Nanoparticles of Sulfur as Fungicidal Products for Agriculture

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Abstract

Sulfur is a nonmetallic element necessary for life. Sulfur nanopartieles 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. So sulfur nanoparticles would present higher efficacies such as removal of heavy metals, radical-scavenging, antimicrobial activity, antioxidant and antitumor activities. It is used as a fungicide product in agriculture, also used in medicine, to obtain sulfur fertilizers and cosmetics industries, as well as in obtaining nanocomposite lithium batteries. In synthesis of sulfur nanowires with carbon to from hybrid materials with useful properties for gas sensor and catalytic applications.

This work presents the results of obtaining the sulfur nanoparticles, which can be used in agriculture as a fungicide treatment. Sulfur nanoparticles were obtained by modifying the surface of sulfur by various surfactants including cetyltriammoniumbromide (CTABr), Sulfanol, Sodium Ligninsulfonate (CMN), Sodium salt of polynaphthalene sulphonic acid (NNO), water soluble polymer sodium carboxymethylcellulose (NaCMC), mineral mixtures and their compositions. The size and the structure of sulfur nanoparticles were determined by methods as LSA, XRD, SEM. Been studied the value of adsorption at the interface of solid/gas. It is shown that the nanoparticles have a sulfur monoclinic β-form, and their average size is in the range 500-1000 nm. The received products can be considered as perspective forms of application in agriculture.

Introduction

Element Sulfur is naturally, a pale yellow, hydrophobic solid insoluble in water, odorless and brittle, 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 and modification of carbon Nanostructures [3], fungicides in agriculture [4], synthesis of nanocomposites for lithium batteries [5-7], in synthesis of sulfur nanowires with carbon to from hybrid materials with useful properties for gas sensor and catalytic applications [8], in agricultural field, sulfur is used as a fungicide against the apple scab disease under colder conditions [9], in conventional culture of grapes, strawberry, many vegetables, and several other crops. Sulfur is one of the oldest pesticides used in agriculture and it has a good efficiency against a wide range of powdery mildew diseases as well as black spot.

In response to an increasing demand for nanoparticles of sulfur, a natural question arises: why it is better to use nanoparticles of sulfur? From the course of colloid chemistry. It is well known that the size and dispersity of the particles have a direct impact on their properties. The smaller the particle size, the larger the surface area of sulfur particles,

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so there will be more efficiency in application in medicine, cosmetics, etc. Therefore, the synthesis of sulfur nanoparticles is currently an important issue.

Different methods were used for nanosize particle synthesis; among those, microemulsion method is one of the very important methods to control the particle size. But microemulsion itself is a very complicated system, composing 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 literatures available on synthesis of sulfur nanoparticles by different investigators [10-14] in both aqueous and microemulsion phase by different routes. Deshpande et al. [10] have synthesized sulfur nanoparticles from H_2S gas by using 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. [11] have prepared sulfur nanoparticles from sodium polysulfide by acid catalysis in reverse microemulsion technique. They found monoclinic or b-sulfur with an average particle size of around 20 nm. Xie et al. [12] have prepared nanosized sulfur particles from sublimed sulfur. They added aqueous cystine solution drop wise on a saturated alcoholic sulfur solution with constant ultrasonic treatment and cystine-nano-sulfur sol was obtained. S.Roy Choudhury et al. [13] 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. Rajib et al. [14] work, 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.

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

In the present article we consider method of obtaining sulfur nanoparticles by mechanical and ultrasonic grinding, followed by modification of the surface of obtained sulfur by surfactants (CTABr, Sulfanol, CMN, NNO), a water-soluble polymer (NaCMC), mineral mixtures and their

NaCMC/Aerosil sulfur. Then shredded sulfur was dried in the device Christ ALPHA 1-1 LD plus.

Interfacial tension and the critical concentration of surfactant at the water/air compositions. Synthesized nanoparticles of sulfur can be used as a fungicidal agent in agriculture.

