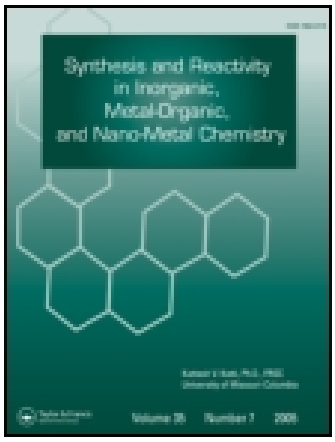

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

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Accepted author version posted online: 30 Oct 2013.Published online: 21 Nov 2013.

To cite this article: Salwa M. I. Morsy & Mohamed M. Ibrahim (2014) Investigation of Cationic Surfactants and Sulfonamides and Their Nanoparticles as Biocides Against Sulfur Reducing Bacteria in the Petroleum Industry, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 44:4, 530-536, DOI: 10.1080/15533174.2013.778877

To link to this article: http://dx.doi.org/10.1080/15533174.2013.778877

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 44:530–536, 2014

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2013.778877

Investigation of Cationic Surfactants and Sulfonamides and Their Nanoparticles as Biocides Against Sulfur Reducing Bacteria in the Petroleum Industry

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A series of cationic ammonium surfactants (1–3) and sulfonamides (4–5) were synthesized and characterized using elemental analysis and FT-IR spectroscopy. The nanostructures of the synthesized surfactants and sulfonamides as silver and zinc nanoparticles (Ag/ZnNPs) were prepared and characterized using transmission electron microscope. The TEM image of AgN-1–3 is a spherical shape with narrow diameter, whereas ZnN-4–6 composites are roughly spherical. The size analysis demonstrated the average diameter of 50–55 nm for the composite. The antimicrobial activity of the synthesized surfactants and sulfonamides as well as their nanostructures were investigated as potential biocides against sulfur reducing bacteria. The values of the inhibition zone diameters are gradually increased by increasing the concentration of the tested biocides and the maximum inhibition diameters for all biocides are obtained at 5 mg/mL. The results also showed that the sulfonamides and their nanocomposites have higher biocidal activities than those of the cationic ammonium surfactants biocides and their nanoparticles.

Keywords biocides, cationic surfactants, petroleum industry, silver and zinc nanoparticles, sulfonamides

INTRODUCTION

Sulfate-reducing bacteria (SRB) in oil environments was rapidly recognized as responsible for the production of H_2S. The formed H_2S is the principal agent in the disastrous effects caused by SRB.[1] It contaminates gas and stored oil, precipitates ferrous sulfide that plugs injection wells, and promotes precipitates ferrous sulfide that plugs injection wells, and promotes corrosion of iron and steel in the absence of oxygen (anaerobic corrosion).[2,3] Another principal mechanism by which SRB are involved in corrosion is their ability to depolarize iron surfaces by consumption of cathodically formed hydrogen.[1] Control of biogenic sulfide production decreases operating costs and can be achieved through the application of biocides.[4] Environmental regulations and development of oil reservoirs in environmentally sensitive areas have spurred the development of easily degradable "green" biocides that are less toxic to higher, no target organisms, such as fish.[5]

Quaternary ammonium salts and their nanoparticles considered efficient inhibitor of SRB[6,7] are also relatively nontoxic and inexpensive and has been successfully used to inhibit sulfide production in oil field settings.[8,9] The efficiency of cationic surfactants is based on their ability to disturb the integral bacterial membrane by a combined hydrophobic and electrostatic adsorption phenomenon at the membrane water interface making disorganization.[10] The cell membrane is predominantly negatively charged as compared with eukaryotic cells.[11]. Hence, the positive charge of the cationic amphiphile facilitates their interaction with the bacterial membrane.

Sulfonamides were the first effective chemotherapeutic agents employed systematically for the prevention and cure of bacterial infections in humans.[12,13] Sulfonamides represent an important class of medicinally important compounds which are extensively used as antibacterial agent. It interferes with *p*-aminobenzoic acid in the biosynthesis of tetrahydrofolic acid, which is a basic growth factor essential for the metabolic process of bacteria.

