Green synthesis of Sulphur Nanoparticles assisted by a herbal surfactant in aqueous solutions

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A novel and green method to synthesise sulphur nanoparticles (SNPs) through precipitation reaction of aqueous sodium thiosulphate catalysed by oxalic acid using a herbal surfactant in aqueous solutions is reported. The herbal surfactant, saponin, was extracted from a native plant called *Acanthe Phylum Bracteatum* grown in Urmia West Azerbaijan, Iran. The SNPs were characterised by dynamic light scattering, scanning electron microscopy, transmission EM, atomic force microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction spectroscopy and Fourier transform infrared spectroscopy. On the basis of the particle characterisation data, the mean size of SNPs was recorded about 40 nm. The monodispersed SNPs owe their size to micelle formation of saponin around the sulphur particles.

1. Introduction: Sulphur occurs naturally as cyclic octatomic molecules with the molecular formula of S_8 which is the best-known among over 30 other sulphur allotropes [1]. Elemental sulphur has numerous applications in construction industry [2] and pharmaceutics [3]. It is used as a component of fertilisers such as calcium sulphate which is the most common fertiliser in agriculture used to improve the nutritious quality of nitrogen and phosphorous fertilisers [4]. Being the main focus of this Letter, nanoscale sulphur has significant application in many areas of modern technology in carbon nanotube modification [5, 6], neutron capturer in cancer therapy [7], antimicrobial and pharmacokinetic purposes [8] and in high-performance lithium–sulphur batteries [9]. Recently, sulphur nanoparticles (SNPs) have been applied to synthesise a nanoporous material for water desalination purposes [10].

In nanoscience, there are three ways to obtain nanoparticles: namely, liquid-phase, gas-phase and vapour-phase methods. The liquid-phase method of synthesis itself includes several other subsequent techniques such as coprecipitation, microemulsion, sol–gel, hydrothermal/solvothermal, microwave, template and biomimetic synthesis. As a well-known method of liquid-phase synthesis, microemulsion shows promising results to achieve nanoparticles through which the particle size is controlled more considerably. It is a system in which two thermodynamically stable and immiscible liquids containing nanosize domains are dispersed such as one or both in the other and are then stabilised by surface active molecules interfacial film [11]. Depending on the continuous and dispersed phases, there are two classes of microemulsion as water-in-oil (w/o) and oil-in-water methods. With regard to all the advantages of microemulsion technique, however, there are some disadvantages and difficulties with the application of this method. The presence of oil, surfactant, co-surfactant and water makes microemulsion a complicated mixture of phases. Moreover, the purification process and difficulties with separation of the synthesised particles, scale up and considerable surfactant consumption are among the main drawbacks of this method [12].

Even though the applications and the need for SNPs in different areas of science are growing increasingly, few procedures have been suggested to obtain them so far. Using the reverse microemulsion in a study, monoclinic SNPs were synthesised by w/o microemulsion technique [13–15]. In 2008, w/o microemulsion was applied to synthesise SNPs from hazardous hydrogen sulphide gas [16]. A few papers have focused on the synthesis of SNPs in aqueous solutions [17, 18]. Recently, a green method has been introduced using a native plant extract limited to Southwestern and Eastern Asia [19]. In 1950, it was proved that large number of SNPs can be synthesised using an economical reactant and following that a method was introduced to synthesise and obtain monodispersed SNPs using inexpensive reactants [20]. In this method, the monodispersed sulphur SNPs were formed through the reaction of sodium thiosulphate ($Na_2S_2O_3$ $5H_2O$) catalysed by hydrochloric acid (HCl). The fundamental concepts in nucleation process of all types of colloidal dispersion using condensation methods were explained thereafter [21]. Following the promises of sustainable chemistry, we introduce a novel, simple, cost-effective, environmentally friendly, and more importantly a green method to synthesise SNPs using a herbal surfactant available almost everywhere in the world. The current synthesis owes its green characteristic to the presence of saponin which is an extract from a plant called *Acanthe Phylum Bracteatum*.

