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Tin Sulfide Nanoparticle Synthesis from Waste Waters

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ABSTRACT

Tin and its derivatives are extensively used in modern technology tools which lead requirement for development of green methods for its waste management and profitable recycling. Presence of tin in water bodies causes enormous environmental concern due to its acute toxicity to living beings. We demonstrate a simple and zero emission process for extraction of tin ions from aqueous solution using dithiocarbamate-based copolymer and its single step quantitative recovery and transformation into SnS nanoparticles. The polymer shows high metal extraction capacity, 1.06 g $SnCl_2$ per gram of polymer. The polymer metal composite and SnS nanoparticles are analyzed using TEM, FTIR, XRD spectroscopy techniques. The FTIR shows formation of Sn-S bonding in the polymer metal composite. This study has implication for cost effective and green approach for purification of water and waste management.

KEYWORDS

Tin Sulfide Nanoparticles; Metal Extraction; Green Chemistry; Hydrothermal Synthesis; Water Purification

1. Introduction

Tin is a high value metal and its compounds are also used in many modern and conventional industrial processes such as lithography, alloys for electronic circuits, reaction catalysis, anti corrosion coating agent, dopant for electrode of modern solar cells [1-7]. The opto-electronic properties of the nanomaterials of tin are adding-in to its industrial demand. The extensive industrial use leads to problems such as leaching of metal in waste water streams [8-11]. This calls for the requirement for waste disposal and efficient recycling of expensive metal and its compounds. Ever since the industrial revolution, several approaches have been developed to address such requirements, for example, electrochemical extraction, sedimentation, co-precipitation etc. [12-16]. However, some of these techniques require expensive equipments and others are inefficient in extraction and most of these do not give high value end product. Therefore, the general industrial setups consider waste disposal as a government imposed auxiliary setup, rather than as a productive secondary setup. So a new removal and extraction technique is required which can efficiently remove metal from the aqueous streams and recover the same in some high value final product [17]. The dithiocarbamate (DTC) based polymers are known for high metal extraction potential [14,18-21]. They form chemical bonds via M-S (DTC) with metals in almost all oxidation states [14,18-21]. Also the dithiocarbamates and related molecules such as xanthates are known to produce metal sulfide nanoparticles in various morphologies such as rods, belts, spherical particles, etc. via thermal decomposition under specific reaction conditions [22-28]. Herein we present a simple and efficient green process for extraction of tin from aqueous medium using a DTC-based polymer P_{A1} and recovery of tin as tin sulfide nanoparticles via thermal decomposition of the Sn-P_{A1} extract. We used the potential of the dithiocarbamate-based copolymer to extract tin chloride through chemical bonding, thereby transforming it into tin sulfide nanoparticles.

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2. Experimental

2.1. Materials and Instruments

All chemicals were purchased from Sigma-Aldrich, Germany. FTIR spectra of all the molecules were recorded in KBr pellets on a Perkin-Elmer spectrum 2000 FTIR spectrometer. Elementar Analysensysteme Gmbh Vario El-III instrument was used for CHNS elemental analysis. TG/DTG curves were simultaneously recorded on PerkinElmer Model TGA-7, USA, under a nitrogen atmosphere at a heating rate of 10˚C·min^{-1} from 20˚C to 800˚C. Transmission electron microscope (TEM) was recorded on Tecnai G2 F30 STWIN. Sample for TEM of the polymer was prepared by suspending P_{A1} in methanol by using ultrasonication at 45 kHz for 15 min and loading them onto the copper grids for TEM.

2.2. Synthesis of the Polymer and Tin Chloride Extraction Process

The dithiocarbamate based polymer P_{A1} was synthesized as described in the literature [14].

