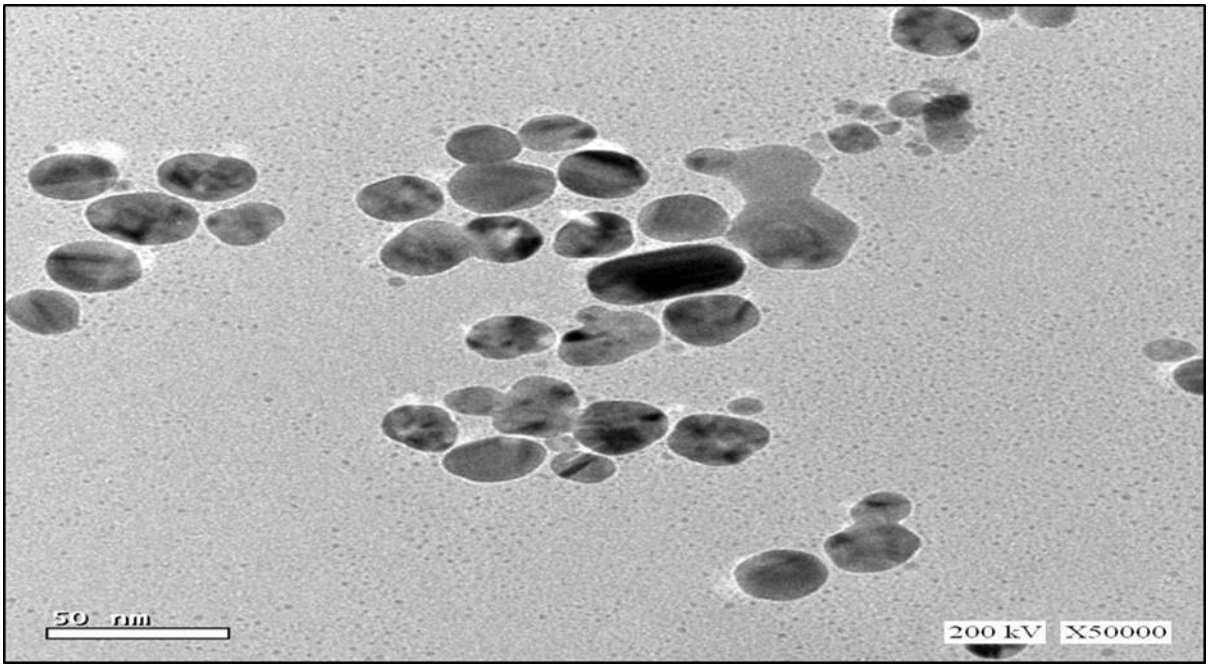


Figure 5b: TEM Image of CuNPs capped by PQ14 surfactant

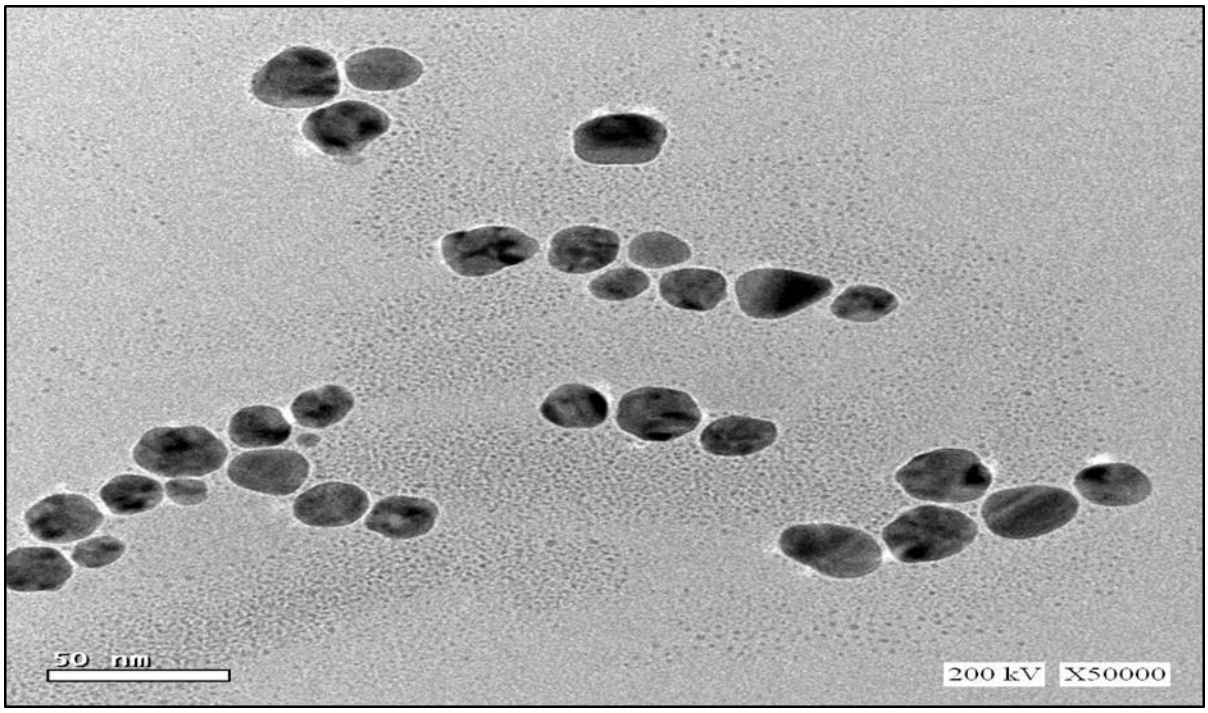


Figure 5c: TEM Image of CuNPs capped by PQ18 surfactant

3.2. Antimicrobial Activity of the Synthesized Cationic Surfactants and Their Nanostructures

The biological activities of the synthesized cationic surfactants (PQ10, PQ14 and PQ18) and their nanostructures with copper nanoparticles was screened against pathogenic Gram-positive (Bacillus subtilis and Staphylococcus aureus), Gram-negative (Salmonella typhimurium and Escherichia coli), bacteria and also, some pathogenic fungi (C. albicans and Asperigllus niger) using the values of the inhibition zone diameter tests and the results are summarized in Table 3. Data in **Table 3** indicating that the synthesized compounds have antimicrobial activity rang from a moderate to slight high effect on Gram negative bacteria and Gram positive bacteria and moderate effect on fungi and high effect on yeast compared to the drug reference used. Where the inhibition zone for Bacillus subtilis ranges from 13–33 mm/mg compared to 26 mm/mg for Chloramphencol drug, for Staphylococcus aureus range from 0–33 mm/mg compared to 25 mm/mg for Chloramphencol drug, for Salmonella typhimurium range from 0–21 mm/mg compared to 28 mm/mg for Cephalothin drug, for Escherichia coli range from 10–26 mm/mg compared to 27 mm/mg for Cephalothin drug, for Candida albicans range from 17–31 mm/mg compared to 28 mm/mg for cycloheximide drug, for Aspergillus niger range from 0–16 mm/mg compared to 26 mm/mg for cycloheximide drug.

The biological activities of surfactants often show a non-linear dependence on their chain length, where bactericides and fungicide activity increase by increasing hydrophobic chain length.

It is clear that the antimicrobial activities are gradually increased by increasing the hydrophobic chain length. The PQ18 surfactant showed the maximum antimicrobial activities against the tested

bacterial strains. That behavior is depending on the surface activities of these biocides. Increasing the hydrophobic chain length increases the adsorption tendency of the biocide molecules at the various surfaces (water or microorganism's membranes).Hence, the potent action of the molecules is increased due to their high population at the cellular membrane [29,30].