The procedure that was employed to synthesise green SNPs in this Letter has some advantages comparing with those introduced previously. In addition to the easy process of synthesis in the aqueous solutions, the oxalic acid ($H_2C_2O_4$ $2H_2O$) used to catalyse the reaction is a weaker acid (pK_a 1.25 and 4.14) which is used as a food additive. Moreover, the use of green surfactant extracted from a plant will sure help the SNPs and the process meet the standards of green chemistry. In a recent work, *A. Phylum Bracteatum* and the saponin extract from that were used in the synthesis of silver nanoparticles [22]. Saponins are glycosides with distinct foaming characteristics which are present in many plants [23]. Even though saponins are regarded as plant-derived surfactants, there are reports of their presence in marine organisms as well [23, 24]. The widespread distribution of saponins in numerous plans all over the world will probably make these surfactants the potential reactants to be used in the synthesis of nanoparticles throughout the world.

2. Experimental results

2.1. Chemicals: All the chemicals were analytical grade. Aqueous $Na_2S_2O_3$ $5H_2O$, $H_2C_2O_4$ $2H_2O$ and ethanol (C_2H_5OH) were purchased from Merck. Saponin was extracted from *A. Phylum Bracteatum* bought from a local herbal market. All the solutions were prepared in double distilled water.

2.2. Extraction of saponin from plant matrix: The saponin in *A. Phylum Bracteatum* was extracted according to the procedure reported in the literature [25]. First, the stem of the plant was grated in order to obtain a fine powder. Later, 5 g of the powder

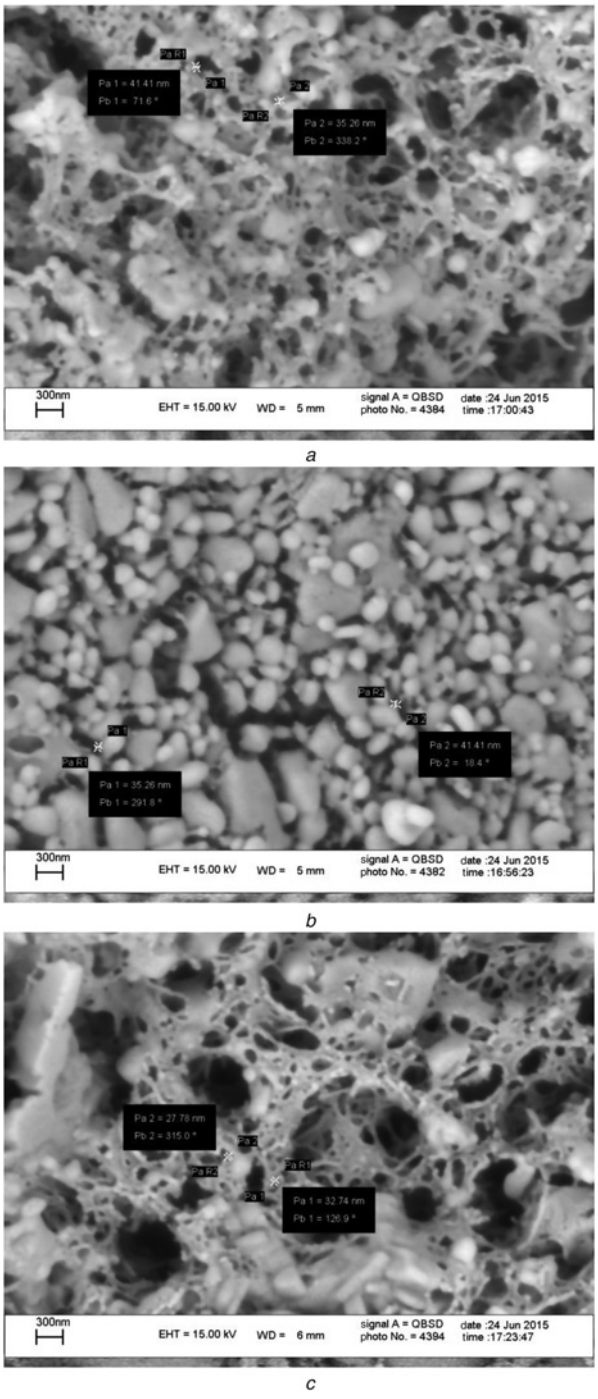

Fig. 1 *SEM micrographs of SNPs using*
a 1CMC of saponin
b 2CMC of saponin
c 3CMC of saponin