The objective of this article is to present novel syntheses and characteristics of cationic ammonium surfactants and sulfonamides and their loaded silver and zinc nanoparticle (Ag/ZnNPs), respectively, were revealed and investigated as potential biocides against SRB.

EXPERIMENTAL

Material and Methods

The chemical structures of the synthesized cationic surfactants (**1–3**) and sulfonamides (**4–6**) were performed using (Vario Elementar Analyzer). The IR spectroscopy was also used to

Received 4 January 2013; accepted 19 February 2013.
This work was financially supported by Taif University, Saudi Arabia, Project No.: 1-433-1819.
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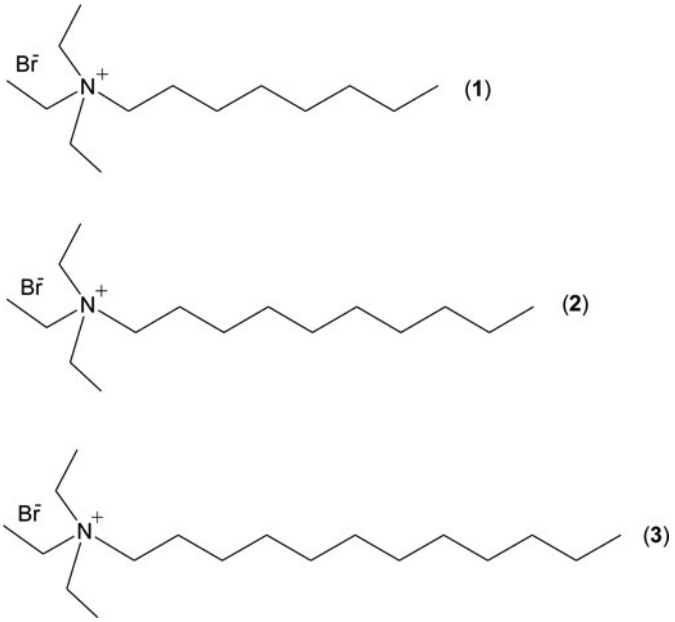
determine the chemical structures of these compounds using Genesis Fourier transformer FT-IR. The size and morphology of silver nanoparticles and the nanostructure of the synthesized quaternary ammonium and sulfonamide biocides with silver and zinc nanostructures were investigated by transmission electron microscope (TEM) using JEM-(Jeol)-2010.

Synthesis

*Synthesis of the quaternary biocides (**1–3**)*

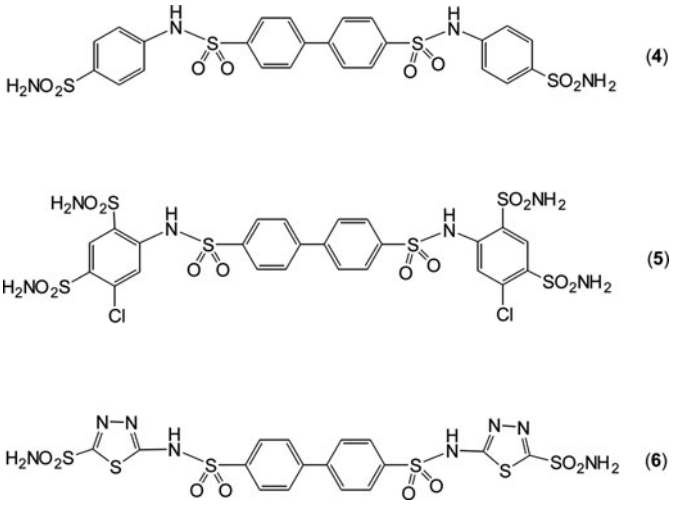
0.1 mol of triethyl amine was refluxed by 0.1 mol of alkyl bromides namely: octyl bromide, decyl bromide, and dodecyl bromide in presence of 100 mL acetone as a solvent for 6 hr.[14] The reaction product (designated as **1–3**) was filtered off and recrystallized twice from acetone, Scheme 1.



SCH. 1. Chemical structures of the synthesized quaternary biocides.