General observation for data in **Table 3** indicates that the Gram- positive bacteria are more resistant to the tested compounds compared with the Gram-negative bacteria. The data provided from the inhibition zone diameter are describing the general behavior of the tested biocides against the different bacterial genera. The results of the antifungal activity obtained from the biological study showed promising features of the tested biocides against the most pathogenic fungal strain (C. albicans).

Table 3: Antimicrobial activity of synthesized surfactants and their CuNPs against pathogenic bacteria, yeast and fungi

Compounds	Bacteria				Yeast	Fungi
	Gram positive		Gram negative			
	Bacillus subtilis	Staphylococcus aureus	Salmonella typhimurium	Escherichia coli	Candida albicans	Aspergillus niger
Control	26	25	28	27	28	26
PQ10	17	20	13	16	25	12
PQ14	23	14	0	10	17	0
PQ18	22	0	0	21	27	0
PQ10-Cu NPs	29	21	21	26	18	16
PQ14-Cu NPs	33	20	15	17	26	14
PQ18-Cu NPs	13	33	15	14	31	12

The bacterial cell membrane is composed of a thick wall containing many layers of peptideglycan and teichoic acids, which are glycerol-ribitol (polyhydric alcohol) through a phosphorus bond surrounded by lipids of lipopolysaccharides and proteins [31, 32]. In Gram positive bacteria **(Figure 6)**, the adsorption is occurred in the lipoteichonic acid layer which is characterized by the charged nature and the ability to interact with the positively charged molecules. While in the Gram-negative bacteria **(Figure 6**), the lipid layer (highly nonpolar layer) is the target of the positively charged biocide molecules. So the mode of action of that type of compounds on different microorganisms can be attributed to the adsorption of amphiphile molecules on the outer cellular membrane of the microorganism due to their amphipathic characteristics. In addition the similarity between the hydrophobic chains and the lipid layers and the building units of the cell membranes and the monosaccharide in these compounds [33]. As a result of that adsorption, the molecules penetrate through the cell membrane; furthermore the positive charges in the cationic molecules neutralize the negative charges on the bacterial cell membranes. Accordingly, the selective permeability which characterizes the outer cellular membrane is completely deactivated [34].