was added to C_2H_5OH (100 ml, 95%). After that, the mixture was sonicated for 15 min at room temperature and stirred at 600 rpm for 1 h. Next, the organic solution phase containing saponin extraction was filtered using filter papers (Whatman No. 2). Finally, the solution was evaporated under vacuum condition at the pressure of 40 mbar at 50°C, so that a fine yellow powder was obtained. It should be mentioned that saponins are thermally stable at the temperatures up to 100°C at which no degradation occurs [26].

2.3. Green synthesis of SNPs: Within the first step and referring to the Critical Micelle Concentration (CMC) value of the extracted saponin (0.53 g/l) [27], 1.06 g/l (equal to two times the CMC value of saponin) was added to 100 ml $Na_2S_2O_3$ $5H_2O$ (5 mM) and stirred at 500 rpm carefully. After that, 100 ml $H_2C_2O_4$ $2H_2O$ (30 Mm) was added to the solution. The solution was left for 30–40 min to reach an equilibrium. It should be mentioned that the temperatures of all the three solutions was kept at 25°C. The reaction between $S_2O_3^{2-}$ and $H_2C_2O_4$ $2H_2O$ is as follows:

$$Na_2S_2O_3 + C_2H_2O_4 \rightarrow Na_2C_2O_4 + SO_2 + S\downarrow + H_2 \quad (1)$$

Finally, the solution was sonicated for 2 min and evaporated under vacuum conditions at 40 mbar and the temperature of 70°C. The resulting precipitation (SNPs) was photographed by scanning electron microscopy (SEM), transmission EM (TEM) and atomic force microscopy (AFM) and characterised using dynamic light scattering (DLS), X-ray diffraction spectroscopy (XRD), energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FT-IR). On the basis of the micrographs and the data provided by the analytical and characterisation techniques, the average particle size of 40 nm was reached.

3. Instrumentation: The characterisation of SNPs was carried out by FT-IR (THERMO NICOLET 730 infrared spectroscope made in USA), DLS (MALVERN Zetasizer Nano S ZEN 1600), XRD (AGINAKO GNR MPD 3000) and EDX analysis (Phoenix). The micrographs of SNPs were provided by AFM (FemtoScan made in Russia) SEM (Zeiss LEO 1430VP) and TEM (PHILIPS CM30 300 kV). The solutions were sonicated using EUROSONIC 4D Euronnda made by Montecchio Precalcino, Italy. The evaporation of the mixtures was carried out by BÜCHI Rotavapor® R-200/205 made in Switzerland.

4. Results and discussion

4.1. Effect of herbal surfactant on particle size: In aqueous solutions, saponin decreases surface tension of water at 25°C which is the temperature at which saponin micelles can form. As it was mentioned earlier, the CMC of saponin is 0.53 g/l at 25°C [27]. The presence of saponin in the solution, its ability to form micelles at this temperature and CMC value make it possible to achieve truly fine and monodispersed SNPs. To reach an optimised CMC value of saponin, and as a result much finer and more homogenous SNPs, three concentrations equal to 1CMC (0.53 g/l), 2CMC (1.06 g/l) and 3CMC (1.59 g/l) of saponin were studied precisely. Figs. 1*a–c* show the SEM micrographs of SNPs synthesised by three CMC values as mentioned above. Fig. 1*a* shows the SEM image of resulting particles using 1CMC (0.53 g/l) of saponin. Although the size of particles is somehow acceptable, fewer particles can be seen which means the surfactant concentration is not adequate to capture and surround as many particles. The SEM micrograph of SNPs with 2CMC of saponin is seen in Fig. 1*b*. As it is seen, the particles spread almost homogenously and big in number with a favourable particle size in nanoscale. The bigger particles to which SNPs are attached probably belong to other organic molecules. Regarding what mentioned and the data provided, the 2CMC value was chosen as the optimised concentration to synthesise green SNPs. Fig. 1*c* shows the SEM micrograph of SNPs prepared by 3CMC of saponin. The picture clearly shows that the increase in concentration of saponin does not result in smaller and finer particles, and since the same result is achieved adding bigger amount of surfactant does not seem sensible. Moreover, the excessive surfactant can restrict particles and reduce their surface area as it traps the particles more in its herbal tissue.