*Synthesis of the sulfonamides (**4–6**)*

A mixture of 0.1 mol of 4,4/-biphenyl-disulfonyl chloride 0.2 mol of 4-aminobenzenesulfonamide, 6-chloro-4-amino benzene-1,3-disulfonamide or 5-amino-1,3,4-thiadiazole-2-sulfonamide, and 0.2 mol of pyridine were refluxed in dry ether (250 mL) for 4 h.[15,16] In case of synthesis of 5-amino-1,3,4-thiadiazole-2-sulfonamide derivative, the Scotten-Baumann conditions were used, and the corresponding amine was dissolved in 15 mL solution 2.5 M NaOH and cooled to –20°C in a salt-ice bath. After the reactions were completed, the solvent was evaporated in vacuum, adjusted to pH 2 with 5 N HCl, and the precipitated bis-sulfonamides were filtered and recrystallized from aqueous ethanol to give biphenyl 1,4-disulfonamide biocides (Scheme 2).



SCH. 2. Chemical structures of the synthesized sulfonamide biocides.

Preparation of the silver nanoparticles

The silver nanoparticles colloidal solution was prepared using the chemical reduction method, which involves reduction of silver nitrate ($AgNO_3$) in distilled water using efficient reducing.[17] In typical experiment, 50 mL of (1 mmol/L) solution of $AgNO_3$ was added to 5 mL of 1% trisodium citrate drop wise under heating and stirring conditions. The reaction was preceded until the color is turned to pale yellow as an evident for the formation of silver nanoparticles.[18]

*Preparation and stabilization of silver nanoparticle by (**1–3**)*

The prepared silver nanoparticles solution (20 mL) was mixed with 5 mL saturated solution of the synthesized quaternary compounds (**1–3**) in deionized water and stirred continuously for 24 h till the yellow color becomes paler. Then the solution was centrifuged at 12000 rpm to obtain the precipitate of quaternary-silver nanoparticles. The precipitate was washed with cold water to remove the unreacted materials. The quaternary-silver nanoparticles solution was used for ultraviolet measurements and TEM image, while the precipitate was used for infrared analysis.[19]

Synthesis of sulfonamide-Zn-nanocomposite

50 mL solution of the different sulfonamides in dimethyl formamide was added to 50 mL suspension of Zn-nanoparticles prepared from the milling of elemental Zn. The concentration of the metal to sulfonamides was 1:3 by weight.[20] The solutions were mixed together and allowed to stir for 24 h at 25°C.

Antimicrobial Studies

The synthesized quaternary ammonium compounds and the sulfonamides and their nanoparticles and nanocomposites were screened for their antimicrobial activity against sulfur reducing bacteria using agar well diffusion method.[21,22]

TABLE 1
The elemental analysis of the synthesized compounds

Compound	M. wt.	Calcd. (Found)					
		C%	H%	N%	Br%	Cl%	S%
1	294.31	57.13 (56.56)	10.96 (10.85)	4.76 (4.71)	27.15 (26.88)	—	—
2	322.37	59.61 (59.01)	11.26 (11.15)	4.34 (4.30)	24.79 (24.54)	—	—
3	350.42	61.70 (61.08)	11.51 (11.39)	4.00 (3.96)	22.80 (22.57)	—	—
4	622.70	46.30 (46.27)	3.53 (3.50)	9.00 (8.96)	—	—	20.57 (20.52)
5	847.72	34.00 (33.77)	23.80 (23.60)	9.91 (9.84)	—	8.36 (8.30)	22.70 (22.54)
6	638.73	30.09 (29.88)	22.10 (21.90)	17.54 (17.42)	—	—	30.12 (29.91)

Growing of microorganisms

The bacterial strains were cultured on nutrient medium, while the fungi strains were cultured on malt medium. For bacteria, the broth media were incubated for 24 h. As for fungus, the broth media were incubated for approximately 48 h, with subsequent filtering of the culture through a thin layer of sterile Sintered Glass G2 to remove mycelia fragments before the solution containing the spores was used for inoculation.