Experimental Procedures

Materials

Crystalline sulfur production LLP "Tengiz Shevroil" (Kazakhstan), cetyltrimethylammonium bromide (CTABr) with a purity of 99% of the company Loba Chemie Pvt. Ltd., (India), sulfanol (Alkilbenzolsulfanat sodium) with a purity of 99% of the company "Unilever Research Laboratory Port Sunlight, Birkenhead, Cheshire, England". Sodium Ligninsulfonate (CMN) from fuCheng Chemical plants (China). Sodium salt of polynaphthalene sulphonic acid (NNO) and sodium carboxylmethyl cellulose (NaCMC) with 99% purity from Tianjin Heowns Biochem. LLC., (China). Aerosil (SiO_2) with 95% purity from Tianjin Heowns Biochem. LLC., (China). Colloid mill company Fritsch Pulverisettel (Germany). Ultra dispersant KQ-600GKDV (China) Surface tensiometer (DCAT-21, Date physics, Germany).

Particle Synthesis

Nanopowder sulfur was carried out in two stages. In the first stage a mixture of 9.8 g of crystalline sulfur, 0.1 g NaCMC and 0.1 g Aerosil milled in a colloid mill Fritsch Pulverisettel (Germany) for 30 min. The amount of powdered sulfur was 3-7 microns.

In the second stage with an ultra disperser KQ-600GKDV (China), was dispersed 100 ml of the surfactant solution (where the concentration of CTABr and sulfonol is 1 mM, the concentration of CMN and NNO is 3 mM) containing 10 g of modi-

fied composition of border were measured by the method of Vilgemi, Fig. 1. using Surface tensiometer (DCAT-21, Date physics, Germany) at room temperature (28 ± 0,50 C).
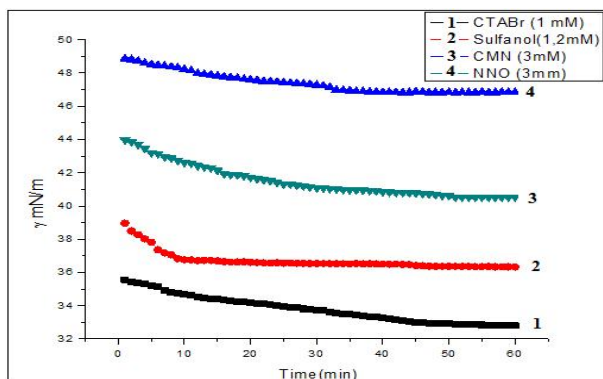

Fig. 1. The influence of the critical micelle concentration of surfactant on the surface tension.

Particle Characterization

The structure sulfur particles was characterized by X-ray diffraction (XRD) using Philips (230 v, 65 KVA) X-ray diffractometer with scanning rate of 0.0020/s in the 2θ range from 100 to 500. Particle size measurement was carried - out bay laser size analyzing (LSA) using Bettersize 2000 analyzer, with the help of cumulates model and intensity distribution. The size and shape of particles were observed under a scanning electron microscope (SEM). And BET surface area measurements.

Results and Discussion

Effect of the Concentration of Surface-Active Substances on the Particle Size of Sulfu

From the literature [15] it is known that nanoparticles of dispersed systems have high surface energy. However, the interaction of the particles by Coulomb forces and the forces of the van der Waals equation causes a reduction in surface energy and the formation of friable aggregates. In addition, because of the capillary pressure of the liquid, there takes place increasing of interaction between the particles of the dispersed phase, which, in turn, leads to compaction of units. In this case, the force of attraction between the particles sized 10 mu.m, in tens time exceeds force of gravity. Formed aggregates are not dissolved due to the repulsive forces.

It is well known that surfactants adsorbed on the surface of the microcrystals of sulfur, reduce the surface tension at the solid/liquid interface. This phenomenon is a good illustration of Rehbinder effect (the phenomenon of reducing the strength of solids by adsorption of surfactants on solid surfaces). Theoretically, the surfactants adsorbed on the pores of the microcrystals of sulfur, facilitate their destruction. First, the surfactant adsorbed in the pores creates a two-dimensional pressure. Second, it contributes to the weakening of intermolecular interactions, to reduce the formation of aggregates and, therefore, increase the number of nanoparticles. Feature of surfactants is 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 the polar groups with the hydrophilic medium determines the specific properties of surfactants.