4.2. Effect of concentration of reagents: The molecular structure of $S_2O_3^{2-}$ in aqueous media with two vacant positions makes it possible

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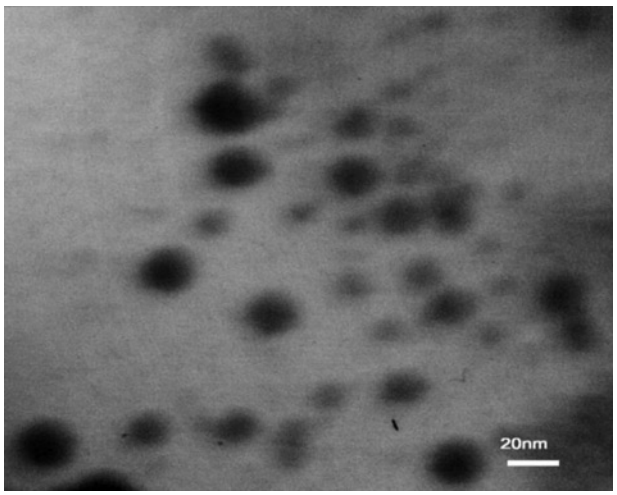

Fig. 2 *TEM micrograph of SNPs with 2CMC of saponin*

for 1 mol $S_2O_3^{2-}$ to react with 1 mol of $H_2C_2O_4$ $2H_2O$ yielding 1 mol of sulphur. In the case of our Letter where the organic di-basic $H_2C_2O_4$ $2H_2O$ ($C_2H_2O_4$) was used to catalyse the reaction, equal ratios of $Na_2S_2O_3$ $5H_2O$ and acid were not capable of starting the precipitation reaction of SNPs due to high pK_a of $H_2C_2O_4$ $2H_2O$. To get an efficient quantity and exact ratios, 1:1–1:10 ratios of $Na_2S_2O_3$ $5H_2O$ and $H_2C_2O_4$ $2H_2O$ in the presence of saponin were closely studied. On the basis of the data by SEM imaging, 1:6 ratio of $S_2O_3^{2-}$ and $H_2C_2O_4$ $2H_2O$ shows the most favourable result with the finest and most homogenous SNPs. The nucleation rate and uniform growth of sulphur particles depend a lot on the initial concentration of $S_2O_3^{2-}$ and $H_2C_2O_4$ $2H_2O$ in the aqueous solutions. The increase in the concentration of sulphur has an extreme impact on the nucleation rate which consequently leads to heterogeneous particle formation. When the initial concentrations of $Na_2S_2O_3$ $5H_2O$ and $H_2C_2O_4$ $2H_2O$ are set at 5 and 30 mM, respectively [12], the appearance of particles makes it possible to stop the supersaturation in solution and following that the nucleation rate falls almost immediately to zero. Therefore, the period of repetitive nucleation becomes so short through controlling the initial concentration of $S_2O_3^{2-}$ and acid. Further experiments show that through using initial concentrations >0.01 M, sulphur particles formation will be too fast resulting in non-uniformity and poly-dispersion of particles. Similar experiments were performed using various acids such as HCl, nitric acid and sulphuric acid. To do so, different ratios (1:1–1:10) of these acids were prepared to react with 5 mM $Na_2S_2O_3$ $5H_2O$. In all reactions, the minimum sulphur nanoparticle size was >200 nm which is far too bigger than the size reached using $H_2C_2O_4$ $2H_2O$.

4.3. TEM image of SNPs: Fig. 2 shows the TEM micrograph of synthesised green SNPs at optimum conditions. The picture clearly shows that the particles spread homogenously. According to picture, the particles are monodispersed and almost 40 nm in size supporting the right choice of saponin concentration in precipitation reaction.

