Cauliflower-like tin sulphide nanoparticles: an amazing material for adsorption of methylene blue dye

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The removal of MB dye from an aqueous solution onto cauliflower-like SnS nanoparticles was investigated. Adsorption parameters including contact time, solution temperature, amount of adsorbent, pH solution and the concentration of substrate were evaluated. The obtained data revealed that SnS nanoparticles are capable of adsorbing organic dyes during several seconds. The cauliflower-like morphology of the nanoparticles, confirmed by scanning electron microscopy, was an important factor for the rapid adsorption of MB dye on nanoparticles. It was found that each particle has been made of several discs with a thickness of 25 nm. This structural property plays an important role in the adsorption. The nanoparticles were reused 18 times without any significant decrease in their adsorption capability.

1. Introduction: The main sources of a variety of environmental pollutions are effluents which have been discharged from industrial plants. One of the major resources that lead to environmental pollutions is dye-containing wastewaters discharged from factories such as in the cosmetic, textiles, paper and plastic industries [1]. During the dyeing process about 15% of the total productions of dyes become residue as dye effluent [2]. These dye molecules are regarded as common water pollutants and their very small amount in water is considerably visible [3].

There are currently more than 100 000 different dyes that are being applied in industries. Most of them have been synthesised artificially with complicated structures [4]. Moreover, these dyes destroy the ecosystem in water by adsorbing sunshine and restraining photosynthesis [5]. Degradation of organic dyes is usually difficult because they have complex structures and high molecular weights. Hence, a variety of techniques have been reported for their removal including oxidation [6], the chemical coagulation [7], membrane separation [8] and adsorption [9, 10]. In sewage treatment, among the many methods, the adsorption technique is considered a superior technology compared with other methods. The adsorption method has some advantages in terms of simplicity, effectiveness, cost, insensitivity to toxic substances and stability at high pH. A most suitable adsorbent material should have the ability of effective and rapid adsorption. Moreover, it should have an excellent reusability capacity and the ability of working in wide working pH ranges aganist the pollutants. Different materials such as diatomite [11], mesoporous silicas [12, 13], metalorganic frameworks [14, 15] and activated carbon (AC) [16], magnetic cellulose beads [17], clays and oil shales [18], covalent triazine framework [19], pillared clays [20] and mesoporous carbon [21] and magnetic zinc ferrite-reduced graphene oxide composite [22] have been applied as adsorbents.

In this Letter we report the synthesis of SnS nanoparticles and its excellent capability for the adsorption of organic dye MB in aqueous solution. Moreover, different parameters such as pH solution, temperature, substrate and the amount of catalyst are examined to find the optimised conditions. These nanoparticles showed excellent adsorption during just some seconds. To the best of our knowledge, this is the first report of SnS nanoparticles as an efficient adsorbent for the removal of organic dyes.

2. Experimental: All reagents and solvents were commercially available and purchased from Aldrich and used as received without further purification.

2.1. Synthesis of SnS nanoparticles: SnS nanoparticles were synthesised through a modified method [23]. First, 30 ml of ethylene glycol was added to two beakers containing 0.226 g of $SnCl2.\ 9H_2O$ and 0.75 g thiourea. Then the mixtures were stirred for half an hour to form a uniform solution. Next, the solution of thiourea was added to the $SnCl_2$ containing solution. The final solution was transformed to a glassy autoclave and kept at 180°C for 24 hours. After this time the obtained precipitate was washed with double-distilled water and acetone. Then the produced nanoparticles were dried at 60°C.

X-ray diffraction (XRD) analysis was performed using Bruker D and Advance X-ray powder diffractometer with graphite monochromatised CuKa1 radiation (k¼1.5406 Å) and the beta filter was used. EDAX analysis was carried out by NEW XL30 144-2.5. UV-vis measurement was carried out by a Varian model Cary 1E UV-visible spectrophotometer.

3. Results and discussion: The X-ray powder diffraction (XRD) pattern of the SnS nanoparticles is shown in Fig. 1*a*. The most intense peaks are (110), (120), (021), (101) and (111), (040), (140) planes which matches well with the NBS Card 39-354. The mean crystallite size diameter (D) of the SnS nanoparticles was found to be <50 nm using the Scherrer equation. Moreover, EDAX analysis confirmed that the produced nanoparticles are only composed of tin and sulphur atoms, indicating that the produced nanoparticles are pure SnS nanoparticles (Fig. 1*b*).