Isotherms of water solutions of sulfonol, CTABr, CMN and NNO are presented in Fig. 2. It can be seen that the shape of the curves correspond to the classical form of the isotherms. Even at low concentrations of sulfonol and CTABr there is a significant decrease in the values of surface tension (72.5 Nm/m to 30.7-35.0 Nm/m).
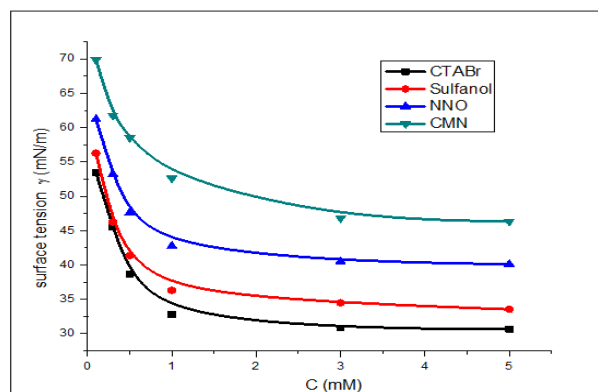

Fig. 2. Effect of surfactant concentration on the surface tension.

Since getting the stable dispersed system largely depends on the size of the dispersed phase, it is appropriate to study the effect of concentration of surfactants on the particle size of sulfur (Fig. 3). The experimental results showed that with the increase of the surfactant concentration there is an increase the size of the sulfur particles. At the critical micelle concentration, there is a minimum value of particle size. Respectively, at 1 mM concentration of sulfonol and CTABr, sulfur particle sizes are in the range 1300-1500 nm, 1700-2000 nm sulfur particles are observed at 3 mM concentrations of CMN and NNO in Fig. 4.
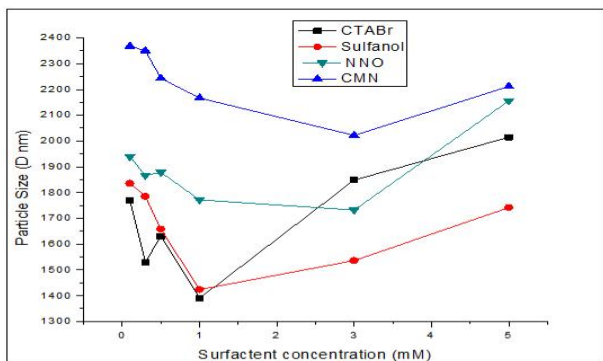
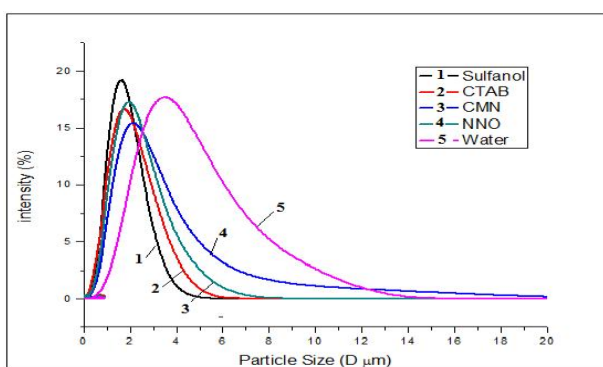Fig. 3. Effect of surfactant concentration on the particle size of sulfur.

Fig. 4. Differential curves of sulfur particles in CMC.

However, the 1300-1500 nm sulfur particles do not form a stable suspension. Apparently, this is a consequence of 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 a 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. To do this, in order to optimize the process, were used composition of water-soluble polymer NaCMC/surfactant at the concentration of surface-active substances, equal to their CMC.

Sodium carboxymethyl cellulose is not a surfactant at the water/air medium, but like any other polymer, it has adsorbent properties on the surface of solids. Figure 5 shows that the composition of surfactant/NaCMC significantly reduce the size of the particles of sulfur. Fig. 6 shows 1100-1400 nm sulfur particles are obtained when modifying it with the composition of sulfur sulphonol/NaCMC at a

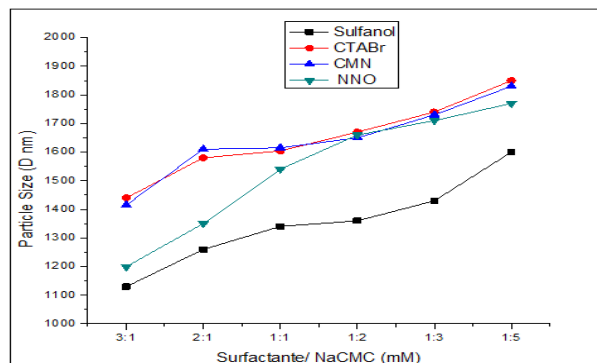ratio of 3:1, and with the compositions NNO and CMN/NaCMC at a ratio of 1:1 in.