4.4. AFM image of SNPs: To study the morphology of SNPs, we also took the advantage of AFM technique. Figs. 3*a–c* show the

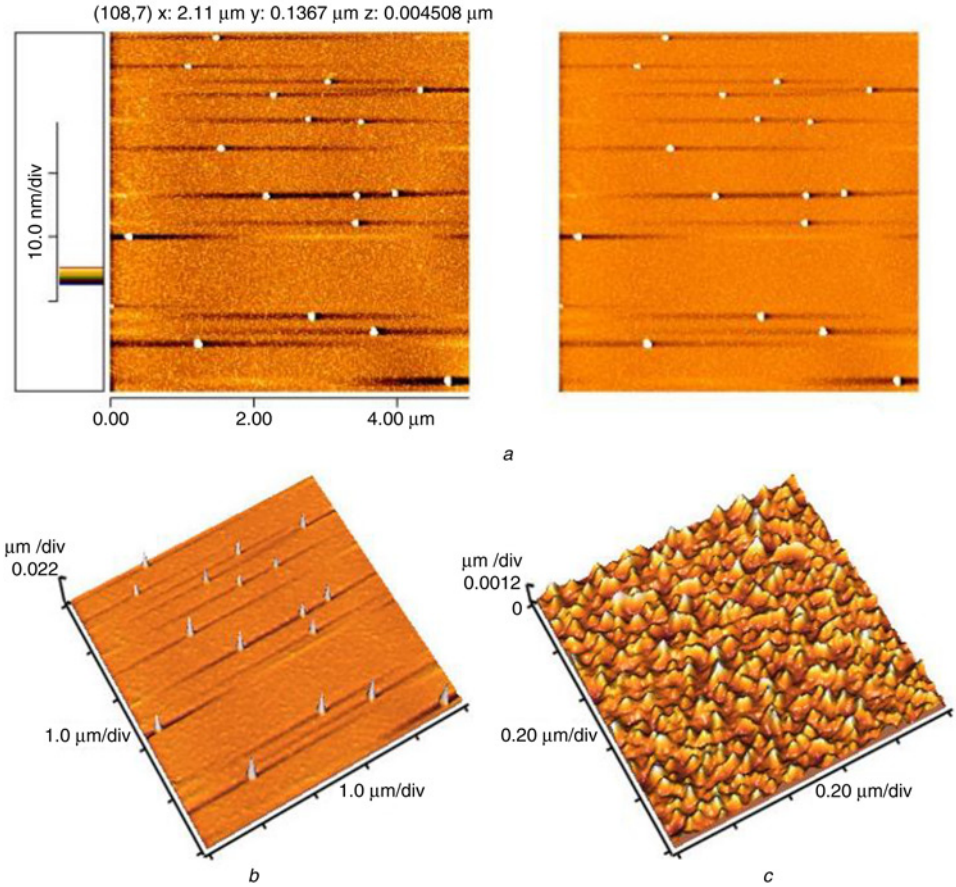

Fig. 3 *AFM images of SNPs using 2CMC of saponin*
a 2D topographic view of SNPs
b 3D view of SNPs
c 3D view of surface roughness

