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Synthesis and characterization of sulfur nanoparticles with WSP/surfactants mixtures

Abstract: Sulfur nanoparticles display unique physical and chemical feature because of effects such as the quantum size effect, mini size effect, surface effect, and macro-quantum tunnel effect. Therefore, sulfur nanoparticles would present higher efficacies such as removal of heavy metals, radical-scavenging, antimicrobial activity, antioxidant and antitumor activities. They have been using as a fungicide product in agriculture and medicine; to obtain sulfur fertilizers and cosmetics industries, as well as in obtaining nanocomposite lithium batteries; to form stable carbon chains such as C_3S and C_5S for obtaining hybrid materials with useful properties for gas sensor and catalytic applications. This work presents the results of obtaining sulfur nanoparticles, which can be used in agriculture as a fungicide treatment. Sulfur nanoparticles were obtained by modifying the surface of sulfur by various water-soluble polyelectrolyte (WSP)/surfactant mixtures including NaCMC/CTAB, PDADMAC/SDBS, NaCMC/Triton X-100 (TX-100). The size and the structure of sulfur nanoparticles were determined by methods as LSA, XRD, SEM. It is shown that the nanoparticles have a sulfur monoclinic α-form, and their average size is in the range of 100-300 nm. The received products can be considered as perspective forms of application in agriculture and medicine.

Key words: sulfur nanoparticles, surfactant, aqueous surfactant solution, water-soluble polyelectrolytes adsorption, surface tension.

Introduction

Sulfur is the tenth most common element by mass in the universe and the fifth most common on Earth. Though sometimes found in pure, native form, sulfur on Earth usually occurs as sulfide and sulfate minerals. Chemical and, biologically active element, It displays three allotropic forms: orthorhombic, monoclinic and amorphous. The orthorhombic form is the most stable form of sulfur. it is widely used in many fields, such as the production of sulfuric acid, chemistry fiber, nitrogenous fertilizer, plastics, antimicrobial agents and rubber, pharmaceutical industry, and bioleaching processes, pulp and paper industries, and different other agrochemical industries [1-2]. The sulfur nanoparticles have many practical important applications such as synthesis of nanocomposites for lithium batteries [3-6], fungicides in agriculture [7], synthesis and modification of carbon nanostructures [8], synthesis of sulfur nanowires with carbon to form hybrid materials with useful properties for gas sensor and catalytic applications [9], in road construction, as a bitumen modifier [10], in the agricultural field, sulfur is used as a fungicide against the apple scab disease under colder conditions [11], The smaller of particle size, the larger surface area of sulfur particles, so there will be more efficiency in an application in medicine, cosmetics, agriculture, etc. Therefore, the synthesis of sulfur nanoparticles is currently an important issue.

Different methods were used for nanosize particle synthesis, among those: the microemulsion method is one of the very important methods to control the particle size. Nevertheless, microemulsion itself is a very complicated system, composed of oil, surfactant, co-surfactant and aqueous phases

with the specific compositions. The main disadvantages of the microemulsion method are the difficulties in process scale-up, separation and purification of the particles from the microemulsion, and finally, this method is consumed huge amounts of surfactants. Despite many exciting applications, there are only a few recent kinds of literature available on the synthesis of sulfur nanoparticles by different investigators [12-16] in both aqueous and microemulsion phase by different routes. Deshpande et al. [12] have synthesized sulfur nanoparticles from H_2S gas by using the biodegradable iron chelate catalyst in reverse microemulsion technique. They found a-sulfur or rhombic sulfur of average particle size 10 nm with a particle size range of 5-15 nm. They have also studied the antimicrobial activity of sulfur nanoparticles and shows it is very much effective, especially when the particle size is low. Guo et al. [13] have prepared sulfur nanoparticles from sodium polysulfide by acid catalysis in the reverse microemulsion technique. They found monoclinic or b-sulfur with an average particle size of around 20 nm. Xie et al. [14] have prepared nanosized sulfur particles from sublimed sulfur. They added aqueous cysteine solution dropwise on a saturated alcoholic sulfur solution with constant ultrasonic treatment and cysteine – nano-sulfur sol was obtained. S.Roy Choudhury et al. [15] get 20-50 nm particles of sulfur interaction sodium polysulfide and ammonium polysulfide with formic acid and further stabilization of the sulfur polyethyleneglycol-400. The same authors established the biological activity of the synthesized nanoparticles of sulfur. By the research of Rajib et al. [16], sulfur obtained by conducting the reaction of sodium thiosulfate interaction with various inorganic and organic acids. Subsequently, the same authors synthesized sulfur particles with particle sizes in the range of 30-60 and 200-300 nm, by modifying the sulfur with various surfactants.