Measurements of resistance and susceptibility

For preparation of discs and inoculation, 1 mL of inocula were added to 50 mL of agar media (40°C) and mixed. The agar was poured into 120 mm Petri dishes and allowed to cool at room temperature. Wells (6 mm in diameter) were cut in the agar plates using proper sterile tubes. Then, holes filled up to the surface of agar with 0.1 mL of the tested biocides dissolved in DMF (1 mg/mL DMF). The plates were left on a leveled surface, incubated for 24 h at 37°C and then the diameter of the inhibition zones were measured.[23] The inhibition zone formed by these compounds against the particular test bacterial strain determined the antibacterial activities of the synthetic compounds. The mean value obtained for three individual replicates was used to calculate the zone of growth inhibition of each sample. Microorganisms The biocidal activity of the synthesized compounds and their nanostructures were tested against Desulfomonas pigra ATCC 29098.

Minimum inhibitory concentration

The antimicrobial activity of the tested biocides against the SRB bacteria was expressed as the minimum inhibitory concentration (MIC) values, defined as the lowest concentration of compounds inhibiting the development of visible growth after 24 h of incubation. The MIC values were determined by dilution method.[22] The compounds tested were dissolved in a mixture of distilled water/alcohol (3/1; v/v) at various concentrations and the 1 mL aliquot of the biocides solutions was added to the 14 mL agar media. The final concentrations of the tested biocides in the medium were 300, 200, 100, 40, 20, 10, and 4 mg/mL.

RESULTS AND DISCUSSION

Structure Confirmation

The microelemental analysis showed that the calculated and the found ratios of the different elements in the compounds are near to each other by the ratio of 99% (see Table 1). That showed the purity of the prepared compounds. Their IR spectral bands (Table 2) showed the presence of the absorption bands at 2950, 2790, and 3040 cm^{-1}, which confirmed the presence of the methyl (CH_3), methylene (CH_2), and positively charged nitrogen groups (N^+). The obtained data showed that the synthesized compounds have identical structures as represented in Schemes 1 and 2.

TABLE 2
FTIR spectral bonds of the synthesized compounds

Compound	CH_3	CH_2	R_4N^+	Aromatic (CH)	SO_2	NH	NH_2
1	2950	2790	3040	—	—	—	—
2	2940	2810	3040	—	—	—	—
3	2954	2800	3040	—	—	—	—
4	—	—	—	3075	1162, 1332	3260	3279, 3380
5	—	—	—	3082	1142, 1315	3248	3277, 3385
6	—	—	—	3058	1187, 1342	3255	3270, 3394

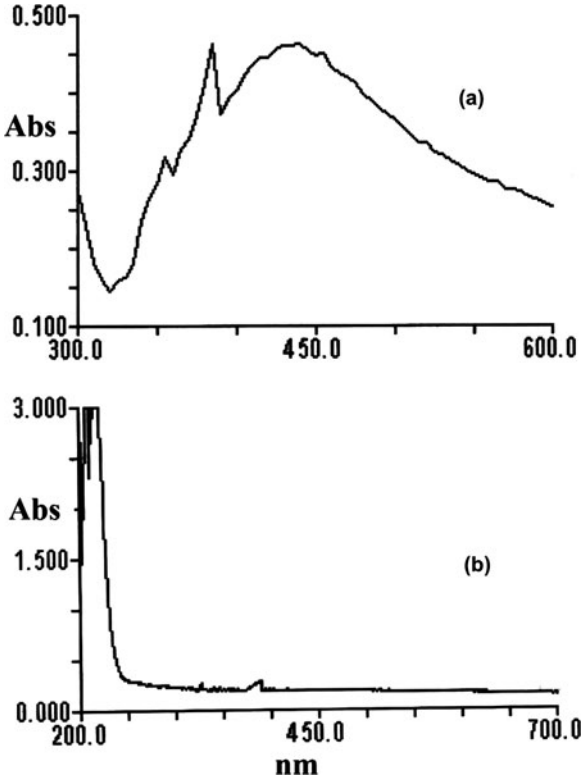


FIG. 1. (a) UV spectra of the silver nanoparticles; (b) UV spectra of silver nanoparticles loaded with the quaternary ammonium biocides.