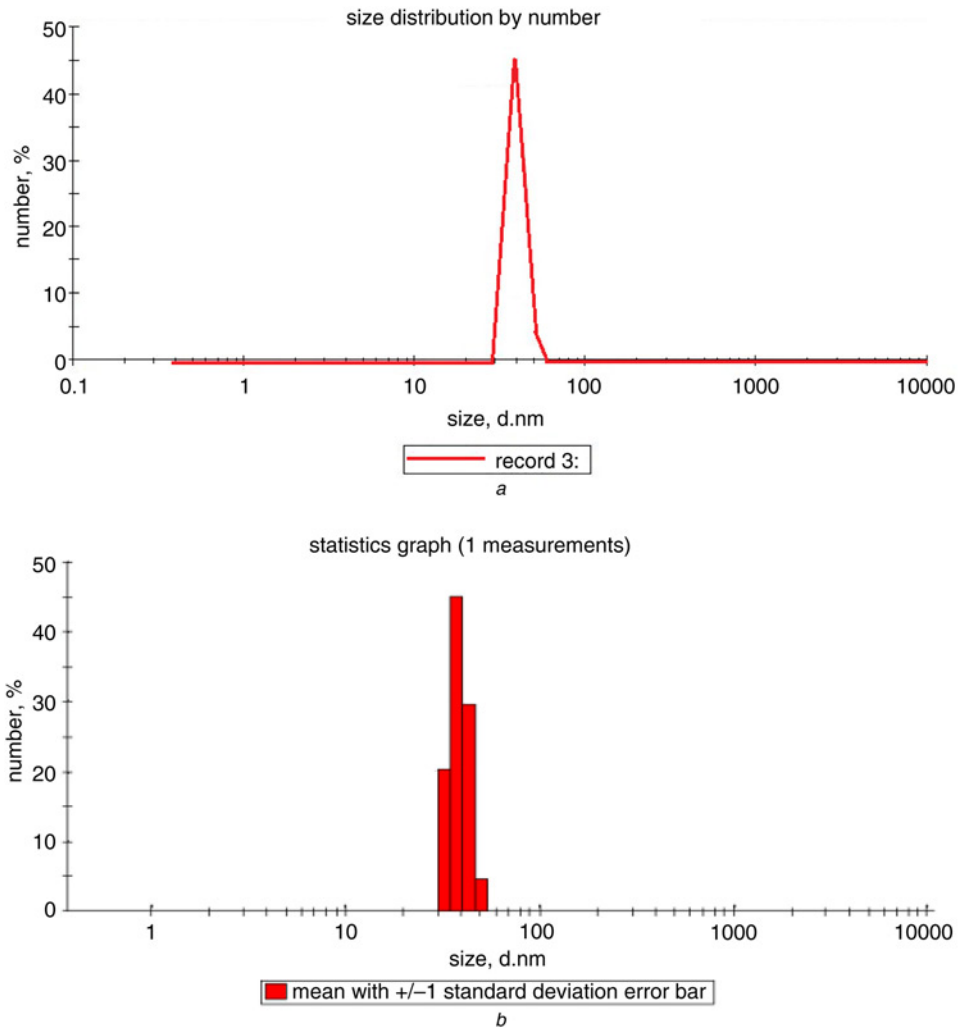

Fig. 4 *DLS analysis of SNPs using 2CMC of saponin*
a Size distribution report by number
b Size statistics report by number

AFM micrographs of SNPs. On the basis of the values of X (2.11 μm), Y (0.1367 μm) and Z (0.004508 μm) seen in Fig. 3*a*, the SNPs have the root mean square roughness of 3.027 nm, mean roughness (R_a) of 2.489 nm and particle size of 28.05 nm on average. Fig. 3*b* shows a three-dimensional image and a better view of the particles morphology which supports the data provided by TEM and SEM. The small value of Z-height (0.0012 μm/div) in Fig. 3*c* supports the fact that particles are smaller in size.

4.5. DLS size distribution analysis: Sample preparation for DLS analysis was carried out by diluting 100 μl of the colloidal solution containing SNPs to 1 ml with double distilled water. The resulting solution was sonicated for 15 min at 25°C. Fig. 4*a* shows size distribution of SNPs by number. As it is seen in the graph, 99.7% of the particles are 39.2 nm in diameter on average supporting the fact the SNPs are distributed homogeneously within the solution. Fig. 4*b* shows the size statistics reported by number. According to the statistics, 20.3% of the SNPs have the smallest size of 32.7 nm. Being the highest in number, 45.2% of particles are 37.8 nm in diameter, 29.6% of the SNPs are 43.8 nm and the least amount of the particles (4.6%) are 50.7 nm in diameter. On the basis of the data provided the mean size of 41.25 nm is obtained.