However, despite the existence of different ways to get sulfur nanoparticles, they all have drawbacks. Namely: the multi-stage process, the use of various inorganic and organic acids, which requires multiple-treatment, significant harm to the human body when using poisonous gases, such as hydrogen sulfide.

In This study presents the method of obtaining sulfur nanoparticles by mechanical and ultrasonic grinding, Sulfur nanoparticles were obtained by modifying the surface of sulfur by various mixtures water-soluble polyelectrolytes (WSP)/surfactants including NaCMC/CTAB, PDADMAC/SDBS), NaCMC/TX-100, The size, surface tension at the water/air and the structure of sulfur nanoparticles were determined by methods as LSA, DCAT-21-Date physics, XRD, SEM.

Materials and methods

Crystalline sulfur production of LLP "Tengiz Shevroil" (Kazakhstan), cetyltrimethylammonium bromide (CTAB) with a purity of 99 % of company Loba Chemie Pvt. Ltd., (India), Triton X-100 (TX-100) and sodium dodecylbenzene sulfonate (SDBS) with a purity of 99% of company "Unilever Research Laboratory Port Sunlight (England), sodium carboxymethyl cellulose (NaCMC), polydiallyldimethylammonium chloride (PDADMAC) with 99% purity from Tianjin Heowns Biochem. LLC., (China). Were used as materials Bettersize-2000 (China), scanning electron microscope (SEM)-Auriga cross-beam, infrared spectroscopy, Colloid mill company Fritsch Pulverisettel (Germany). Ultra dispersant KQ-600GKDV (China) Surface tensiometer (DCAT-21, Date physics, Germany).

Synthesis of sulfur nanoparticles. Preparation of sulfur nanopowder was carried out in two stages: In the first stage, 10 g of crystalline sulfur was milled in a colloid mill Fritsch Pulverisettel (Germany) for 30 min. Size of the sulfur powder was 10-100 microns. In the second stage, the milled sulfur powders were dispersed into 100 ml of WSP/surfactants mixtures solution (where the concentration of mixtures NaCMC/CTAB and PDADMAC/SDBS was 1mM and the concentration of NaCMC/TX-100 was 0.1 mM) with an ultrasonic disperser KQ-600GKDV (China), Then the crushed sulfur was dried in the device Christ ALPHA 1-1 LD plus (Germany) [17].

The interfacial tension and critical concentration of WSP/surfactant mixtures at the water/air interface measured by the method of Vilgemi, using surface tensiometer (DCAT-21, Date physics, Germany) at room temperature (28 ±0.5 0C).

Characterization of sulfur nanoparticles. Crystal structure of sulfur nanoparticles was characterized by X-ray diffraction (XRD) using Philips (230 v, 65 KVA) X-ray diffractometer with the scanning rate of 0.0020 /s in the 2θ range from 100 to 500. Particle size measurement was carried out by laser size analyzing (LSA) using Bettersize-2000 laser particle size analyzer. The shape of sulfur nanoparticles was observed with a scanning electron microscope (SEM).