Ultraviolet Spectroscopy (UV)

It is observed from Figure 1 the presence of a strong absorption peak at approximately wavelength 430 nm and intensity of 0.49 absorbance intensity from the surface Plasmon resonance of nanosized silver particles.[24,25] The good symmetric absorption peak implies that the size distribution of the nanoparticles is narrow.[26] The loading of the quaternary ammonium biocides on the silver nanoparticles solution disappear the peak at 430 nm as shown in Figure 1. That is due to the reduction of the negative charge on the colloidal particles. Metal particles in their aqueous colloidal dispersions are usually acquiring negative charges due to the adsorbed anions around the particles.

Transmission Electron Microscope (TEM)

The size and morphology of silver nanoparticles and the nanostructure of the synthesized quaternary ammonium and sulfonamide biocides with silver and zinc nanostructures were investigated by TEM. The TEM image reduced of the silver nanoparticles (Figure 2) indicates that these silver particles are spherical shape with narrow diameter.[27] The particles size distribution of the quaternary biocides **1** and **2** capped silver nanoparticles (Figures 3 and 4) indicate that the size distribution of silver nanoparticles is narrow sphere. These figures showed the spherical silver nanoparticles with a corona of the quaternary surfactants, which related to the self-assembling of

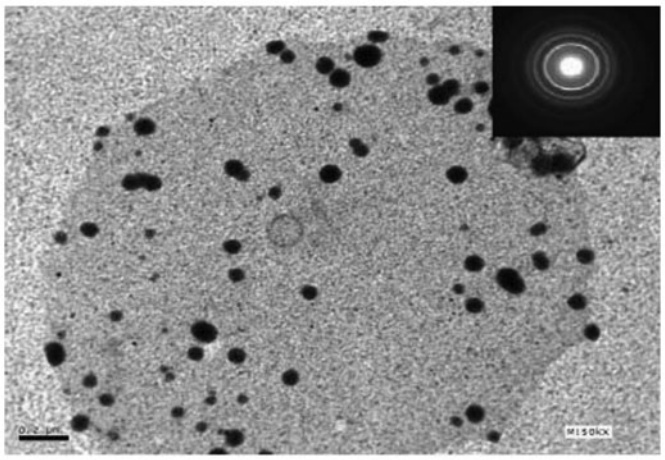


FIG. 2. TEM of the reduced silver nanoparticles.

the surfactant molecules on the silver nanoparticles. The TEM images further revealed the stabilization of silver nanoparticles due to interaction with the quaternary biocide molecules. Figures 5–7 show the TEM micrograph of the Zn-nanoparticle composite, showing that the particles were roughly spherical. The size analysis demonstrated the average diameter of 50–55 nm for the composite.

Antimicrobial Activities

The biocidal activities of the synthesized quaternary ammonium biocides and their silver loaded nanoparticles and the sulfonamides and their zinc nanocomposites in terms of the inhibition zone diameter (in mm) and MIC were determined and the results were listed in Table 3 and 4, respectively.

It is clear that the values of the inhibition zone diameters are gradually increased by increasing the concentration of the tested

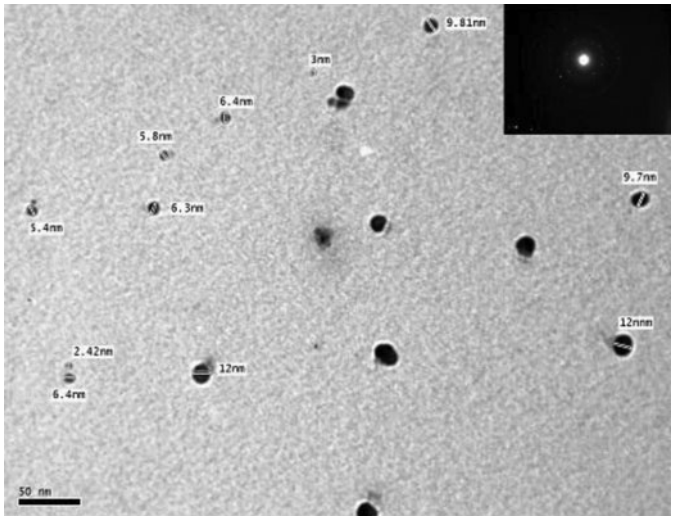


FIG. 3. TEM of the decyl triethyl ammonium bromide capped silver nanoparticles.