Polydispersity value of the particles which is a measure of the width of the particle size distribution is calculated using the equation below

$$\mathrm{PdI} = \left(\frac{\sigma}{d}\right)^2 \tag{2}$$

where PdI is the polydispersity, σ is the standard deviation and d is the mean size. The standard deviation of SNPs size is calculated via (3)

$$\sigma = \sqrt{\frac{1}{N}\sum_{1}^{N}(x_i - d)^2} \tag{3}$$

where N is the number of particle size values and x_i is the particle size. On the basis of the data, the mean size of the particles is calculated as 41.25 nm with the standard deviation of 6.7 nm. According to (2), the PdI value of 0.02 is obtained. The PdI values <0.1 support the fact that the green SNPs are monodispersed and there is almost no agglomeration following the synthesis.

4.6. EDX analysis: The evaluation of purity and composition of SNPs was done by EDX spectroscopy. Fig. 5 shows EDX analysis spectrum of the particles. As it is shown, the peaks prove the presence of elemental sulphur and its purity as well. The

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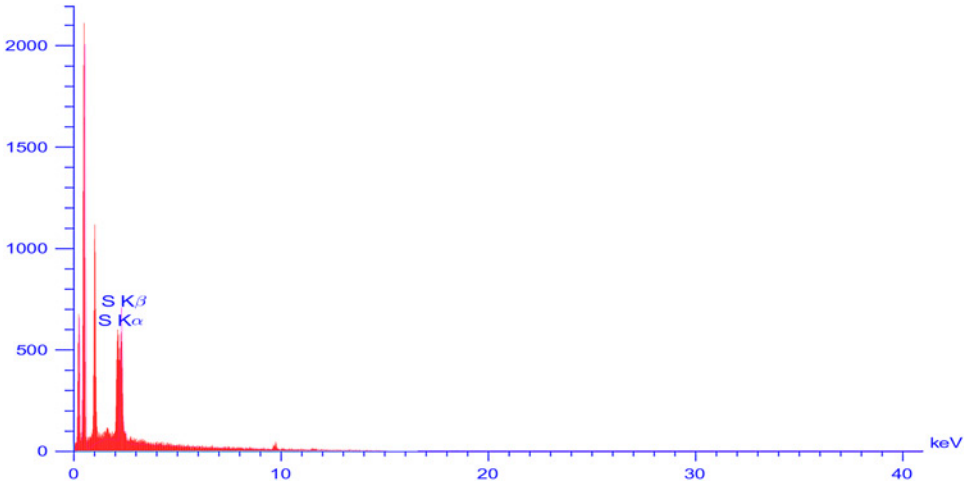

Fig. 5 *EDX analysis of SNP*

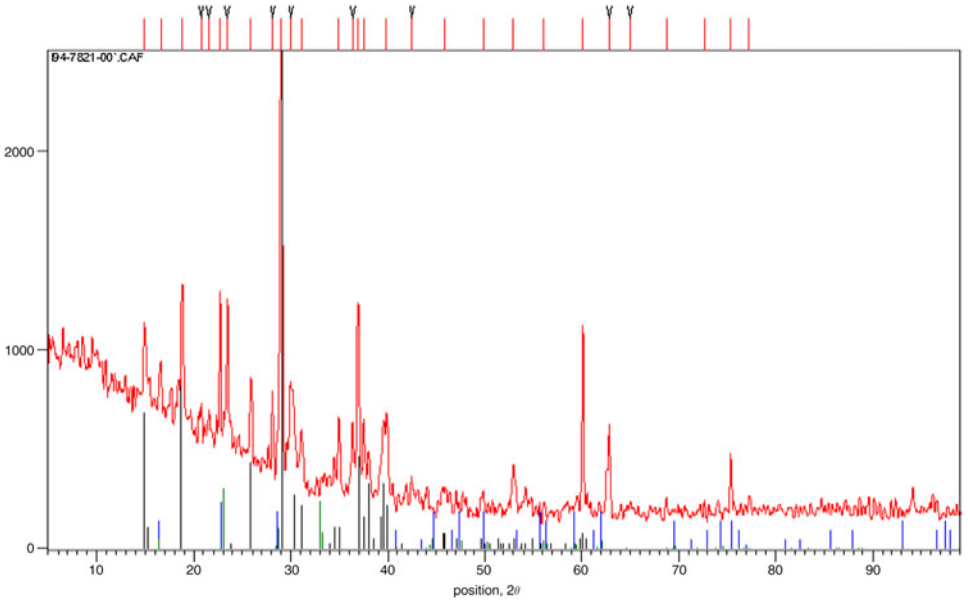

Fig. 6 *XRD analysis of SNPs*

spectral data of SNPs match the results of previous works of sulphur nanoparticle synthesis [16].