Results and discussion

Effect of WSP/surfactant mixtures concentration on the surface tension. The tensiometric plot of

CTAB, SDBS, and TX-100 shows a sharp decrease in surface tension with a slight increase in [CTAB, SDBS and TX-100] up to cac, then it approximately keeps constant giving 'first plateau' until critical saturation concentration csc. A further decrease in surface tension is observed up to cmc, beyond which they further stabilize, giving 'second plateau' due to the formation of free micelles in the solution [18-19]. The plot of CTAB (Figure 1 A-1), SDBS (Figure 2 B-1) and TX-100 (Figure 3 C-1) in pure water shows only one critical concentration (i.e., at cac), while in the presence of NaCMC, PDADMAC three critical concentrations (first at cac, second at csc and third at cmc) are observed. This indicates the influence of NaCMC, PDADMAC in the solution and theirs association with the cationic surfactant CTAB, anionic surfactant SDBS and nonionic surfactant TX-100. csc represents the critical saturation concentration of the surfactant (Figure 1 A-2, Figure 2 B-2, Figure 3 C-2) when all the binding sites on polyelectrolyte are saturated due to adsorption of CTAB, SDBS and TX-100 over polymer backbone. During this association process (at first plateau), the surface tension of the solution is almost constant as the added surfactant get associated with the water-soluble polyelectrolyte molecules in the solution and surfactant free molecules are not available to affect the surface properties of the solution. When all the binding sites on polyelectrolyte molecules are saturated with surfactant molecules, surface tension starts decreasing with increase in CTAB, SDBS and TX-100 concentration further till a certain concentration, termed as critical micelle concentration (cmc) is reached. At cmc, the micellization of polymer bound surfactant occurs resulting in the formation of insoluble WSP/surfactant mixtures. This suggests that the WSP/surfactant mixtures also undergoes a two-stage interaction process where the surfactant binds to the polyelectrolyte due to electrostatic attraction; thereafter, the micellization of polymer-bound surfactant molecules occurs as reported in the literature [20, 21]. As experimental results (Figure 1,2,3) show the minimum surface tension values (γCMC) for NaCMC(0.01%)/TX-100(0.1mM),; PDADMAC (0.01%)/SDBS(1 mM) and NaCMC(0.01%)/CTAB(1 mM) are 40.35, 45.7 and 42.8 Nm/m, respectively.

Effect of the concentration of WSP/ surfactants mixtures on the particle size of sulfur. It is well known that WSP/surfactant mixtures adsorbed on the surface of sulfur microcrystals, reduce the surface tension at the solid/liquid interface. This phenomenon is a good illustration of the Rehbinder effect**.** Theoretically, the WSP/surfactant mixtures adsorbed on the pores of sulfur microcrystals, facilitate their destruction. Firstly the WSP/surfactant mixtures adsorbed in the pores which creates a two-dimensional pressure. Secondly, it contributes to the weakening of intermolecular interactions, to reduce the formation of aggregates, therefore, increase the number of nanoparticles (Fig. 4). The Feature of WSP/surfactant mixtures are the presence of polar (hydrophilic) and non-polar (hydrophobic) groups. Simultaneous adsorption of non-polar groups on the surface of the solid phase and the interaction of polar groups with the hydrophilic medium determines the specific properties of surfactants.

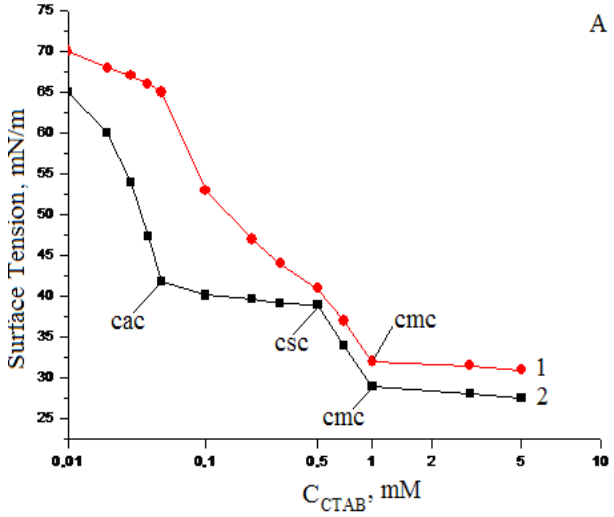


Figure 1 – Variation of surface tension (γ) with CTAB concentration in pure water (1), and 0.01 % NaCMC aqueous medium (2) at 25 ^{0}c