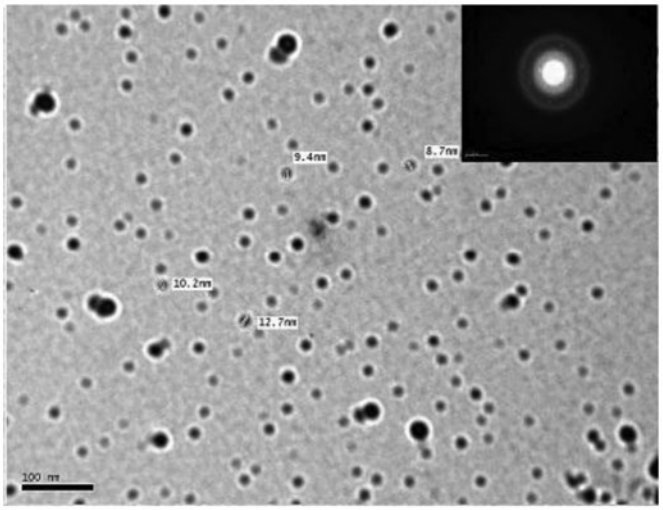


FIG. 4. TEM of the dodecyl triethyl ammonium bromide capped silver nanoparticles.

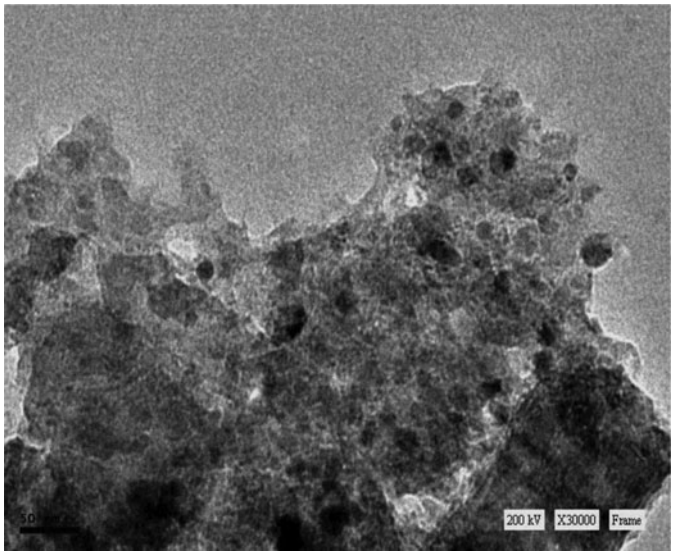


FIG. 6. TEM of biphenyl 1,4-disulfonamide biocides **5**.

biocides and the maximum inhibition diameters for all biocides are obtained at 5 mg/mL. It is also clear that the antimicrobial activities are gradually increased by increasing the alkyl chain length. The dodecyl derivative.[3] showed the maximum antimicrobial activity against the tested bacterial strain (Desulfomonas pigra ATCC 29098). The shorter alkyl chain length derivatives[1–3] showed lower biocidal activity in terms of inhibition zone diameter.[28–31] The biocidal tests were done in dimethyl formamide as a solvent. The DMF has no effect on the growth of the tested bacterial strains as described in recent works. The inhibition zone diameter tests were done for the silver nanoparticles loaded quaternary biocides (AgN-**1–3**) against the SRB bacteria (Desulfomonas pigra ATCC 29098). The obtained results showed the high potency of the nanoparticle-quaternary biocides compared to their quaternary biocides in the molecular from. The inhibition zone diameters were nearly double, which indicates the increasing efficiency of the nanoforms of the biocides in overcoming the fatal effect of the SRB bacteria in the infected area especially in the oilfields. The values of the inhibition zone diameter of the sulfonamides[4–6] were listed in Table 3. It is clear that the inhibition zone diameters range between 14–17 mm at 1 mg/mL and 17–21 mm at 5 mg/mL. that is considerably large values compared to the quaternary ammonium biocides. That showed the high inhibiting effect of the sulfonamide biocides, which can be attributed to the presence of the sulfur atoms in the chemical structures of these biocides[32,33]