To investigate the morphology of the produced nanoparticles, scanning electron microscopy (SEM) images were obtained (see Fig. 2). The images show that the nanoparticles have a cauliflower-like morphology. The average diameter of the SnS nanoparticles

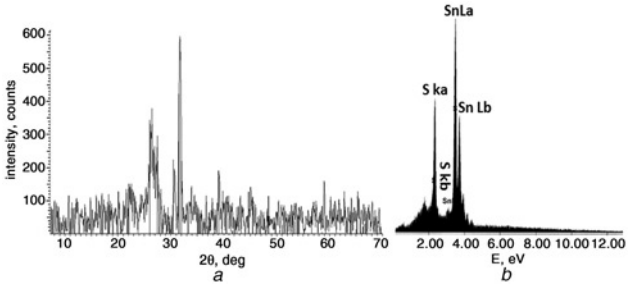

Figure 1 *XRD pattern (Fig. 1a) and EDAX analysis of SnS nanoparticles (Fig. 1b)*

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is <50 nm. As observed, these nanoparticles have several discs aggregated with each other with a thickness of 25–30 nm, which are a good site for adsorption of organic dyes.

4. Adsorption efficiency: A study of adsorption was carried out for the removal of MB dye solution onto the synthesised SnS nanoparticles. Adsorption parameters including contact time, solution temperature, amount of adsorbent, pH solution and the concentration of substrate were evaluated. The absorbance was recorded at a wavelength of 664 for MB and the removal percentage of MB was evaluated by the UV-vis spectrophotometer at continuous time interval times (20 s).

Routinely, to obtain the optimised time for adsorption removal, 30 ml of MB solution with a concentration of 20 ppm was provided. Then, 0.02 g of adsorbent (SnS NPs) was added to the solution and exposed to ultrasound irradiations. The results are shown in Fig. 3*a*. As it is observed, a maximum adsorption (89.7%) is obtained immediately at the first 20 s. Then the removal remains constant. It seems that after this period of time the surfaces of the nanoparticles are completely covered by MB dye and the adsorption of the dye does not occur anymore.

In another experiment the effect of the amounts of adsorbents was investigated in optimum time (Fig. 3*b*). To do this, 30 ml of MB dye solution (20 ppm) was provided and mixed with different amounts of adsorbent (SnS NPs). The adsorbent was dispersed ultrasonically. It can be determined that by increasing the amount of adsorbent up to 0.02 g the adsorption removal is increased, but then by adding the adsorbent into the solution the adsorption is decreased. Hence, the optimum amount of adsorbent to reach maximum adsorption is 0.02 g.

To evaluate the effect of temperature on the adsorption efficiency of the nanoparticles, a wide range of temperatures was set. Fig. 4*a* shows the results of experiments run at 20°C to 60°C. The amount of used catalyst is 0.02 g (optimum amount) and the concentration of MB dye is 20 ppm. By raising the temperature from 20°C to 60°C the adsorption is increased from 87.9% to 93%. As shown, there is no significant efficiency (only 5%) in adsorption by raising the temperature from 20°C to 60°C.

To find the effect of pH on the adsorption removal of MB dye on SnS nanoparticles an experiment was carried out in acidic, basic and neutral solutions ranging from 2 to 10 under ultrasound irradiation (Fig. 4*b*). The Figure shows that by increasing the pH value from acidic to the neutral and basic pH, the adsorption of MB on the adsorbent (SnS NPs) is increased. At higher pH values the adsorption of MB dye is more increased than the acidic and neutral pH. Since the MB is a cationic dye, it is well adsorbed onto the adsorbent in higher solution.