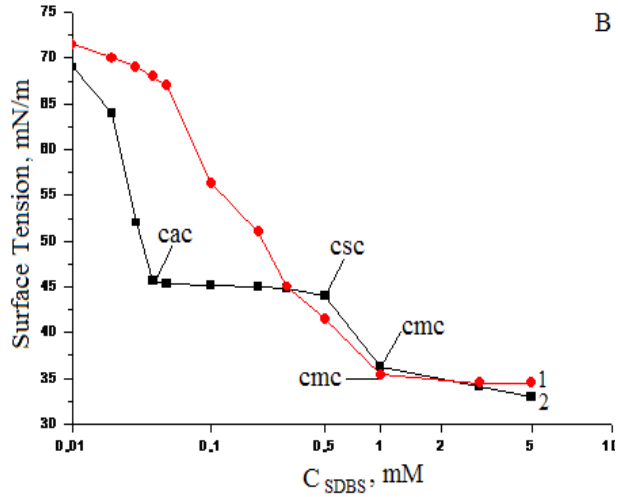


Figure 2 – Variation of surface tension (γ) with SDBS concentration in pure water (1), and 0.01 % PDADMAC aqueous medium (2) at 25 ^{0}c

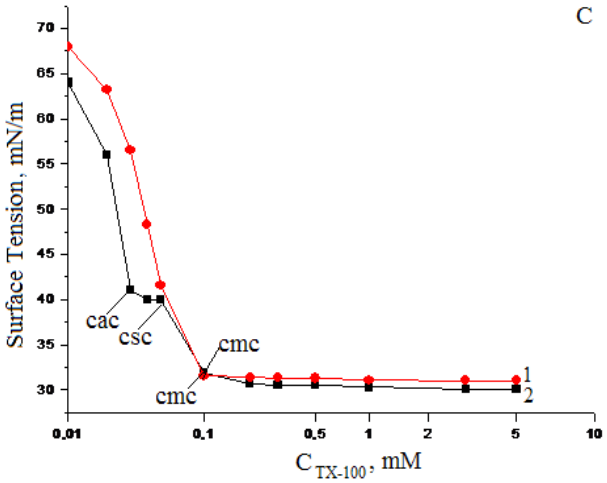


Figure 3 – Variation of surface tension (γ) with TX-100 concentration in pure water (1), and 0.01 % NaCMC aqueous medium (2) at 25 ^{0}c

However, the 300-500 nm of sulfur particles do not form a stable suspension. Apparently, this is a consequence of the predominance of hydrophobic interactions in the highly polar aqueous environment. Therefore, even with stirring sulfur aggregates are not destroyed. Mechanical effects (intense mixing) can lead to an imbalance of the adsorbed particles on the surface of colloidal stabilizers (modifiers). Thus destabilized particles are able to interact with each other at distance of intermolecular forces and may converge by the forces of gravity. Consequently, to obtain a stable suspension of sulfur, you should use the smallest particle size.

The last time in the industry is widely used by water-soluble polyelectrolyte/surfactant mixtures as additives. When we add WSP to a particular ionic surfactant solution, it has been observed that surface tension and contact angle values are reduced. This happens because the presence of WSP decreases the repulsion between the head groups. As the repulsion decrease, the cmc decrease, too. So the addition of WSP can give a more economical way of using the surfactants for decreasing the contact angle, particle size and altering the wetting property. [22-23]. WSP/surfactant composition influence to reduce sulfur particles through adsorption on the crystalline sulfur pores. In the study, 0.01% of the water-soluble polyelectrolyte solution was used. It is proved in the literature [19] that the better adsorb on the substance surface due to polyelectrolytes of this concentration allow reducing the surface tension of the water. In this reason, the use of WSO/ surfactant mixtures reduces sulfur particle size. this work was use mixtures (NaCMC (0.01%) /CTAB, PDADMAC (0.01%)/SDBS, NaCMC(0.01%)/ TX-100) Fig. 5 shows the Effect of the concentration of WSP/surfactant mixtures on the particle size of