100 mg P_{A1} was soaked with slow stirring in 100 ml water for about 1 hrs at room temperature. 10 mM solution stock solution of tin chloride was prepared by mixing 2.25 g $SnCl_2{\cdot}2H_2O$ in 1000 ml water. After soaking the P_{A1} in water, 100 ml of the stock solution was added to the P_{A1} slurry followed by stirring for 2 hrs. Then it was filtered to extract the Sn-P_{A1} composite. It was characterized by FTIR, XRD and TEM with EDX. The filtrate was analysed for the concentration of Sn using atomic absorption spectroscopy. The amount of metal salt (in grams) absorbed by 1 g of P_{A1} is stated as the maximum loading capacity (MLC) of P_{A1}. This is calculated by following formula:

$$\text{MLC} = \frac{(\text{grams of metal salt taken} - \text{grams of metal salt remained})}{(\text{grams of } P_{A1} \text{ taken})}$$

2.3. Synthesis of Tin Sulfide Nanoparticles

The 10 mg filtered Sn-P_{A1} composite was poured into a 25 ml TEFLON lined stainless steel hydrothermal bomb and approximately 15 ml water was added to it. The mixture was vigorously shaken using a 45 kHz ultrasonicator for 5 min at room temperature. Than the hydrothermal bomb was sealed tightened using its attachments and placed in an oven for 10 hrs at 125˚C. After 10 hrs heating the hydrothermal bomb was allowed to cool naturally. Then the product was extracted by centrifugation at 10,000 rpm and washed several times with water. The product was dried by keeping it for a week in vacuum desiccator. The product was analyzed using XRD and TEM imaging with EDS.

3. Results and Discussion

Figure 1(a) shows highly porous structure of P_{A1} which gives it high surface area for metal ligation. This allows P_{A1} to extract large amount of tin from the aqueous solution. **Figure 1(b)** shows dark patches of Sn bonded with the P_{A1} all over the polymer surface.

This illustrates the high potential of the metal absorption by the P_{A1}. The EDS (**Figure 1(c)**) of a selected area on the Sn-P_{A1} composite shows highest concentration of Sn in the composite among all the elements present in it. There are peaks with respect to the Cu which are due to the copper grid used for the TEM imaging. The Sn-P_{A1} composite was also analyzed by atomic absorption spectroscopy (AAS) and CHNS elemental analysis (**Table 1**)

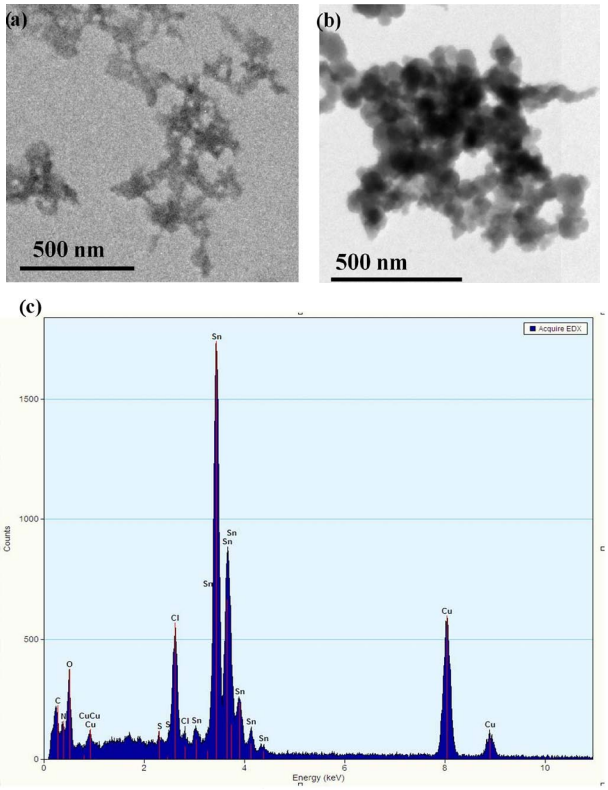

Figure 1. (a) TEM image of P_{A1} showing its porous structure; (b) TEM image of Sn-P_{A1} composite showing large amount of Sn bonded with the P_{A1} all over its surface; (c) EDS of a selected area on the Sn-P_{A1} composite showing amount of Sn attached with the P_{A1}.