Hence, the vital transportation of essential components, bioreactions and activities of the cell are disturbed, causing death for these microorganisms.

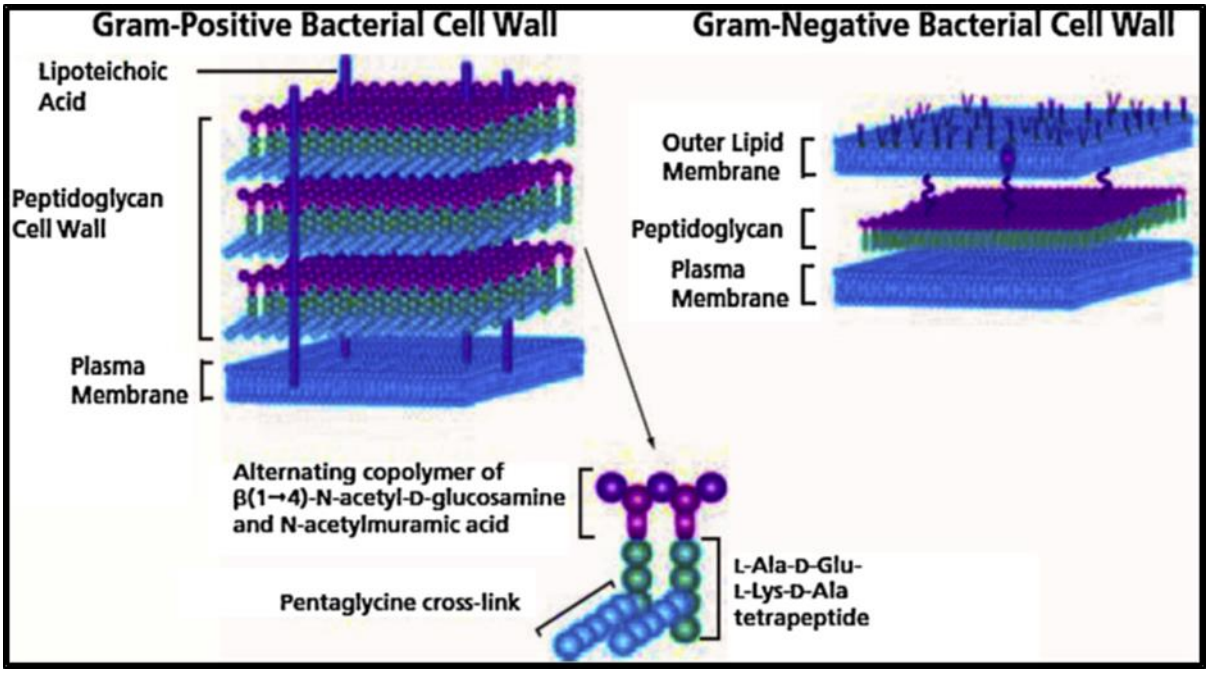


Figure 6: Structure of the bacterial cell walls

By inspection data in **Table 3**, the biological activity of copper nanoparticle stabilized by synthesized cationic Thiol polyurethane surfactants higher than corresponding synthesized cationic Thiol polyurethane surfactants, this can be attributed to copper nanoparticle alone has biological activity, so prepared surfactant capped copper nanoparticles have higher activity, this can be attributed to the higher surface area of prepared nanoparticles and the acquired positive charge of prepared copper nanoparticles in addition positive charge of cationic surfactants, where these positive charge facilitate adsorption at negative cell wall membrane of bacteria. In addition to the bactericidal effect of metal nanoparticles has been attributed to their small size and high surface to volume ratio, which allows them to interact closely with microbial membranes and is not merely due to the release of metal ions in solution. A cell wall is present around the outside of the bacterial cell membrane and it is essential to the survival of bacteria.

4. Conclusion

The main conclusions are as the following:

- The results indicate formation and stabilization of copper nanoparticle using synthesized cationic surfactants.

- By increasing the hydrophobic chain length of the synthesized cationic surfactants, the stability of prepared CuNPs increase.
- The antimicrobial activities of the compounds toward bacteria and fungi were high compared to the drug used.
- The antimicrobial activity depended on the chemical structure of the synthesized surfactants.
- The copper nanoparticles of the stabilized surfactants increase their biological activity.

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