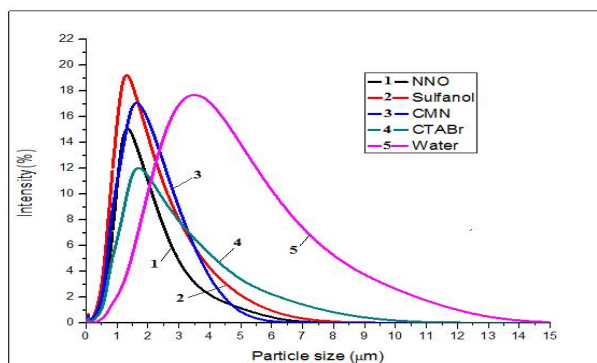Fig. 5. Effect of surfactant composition / polyelectrolyte (NaCMC) on the particle size of sulfur.

Fig. 6. Differential curves of particle size of sulfur-modified compositions surfactant/polyelectrolyte (NaCMC) with optimal (3:1) ratio of the components.

When using the composition of CTABr/NaCMC 3:1, there was an increase of sizes of the particles of sulfur. Increasing the concentration of polyelectrolyte leads to increased formation of a complex of oppositely charged CTABr and NaCMC. Hydrophobic interaction of macromolecules of formed polyelectrolyte complex with particles of sulfur increases the force of gravity, therefore, it enhances sedimentation of weighted dispersed particles.

Effect of Surfactants, Polyelectrolytes and Mixtures of Mineral Compositions on the Particle Size of Sulfur

Drying, previously obtained hydrophilic sulfur particles modified with composition of surfactant/NaCMC, due to evaporation of water, in the system enhances the action of capillary forces. This facilitates the formation of dense aggregates of sulfur. In practice, to prevent adhesion of the particles

of sulfur, we use mineral mixtures such as diatamit, aerosil, kaolin. These substances do not adversely affect on the growth and fertility of the plant, so as the stabilizer of sulfur suspension, we selected aerosil.

Figure 7 shows the results of studies of the effect of Aerosil (d = 30-40 nm) on the particle size of sulfur. It can be seen that with the increase of percentage of Aerosil, sulfur particle sizes increases. The smallest size of the sulfur particles are observed at a concentration of 1% Aerosil, the particle size of sulfur 500-1000 nm Fig. 8. At the same concentration of the stabilizer was obtained stable suspension of sulfur. This result suggests the possibility of use.
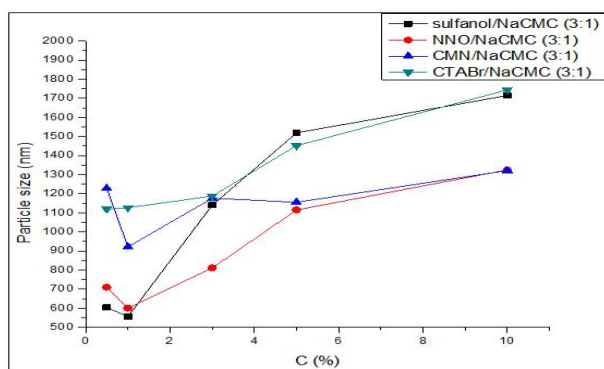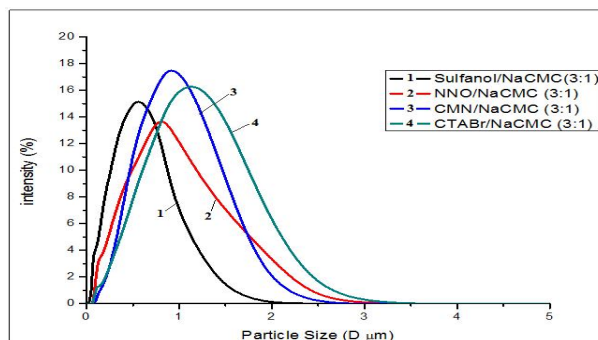

Fig. 8. Differential curves of sulfur particles in the presence of 1% Aerosil.