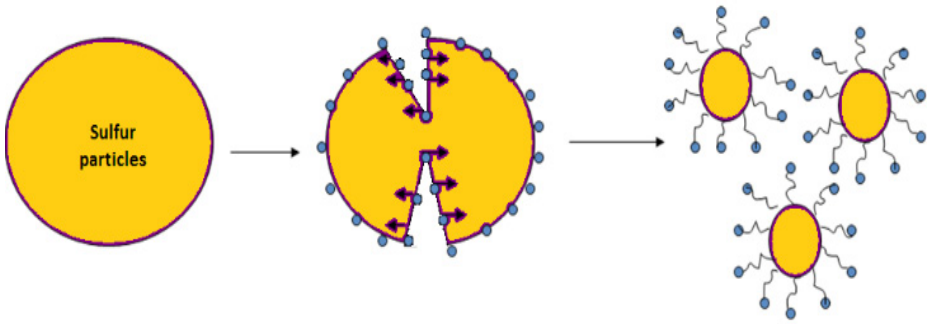
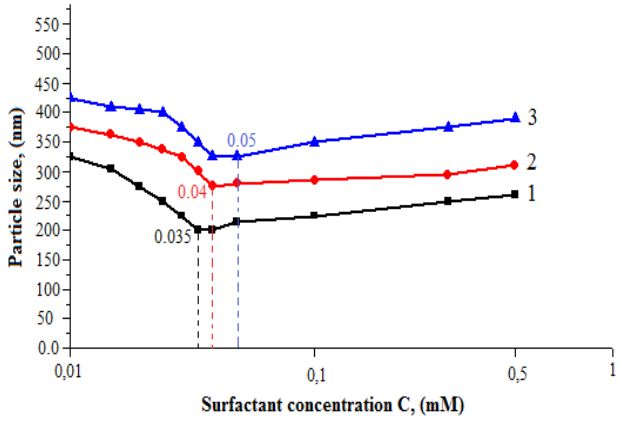


Figure 4 – Adsorption of WSP/surfactant mixtures solution on the pores of the microcrystals of sulfur

sulfur. Experimental results showed that with the increase of surfactant concentration, decrease sulfur particle size. At the CMC, there are minimum value of sulfur particle size at 0.035, 0.04, 0.05 mM, concentration of NaCMC/TX-100, PDADMAC/SDBS and NaCMC/CTAB respectively, sulfur particle sizes are in the range of 200-350 nm.

Figure 6 shows comparisons of particle size distribution among three of WSP/surfactant mixtures used in the study. NaCMC/TX-100, PDADMAC/ SDBS, and NaCMC/CTAB have a different size distribution, TX-100 having little sharp distribution than the other two WSP/surfactant mixtures but the change is not very significant.



1- NaCMC(0.01%)/TX-100;2-PDADMAC(0.01%)/SDBS,
3- NaCMC (0.01%)/ CTAB

Figure 5 – Effect of concentration
of WSP/ surfactant mixtures on the sulfur particle size

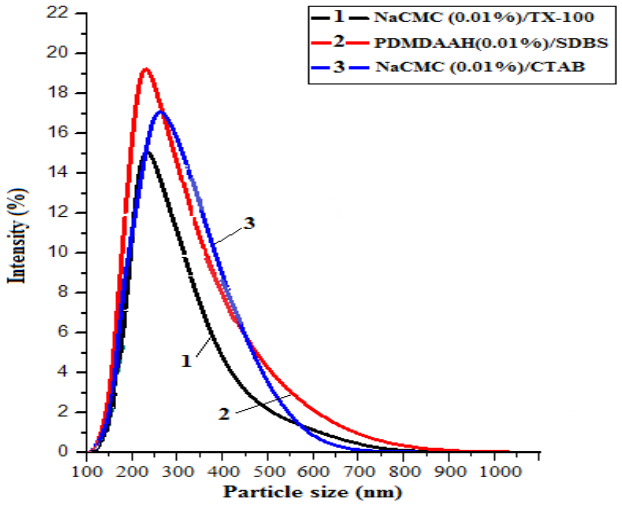


Figure 6 – Differential curves
of sulfur particles in of mixtures WSP / surfactants