Table 1. CHNS elemental analysis of P_{A1} and Sn-P_{A1} composite.

	%C	%H	%N	%S
Calculated P_{A1}	23.077	2.885	35.897	30.769
Observed P_{A1}	22.181	2.922	33.743	32.271
Observed Sn-P_{A1}	11.728	1.57	18.884	16.052

to determine the concentration of Sn in the composite. The results of AAS shows about 32.6% Sn (w/w) in the Sn-P_{A1} composite. Also the analysis of the filtrate showed significant removal of Sn as the concentration of Sn lowered from 10 mM to 4.4 mM by 100 mg P_{A1}. This means 100 mg P_{A1} extracted 56% of the tin chloride from the water in single wash *i.e.*, 100 mg bonded with 106.2 mg $SnCl_2$. This gives MLC for the P_{A1} 1.06 g/g of P_{A1}. This value is one of its highest performance when compared to the MLC with other heavy metals. [14] The CHNS elemental analysis of the P_{A1} and Sn-P_{A1} also suggests about 51.8% (w/w) of $SnCl_2$ in the Sn-P_{A1}. This gives 32.4% (w/w) of Sn in Sn-P_{A1},which is in good agreement with the AAS results.

The filtrate was treated with another set of 100 mg P_{A1} for complete recovery of the tin ions present in the solution. The AAS results of the second cycle showed less than 0.01 mM concentration left in the solution. Thus achieving more than 99.9% recovery of the tin ions from the solution.

Figure 2 shows powder XRD of the polymer (black color) having a broad peak at 2θ = 35.8˚ [29,30]. As per the Scherrer equation the broad peak width is inversely proportional to crystallite size [31]. This is in agreement with the high porosity of the polymer structure as seen in its TEM. The XRD pattern of the Sn-P_{A1} composite has dual character of the P_{A1} and the Sn bonded with the P_{A1}. The new peaks in the XRD pattern of Sn-P_{A1} composite show resemblance with that of the SnS and SnS_2. This indicates the ligation of DTC groups present in the P_{A1} with the Sn [28-30].

The FTIR of the P_{A1} (**Table 2**) shows characteristic bands with respect to the dithiocarbamate, thiourea and hydrazone functional groups along with the imine bonds. The Sn-P_{A1} composite shows blue shift in the bands of C=N, C=S, N-H and N-N this is attributed to the ligation with of lone pair of electrons of N atom of C=N and S atom of C=S which enhances the bond strength of these bonds. Whereas the characteristic band and shoulder of the dithiocarbamate bonds at 1000 cm^{-1} and 925 cm^{-1}, respectively shows significant changes as the shoulder is absent in the Sn-P_{A1} composite. Also the asymmetric stretching band shows a blue shift. This indicates bidentate ligation along with other multiple modes of ligation of S with the Sn [14,18,19,32].

The TG/DTA of the P_{A1} shows its thermal degradation starts at 140˚C under N_2 atmosphere [14]. However under high pressure in hydrothermal process this degradation would folow different mechanism. It is observed that hydrothermal treatment at 125˚C gives enough temperature and pressure for cleavage of polymer and formation of tin sulfide. This treatment of the Sn-P_{A1} composite gives SnS nanoparticles which may be seen in the SEM image (**Figure 3(a)**). The nanoparticles are homogenous

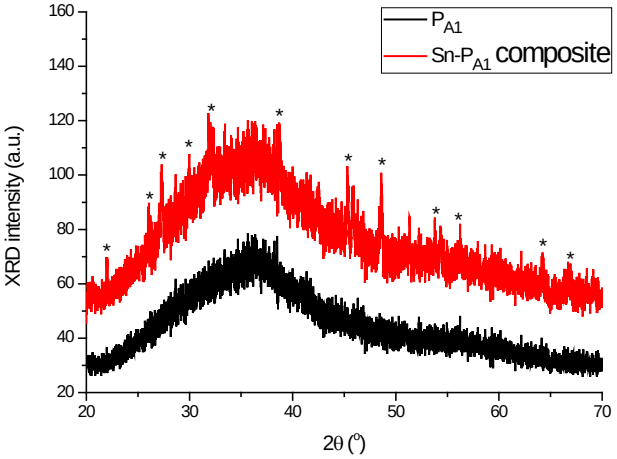

Figure 2. Powder-XRD of P_{A1} and Sn-P_{A1} composite, the stared peaks are from Sn bonded with the polymer.