XRD and SEM Analysis of the Sulfur Particles

The XRD analysis of sulfur nanoparticles synthesized in aqueous surfactant solution is shown in Fig. 9 the position and intensities of the diffraction peaks of all samples were compared with standard β-sulfur particle diffraction pattern.

The determination of the mean particle diameter (D) was done by the XRD analysis using Debye-Scherrer formula, $D = \frac{k\,\lambda}{\beta cos\theta}$, where D is the crystallite size, k the Scherrer constant usually taken as 0.89, λ the wavelength of the X-ray radiation (0.154056 nm for Cu Kα), and β is the full width at half maximum of the diffraction peak measured at 2θ.

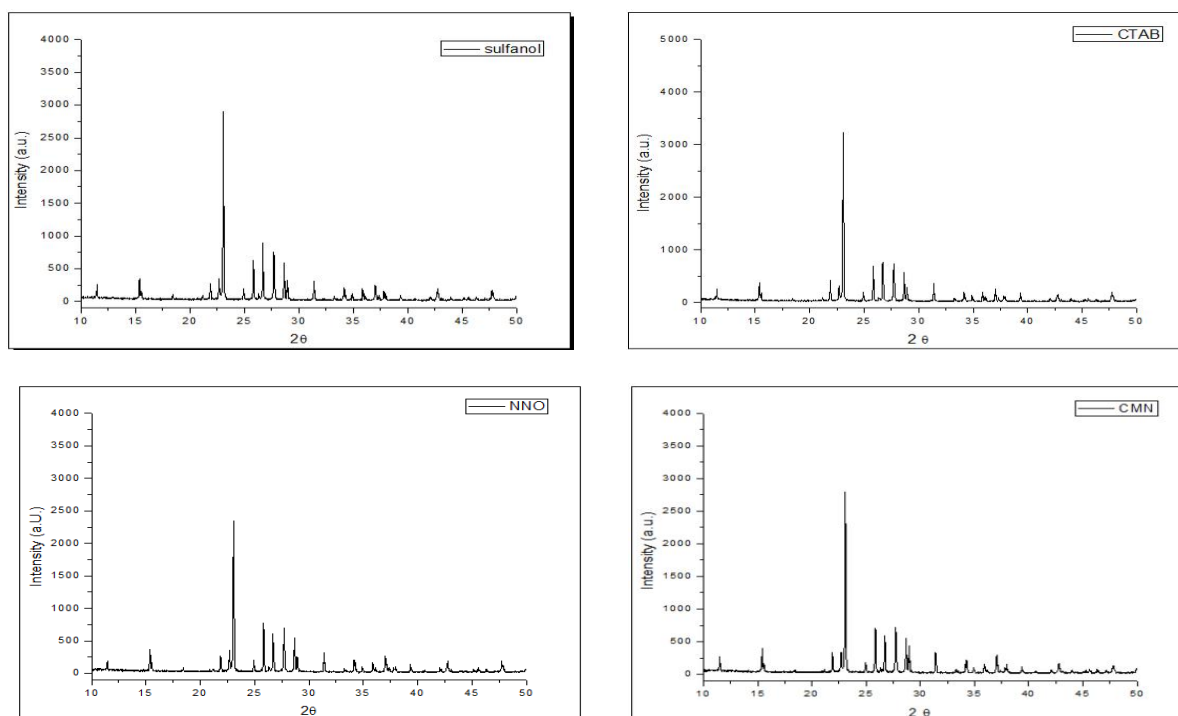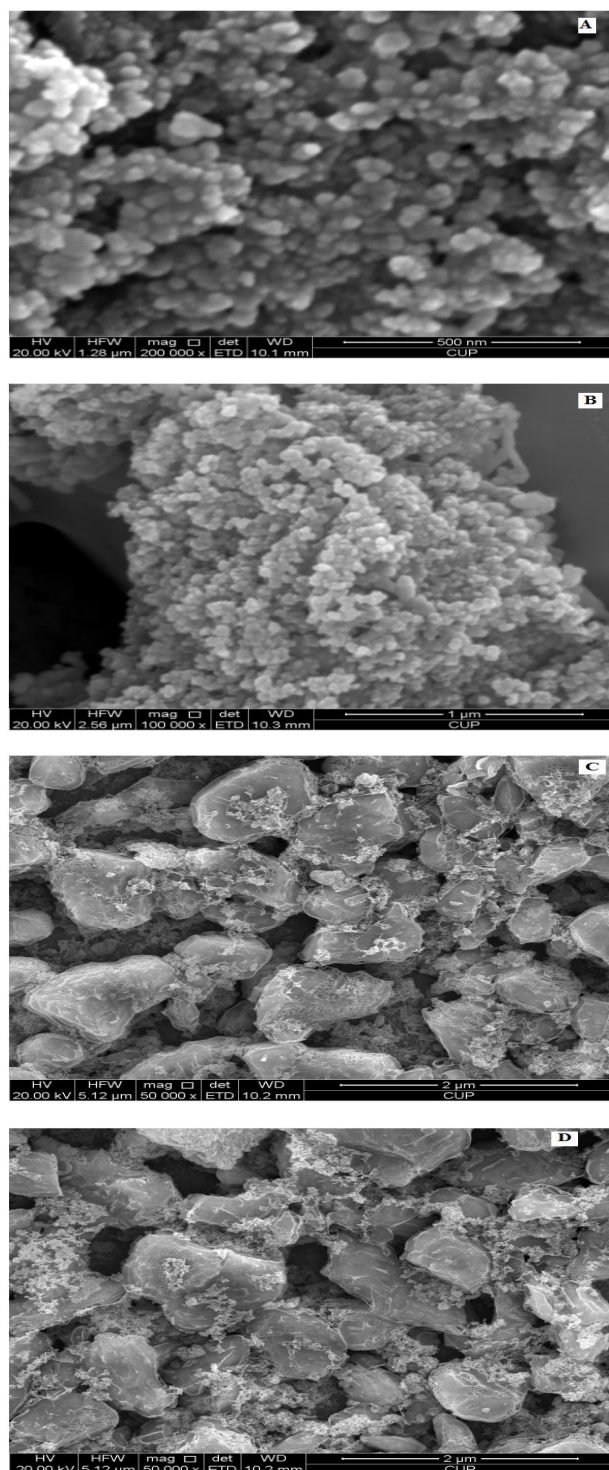Fig. 7. Effect of Aerosil on modified surfactant composition / NaCMC sulfur particles.