XRD and SEM analysis of the Sulfur particles. Determination of particle diameter (D) was done by the XRD analysis using Debye-Scherrer formula,

$$D = \frac{\kappa\lambda}{\beta cos\theta}$$

Where D crystallite size, *k* – Scherrer constant usually taken as 0.89, λ – wavelength of the X-ray radiation (0.154056 nm for Cu Kα), and α is the full width at the half maximum of the diffraction peak measured at 2θ the position and intensities of the diffraction peaks of all samples were compared with standard α-sulfur particle diffraction pattern (24).

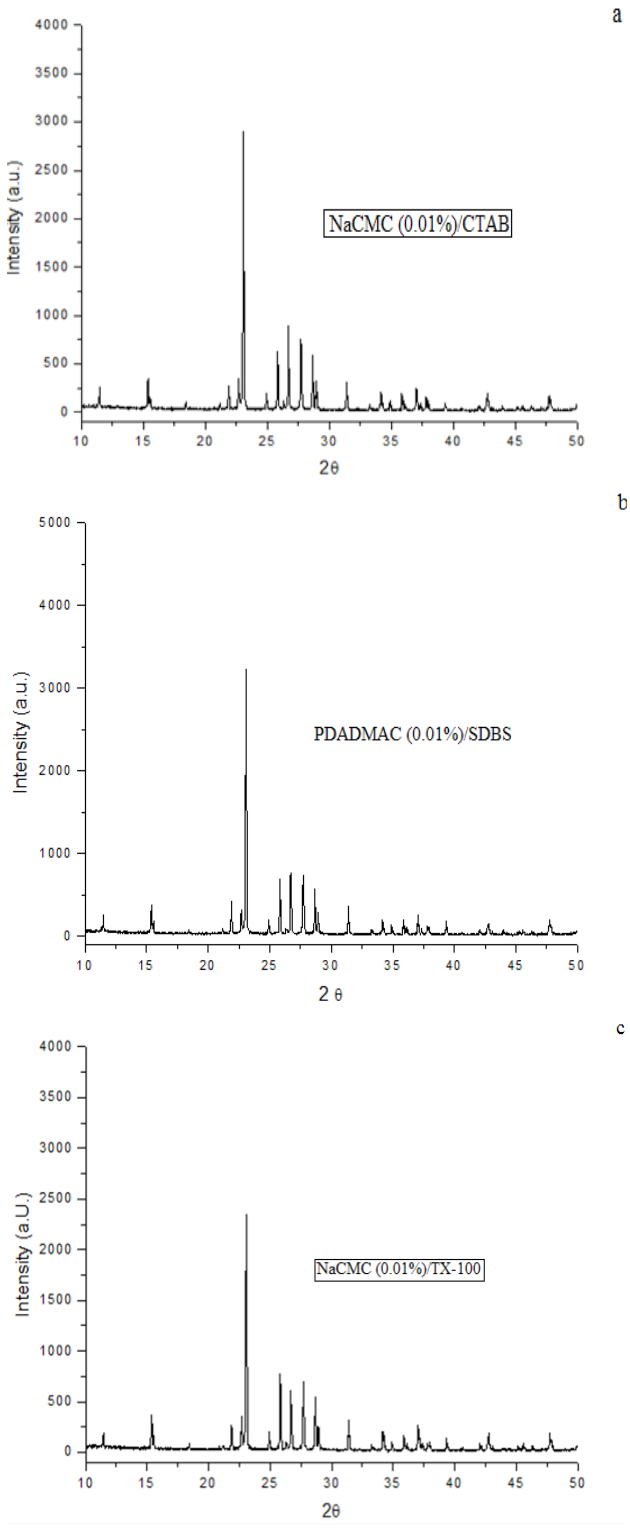
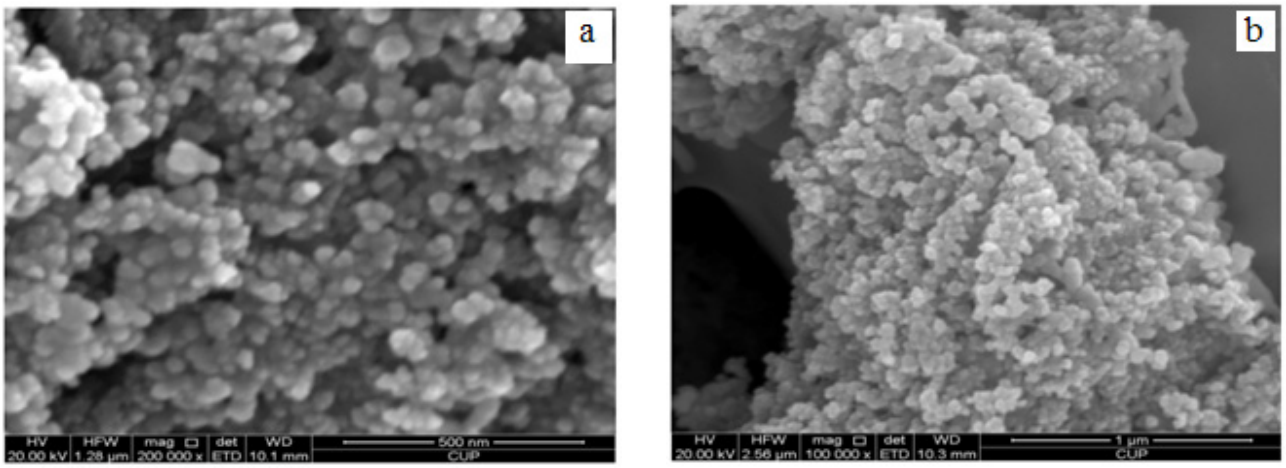