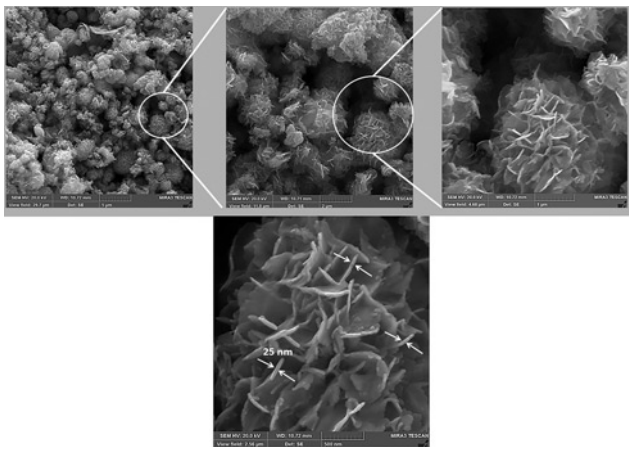

Figure 2 *SEM images of cauliflower-like SnS nanoparticles*

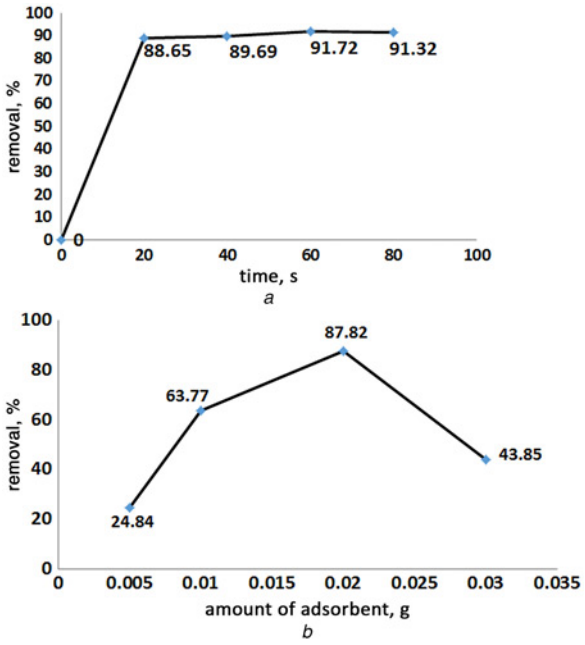

Figure 3 *Effect of time (Fig. 3a) and the amount of adsorbent on the percentage removal of MB dye under ultrasound irradiation (Fig. 3b)*

Finally, the adsorption capability of SnS NPs was investigated in different concentrations of MB. In this part different concentrations of MB solution (10, 20, 30 and 40 ppm) were provided and each separately mixed with 0.02 g of adsorbent. The mixture was sonicated for 20 s. After this period, the absorbance was measured by the spectrophotometer and the adsorption removal was calculated (Fig. 5*a*). As seen, in the solution of 10, 20 and 30 ppm of MB dye the adsorption removal is 88.37, 87.82 and 85.71, respectively. It is seen that the synthesised cauliflower-like nanoparticles have a capability of the adsorption of MB dye in a wide range of concentrations. However, in higher concentrations (40 ppm) and in the contact time of 20 s the adsorption removal of MB is low (15.93%). However, with increasing the contact time of MB and the nanoparticles from 20 to 210 s, the percentage of removal

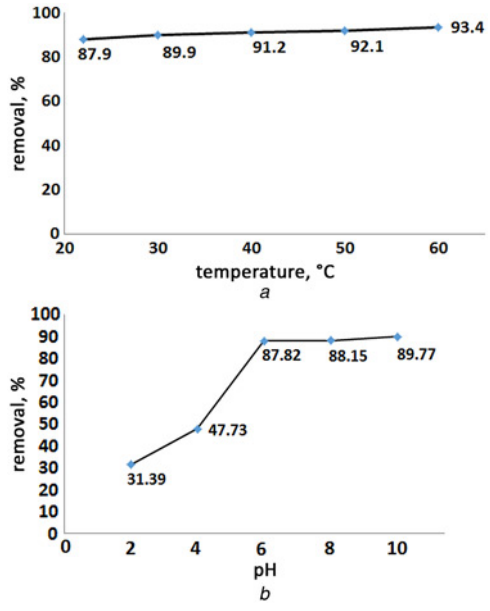

Figure 4 *Effect of temperature (Fig. 4a) and pH (Fig. 4b) on the removal of MB dye*

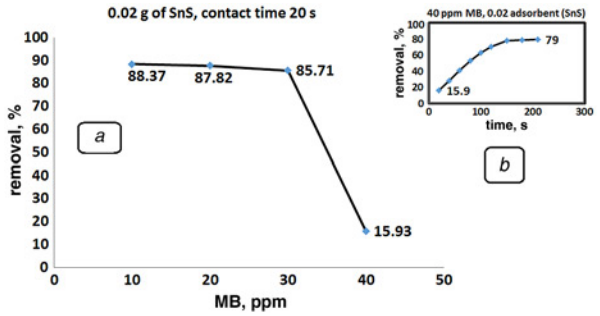

Figure 5 *Adsorption capability of the SnS nanoparticles in different concentrations of MB dye (Fig. 5a) and effect of contact time (Fig. 5b)*

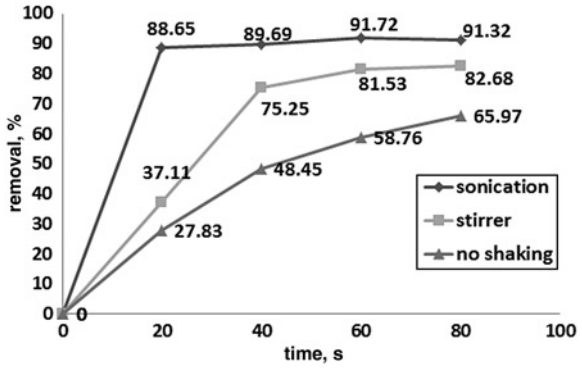

Figure 6 *Effect of ultrasound irradiation, stirring and motionlessness on the adsorption of MB dye on SnS NPs*

reaches 79% (Fig. 5*b*). The results indicate that the synthesised nanoparticles have the capability of adsorbing MB in higher concentrations, which can probably be attributed to the cauliflower-like morphology of the nanoparticles having several disks aggregated with each other with thickness of 25–30 nm, which are a good site for the adsorption of organic dyes.