Fig. 9. XRD pattern of sulfur nanoparticles: in different surfactant media.

Analysis by Scanning Electron Microscope (SEM)

Figures 10A-D show the SEM images of sulfur particle synthesize by surfactants CTABr, Sulfanol, CMN and NNO.

A – CTABr, B – Sulfanol, C - CMN, D – NNO

Fig. 10. SEM micrographs of sulfur nanoparticles.

Conclusions

On the basis of these experiments, it was found that the modification of the surface of the sulfur by surfactants reduces the size of the particles of sulfur. In particular, in the presence of CTABr and sulfonol at the concentration 1 mM, the particle sizes of sulfur are in the range 1300-1500 nm, the 1700-2000 nm sized sulfur particles are obtained in the presence of CMN and NNO at the concentration 3 mM.

The use of polyelectrolyte complexes surfactant/NaCMC as modifiers-leads to a lot reduction in the size of the particles of sulfur: 1100-1400 nm sulfur particles are obtained at a ratio of 3:1, when modifying of sulfur, with the composition sulphonol/NaCMC and at a ratio of 1:1 with compositions NNO and CMN/NaCMC.

Adding 1% of the mineral Aerosil in the suspension of sulfur, at the same time reduces the amount of sulfur particles and stabilizes the system.

The obtained results allow the synthesis of fungicidal preparation, used in agriculture – sulfur nanoparticles modified with surfactants and compositions of surfactant/NaCMC.

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