Figure 7 – XRD pattern of sulfur nanoparticles:
surfactant and mixture WSP/surfactant media

The XRD analysis of sulfur nanoparticles synthesized in WSP/surfactant mixtures are shown in Figure 5, which are a,b and c, the XRD pattern of sulfur particles indifferent in the presence of WSP/surfactant mixtures media, respectively. The positions and intensities of the diffraction peaks have the same means with the literature values for orthorhombic or a-phase sulfur on S_8 structure (74-1465 from JCPDS PDF Number). The XRD samples are prepared by successive washing by fresh water, so it was got an only pure sulfur peak.

Analysis by scanning electron microscope (SEM). Figs. 8 A-B show the SEM images of sulfur particles synthesize by mixtures of WSP/Surfactant (NaCMC/CTAB, PDADMAC/SDBS) (A, B images) have had uni-α-form, too. From the figure, it is clear that the sulfur particles are the almost spherical shape and uniform size.



a– NaCMC/CTAB, b-PDMDAAX/SDBS

Figure 8 – SEM micrographs of sulfur nanoparticles

Conclusions

Thus, the experimental results showed the minimum surface tension values (γCMC) for NaCMC(0.01%)/TX-100(0.1mM),; PDADMAC (0.01%)/SDBS(1 mM) and NaCMC(0.01%)/CTAB(1 mM) are 40.35, 45.7 and 42.8 Nm/m, respectively. The use of mixtures NaCMC/CTAB, PDADMAC/SDBS and NaCMC/TX-100 as modifiers lead to a lot reduction in the size of sulfur particles were obtained. There is the minimum value of the size of sulfur particle at concentration of 0.035, 0.04 and 0.05 mM of NaCMC/TX-100, PDADMAC/SDBS and NaCMC/CTAB with sulfur particle sizes in the range of 200-350 nm. The size, crystal structure and morphology of sulfur nanoparticles were determined by methods of laser size analyzing (LSA), X-ray diffraction (XRD) and scanning electron microscope (SEM). It was found that the nanoparticles had a sulfur monoclinic α-form structures, and their average size was in the range of 100-300 nm.

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