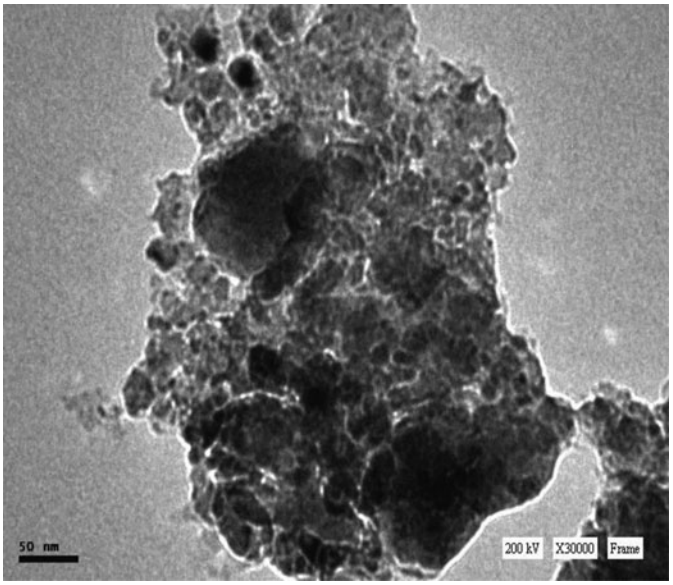


FIG. 5. TEM of biphenyl 1,4-disulfonamide biocides **4**.

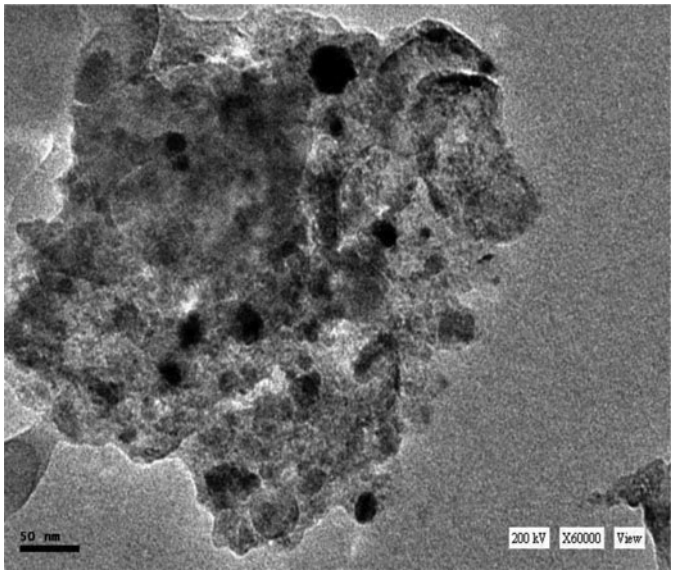


FIG. 7. TEM of biphenyl 1,4-disulfonamide biocides **6**.

TABLE 3
Antimicrobial activities (a,b) in terms of inhibition zone diameter (mm) at different doses (1, 2, 5 mg/mL) of the synthesized quaternary and sulfonamide biocides and their nanostructures against sulfur reducing bacteria (Desulfomonas pigra ATCC 29098)

	Inhibition zone diameter in (mm) at different dose (mg/mL)		
Compound	1 mg/mL	2 mg/mL	5 mg/mL
1	12.3	14	15
2	13.5	15	17
3	14.2	16.3	18
AgN-**1**	22	25	27
AgN-**2**	24	26	30
AgN-**3**	25	29	32
4	14	15.5	17
5	16	17	19
6	17	18.5	21
4-nanocomposite	25	28	31
5-nanocomposite	29	31	35
6-nanocomposite	31	34	39

[a]The data is a mean of five replicates with relative error ∼7%.
[b]The antimicrobial activity expressed as the diameter of the inhibition zone formed in presence of the tested compounds.