Moreover, BET measurement was performed, that showed a slightly high specific surface area of 28.005 m^2 g^{-1} with an average pore diameter of 37.195 nm.

Fig. 6 shows the effect of sonication and stirring on the removal of MB in the presence of SnS nanoparticles. The experiment was carried out in a motionless state without using a stirrer. As observed, under ultrasound irradiation the best result is obtained. During the first 20 s about 90% of MB is removed by adsorption on the nanoparticles. It is seen that in the motionless state the adsorption is 65% after 80 s. Hence, by applying ultrasound irradiating the maximum adsorption is obtained during 20 s, but maximum adsorption is obtained during 60–80 s by stirring.

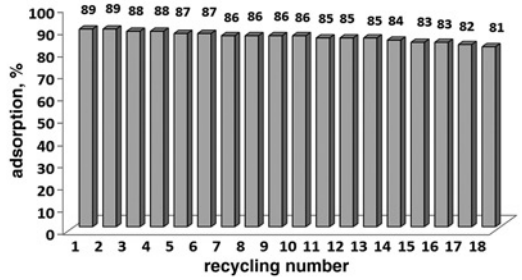

Figure 7 *Reusing of cauliflower-like nanoparticles in adsorption of MB dye*

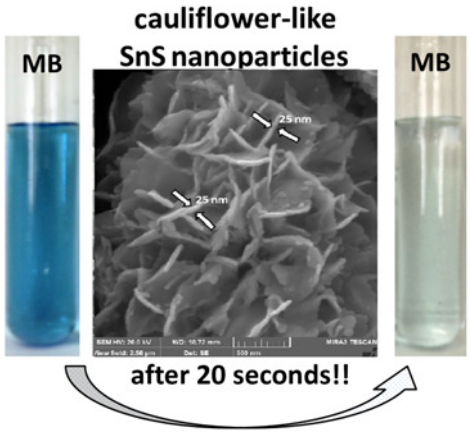

Figure 8 *Graphical process of MB adsorption by cauliflower-like SnS nanoparticles*

Table 1 Comparision of current work with some reported works

Adsorbent	Capacity	Time	Ref.
diatomite	34 mg/g	350 min	[11]
banana peel	0.1808mg/g	50 min	[24]
orange peel	0.0647 mg/g	50 min	[24]
CFT	1 mmol/g	55 min	[19]
SnS NPs	24.34 mg/g	20 s	current work

4.1. Desorption/adsorption test and recycling of the adsorbent: The desorption/adsorption test was carried out to investigate the capability of the synthesised nanoparticles for further use. After adsorption of the MB onto the adsorbent, they were centrifuged and separated from the solution and sonicated for 5 min in acetone. In this process the adsorbed MB dye on the nanoparticles was desorbed from the surface of the nanoparticles. Then the nanoparticles were applied again in the desorption process. As the graph shows, the used nanoparticles were capable to be used 18 times without significant decrease in the adsorption process (Fig. 7).

Fig. 8 represents the photograph for removal of methylene blue adsorbed by the cauliflower-like SnS nanoparticles. As observed, the solution of 20 ppm MB becomes colourless during 20 s. This capability relates to the morphology of the nanoparticles which provides a high surface area for adsorption.

To show the higher adsorption capacity of the synthesised cauliflower-like SnS NPs, the current work is compared with some reported works (Table 1). As seen, the SnS NPs have high adsorption capacity in comparison with banana peel and orange peel. Moreover, the capacity of diatomite is 34 mg/g but in 350 min. As shown, the SnS NPs have a capacity of 24.34 mg/g during 20 s which is comparible with other works.

5. Conclusion: In summary, cauliflower-like SnS nanoparticles were synthesised by a hydrothermal method. An excellent application of these nanoparticles was evaluated in the removal of organic MB dye from the aqueous solution. These nanoparticles showed a maximum removal in normal conditions without any pH adjustment, or temperature setting. Moreover, the synthesised nanoparticles could be easily separated by centrifugation during the experiments. The adsorption of other organic dyes and existent harmful materials in ecosystems is of much interest and further study of the application in these fields is in progress.

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