Table 2. FTIR observation table for P_{A1} and Sn-P_{A1} composite.

Molecules	*ν*(N-H)	*ν*(C=N)	*ν*(N-N)	*ν*(C=S)	*ν*(S=C-S)
			$\nu \cdot cm^{-1}$ (wavenumber)		
P_{A1}	1600	1546	1142	1050	(as, b) 1000 (ss, sh) 925
Sn-P_{A1}	1620	1560	1180	1090	(as) 1050

as = antisymetric stretch, ss = symmetric stretch, sh = shoulder, b = broad as = antisymetric stretch, ss = symmetric stretch, sh = shoulder, b = broad.

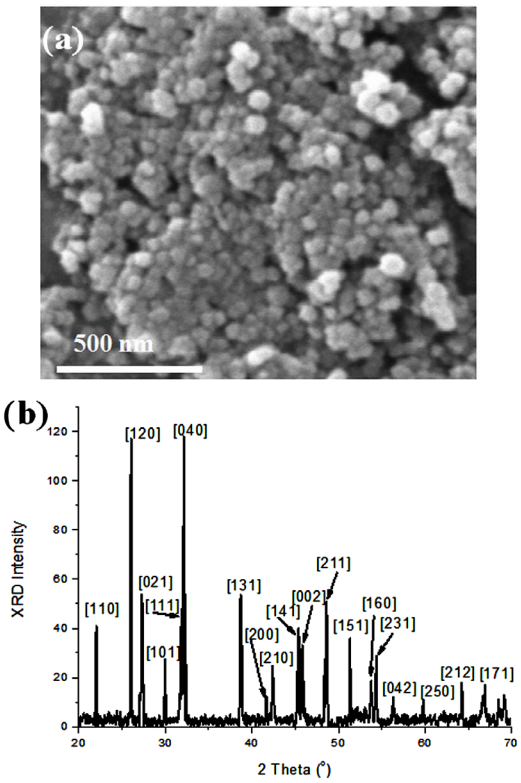

Figure 3. SEM image of SnS synthesized from Sn-P_{A1} composite via hydrothermal treatment.

in spherical shape with particle size < 100 nm. The XRD pattern (**Figure 3(b)**) of the SnS nanoparticles shows various peaks corresponding to the orthorhomic crystalline phase of the SnS which are in good agreement with the literature values (JCPDS 39-354).

The hydrothermal treatment cleaves the polymer into small water soluble fragments and SnS nanoparticles were collected as precipitates with isolated yield of 97.2%. The washings of the experiment was analysed by spot test for various organic functional groups. These experiments show presence of thiocynide and hydrazones functional groups. Further analysis of the washings are still going on as we would like to find some meaningful treatment of this by product of the reaction. However the synthesis of the SnS nanoparticles was emission free as no byproducts were allowed to leach in the environment (major advantage of closed vessel hydrothermal processes).

4. Conclusion

We successfully demonstrated a simple method for the purification of industrial waste water stream having heavy metal impurities. The tin chloride was efficiently extracted by the polymer at a high metal loading capacity of 1.06 g/g of the polymer. Moreover, the sensitivity of the polymer was also quite high for the ultra low concentration of the tin chloride as in the second cycle using another set of pure polymer recovered above 99.9% of the tin metal ions. The major advantage of this process is the conversion of the waste metal ions into highly useful SnS nanoparticles through a zero emission process. The hydrothermal processes are known for their energy efficiency and green aspects and hence the present work has a high value for industrial pollution and waste management works. The low economic cost of production of the P_{A1} and the use of simple instruments such as autoclaves make this process eligible for futuristic industrial applications.

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