ion zone diameter are describing the general behavior of the tested biocides against the different bacterial genera. The biocidal activity of the quaternary ammonium compounds (QAS) in some fields is limited due to the developed microbial resistance against QAS after longer periods of applications, their high acute toxicity and low biodegradability.[30]

The mode of action of the quaternary ammonium biocides in the biocidal action is generally accepted that the cationic biocides can adsorb onto negatively charged cell membranes, which will then lead to decrease in the osmotic stability of the cell and leakage of intracellular constituents.[31–33] However, the exact mechanism of the antimicrobial action is still unknown and several other mechanisms that may contribute to the antimicrobial action have also been suggested, such as the formation of an impermeable coat on the bacterial surface,[32] uptake of low molecular weight biocides that will interact with electronegative substances in the cell and inhibition of bacterial growth through chelation of trace metals.[32] The mechanism for the interaction may be different for gram-positive and gram-negative bacteria.

AgN-**1–3** biocides have high potency against the SRB bacteria (Desulfomonas pigra ATCC 29098). That can be attributed to the presence of the alky chains that increase the surface activity of these compounds. This can be explained by the different cell membrane structure of the two bacterial types.[30] The external layer of the outer membrane of the SRB bacteria is almost entirely composed of lipopolysaccharides and proteins that restrict the entrance of biocides and amphiphilic compounds.[30,34] The perturbation of this outer membrane requires a fine tuning of the hydrophobic-hydrophilic balance (HLB).

It is clear that the values of the inhibition zone diameters are gradually increased by increasing the concentration of the tested biocides and the maximum inhibition diameters for all biocides are obtained at 5 mg/mL. It is also clear that the antimicrobial activities are the maximum antimicrobial activity against the tested bacterial strain (Desulfomonas pigra ATCC 29098). The shorter alkyl chain length derivative[1] showed lower biocidal activity in terms of inhibition zone diameter.[35–37] The biocidal tests were done in dimethyl formamide as a solvent. The DMF has no effect on the growth of the tested bacterial strains as described in recent works.[38]

TABLE 4
Minimum inhibitory concentration values (μM) of the synthesized quaternary and sulfonamide biocides and their nanostructures against sulfur-reducing bacteria (*Desulfomonas pigra* ATCC 29098)

Dose, mg/mL	Minimum inhibitory concentration (μM)
1	>600
2	>600
3	>600
AgN-**1**	200
AgN-**2**	100
AgN-**3**	50
4	300
5	300
6	150
4-nanocomposite	100
5-nanocomposite	50
6-nanocomposite	25

[a]The data is a mean of five replicates with relative error ∼7%.

MIC values for the synthesized quaternary biocides 1–3 are summarized in Table 4. The tested biocides show high activity level against SRB bacteria (Desulfomonas pigra ATCC 29098) with MIC values >600 mg/mL (Table 4). The MIC values for the synthesized quaternary ammonium biocides in the form of the nanoparticles (AgN-**1–3**) are summarized in Table 4. While, in case of the sulfonamides, the MIC values range between 300 and 150 mM. The MIC values of the zinc nanocomposite loaded of the sulfonamides were decreased considerably to reach to 100–25 mM (Table 4).

Comparing the antibacterial activities of the silver and zinc nanostructures showed that the zinc nanocomposites have higher efficiency as biocide against SRB. That can be attributed to the influence of zinc nanostructures. It was reported that the zinc and zinc oxide nanoparticles and also zinc nanocomposites have high toxicity for the different types of bacteria. Here, the results

showed identical trend in the activity increasing against SRB bacteria.

The results of the biocidal activities of the two types of the synthesized biocides showed their high efficiency as biocides in defeating the growth of the sulfur reducing bacteria in oilfields applications.

CONCLUSION

In this study, we have synthesized two types of the biocides that were quaternary ammonium bromide and sulfonamides in their molecular and nanoparticle forms. The molecular forms of the different biocides showed good biocidal activity against SRB bacteria at 2 and 5 mg/mL. The nanoparticles forms of the different biocides were highly potent against the SRB bacteria than their corresponding molecular form.

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