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 SnCl₂ 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 PA1 and recovery of tin as tin sulfide nanoparticles via thermal decomposition of the Sn-PA1 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. Elemental Analysensysteme GmbH Vario El-III instrument was used for CHNS elemental analysis. TG/DTG curves were simultaneously recorded on Perkin-Elmer 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 PA1 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 PA1 was synthesized as described in the literature [14].
100 mg PA1 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 SnCl₂·2H₂O in 1000 ml water. After soaking the PA1 in water, 100 ml of the stock solution was added to the PA1 slurry followed by stirring for 2 hrs. Then it was filtered to extract the Sn-PA1 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 PA1 is stated as the maximum loading capacity (MLC) of PA1. This is calculated by following formula:

\[ \text{MLC} = \frac{\text{grams of metal salt taken} - \text{grams of metal salt remained}}{\text{grams of PA1 taken}} \]

2.3. Synthesis of Tin Sulfide Nanoparticles
The 10 mg filtered Sn-PA1 composite was poured into a 25 ml TEFLOD 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 PA1 which gives it high surface area for metal ligation. This allows PA1 to extract large amount of tin from the aqueous solution. Figure 1(b) shows dark patches of Sn bonded with the PA1 all over the polymer surface. This illustrates the high potential of the metal absorption by the PA1. The EDS (Figure 1(c)) of a selected area on the Sn-PA1 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-PA1 composite was also analyzed by atomic absorption spectroscopy (AAS) and CHNS elemental analysis (Table 1).

![Figure 1](image)

**Table 1. CHNS elemental analysis of PA1 and Sn-PA1 composite.**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%S</th>
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<tbody>
<tr>
<td>Calculated PA1</td>
<td>23.077</td>
<td>2.885</td>
<td>35.897</td>
<td>30.769</td>
</tr>
<tr>
<td>Observed PA1</td>
<td>22.181</td>
<td>2.922</td>
<td>33.743</td>
<td>32.271</td>
</tr>
<tr>
<td>Observed Sn-PA1</td>
<td>11.728</td>
<td>1.57</td>
<td>18.884</td>
<td>16.052</td>
</tr>
</tbody>
</table>
to determine the concentration of Sn in the composite. The results of AAS shows about 32.6% Sn (w/w) in the Sn-PAl 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 PAl. This means 100 mg PAl extracted 56% of the tin chloride from the water in single wash i.e., 100 mg bonded with 106.2 mg SnCl2. This gives MLC for the PAl 1.06 g/g of PAl. This value is one of its highest performance when compared to the MLC with other heavy metals. [14] The CHNS elemental analysis of the PAl and Sn-PAl also suggests about 51.8% (w/w) of SnCl2 in the Sn-PAl. This gives 32.4% (w/w) of Sn in Sn-PAl, which is in good agreement with the AAS results.

The filtrate was treated with another set of 100 mg PAl 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-PAl composite has dual character of the PAl and the Sn bonded with the PAl. The new peaks in the XRD pattern of Sn-PAl composite show resemblance with that of the SnS and SnS2. This indicates the ligation of DTC groups present in the PAl with the Sn [28-30].

The FTIR of the PAl (Table 2) shows characteristic bands with respect to the dithiocarbamate, thiourea and hydrazone functional groups along with the imine bonds. The Sn-PAl 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-PAl 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 PAl shows its thermal degradation starts at 140°C under N2 atmosphere [14]. However under high pressure in hydrothermal process this degradation would follow 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-PAl composite gives SnS nanoparticles which may be seen in the SEM image (Figure 3(a)). The nanoparticles are homogenous
in spherical shape with particle size < 100 nm. The XRD pattern (Figure 3(b)) of the SnS nanoparticles shows various peaks corresponding to the orthorhombic crystal-line 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 thiocyanide and hydrazonate 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 potential for use in Organic Electronic Applications, Accounts of Chemical Research, Vol. 45, No. 3, 2012, pp. 337-346. http://dx.doi.org/10.1021/ar200119g

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