4.7. XRD analysis: Fig. 6 shows the XRD pattern of green SNPs. If compared with the α-sulphur particle diffraction pattern [16], the position and intensities resulting from the diffraction pattern are perfectly matched. The sharp peaks in the graph demonstrate the highly crystalline orthorhombic SNPs [13]. To determine the mean particle diameter using XRD technique, Debye–Scherrer formula was applied as follows

$$D = \frac{k\lambda}{\beta \cos \theta} \tag{4}$$

where D is the size of crystallite, k is the Scherrer constant of about 0.89, λ is the X-ray radiation wavelength of copper anode with value of 1.5406 Å with the 2θ ranging from 5° to 99° and β is the full width at half maximum of the diffraction peak. On the basis of the calculations from (4), the particle size of 43 nm was gained.

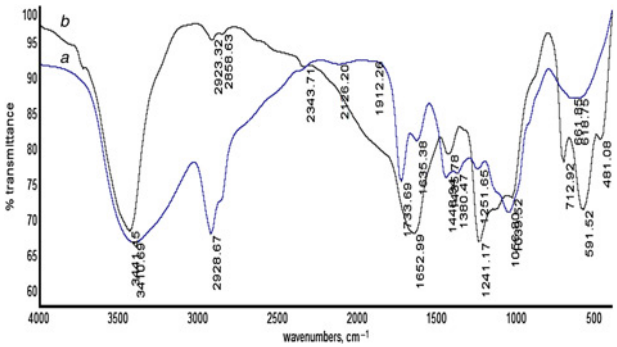

Fig. 7 *FT-IR analysis of*
a Saponin extracted from *A. Phylum Bracteatum*
b Synthesised SNPs

4.8. FT-IR analysis of saponin and SNPs: Among the major factors influencing the size of particles within the reaction process, the herbal surfactant, saponin, plays a significant role. More importantly, saponin is the reactant which characterises the green synthesis in this Letter. Fig. 7 shows the FT-IR spectra of bare saponin [graph (a)] and SNPs [graph (b)]. In graph (a), the broad

absorption peak at 3410.69 cm^{-1} is attributed to O–H stretch band of primary aliphatic alcohols; the sharp peak at 2928.67 cm^{-1} is assigned to C–C of aliphatic hydrocarbons and the absorption at 1733 cm^{-1} is assigned to C=O stretch. The data provided here about the saponin extract from *A. Phylum Bracteatum* is in a good agreement with the FT-IR spectra of saponin in previous studies [26]. In addition to saponin characterisation peaks which were discussed above, all the character peaks of sulphur can be seen in the IR spectra of SNPs in graph (b). The broad peak around 3440 cm^{-1} (O–H stretch band), the sharp peak around 2930 cm^{-1} (C–C aliphatic hydrocarbons) and the absorption at 1733 cm^{-1} (C=O stretch of aliphatic carboxylic acids) demonstrates the presence of surfactant (saponin) as micelles around the particles.

5. Conclusion: In the current Letter, a novel and green method was introduced to obtain SNPs. Limiting the particle size to nanoscale depends on three important factors as the stoichiometric ratio of reagents, temperature, herbal surfactant presence and concentration. In addition to the $Na_2S_2O_3$ $5H_2O$ and $H_2C_2O_4$ $2H_2O$ initial concentrations and ratios, the optimised value of saponin CMC plays a significant role in obtaining SNPs. With regard to all the factors discussed above, the mean particle size of nearly 40 nm was achieved. The analytical data provided by characterisation techniques such as FT-IR, SEM, TEM, XRD, AFM, DLS and EDX are in a good agreement and confirm the synthesis of SNPs via the proposed procedure.

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