Adsorption of Pb^{2+} ions on nanosized γ-Fe_2O_3: formation of surface ternary complexes on ligand complexation

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Abstract

Adsorption of Pb^{2+} ions on the combustion derived nanosized γ-Fe_2O_3 and its thiourea complex composite is reported. The adsorbents upon adsorption of Pb^{2+} ions are characterised by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray microanalysis and infrared spectroscopy techniques. The eluent is characterised by atomic absorption spectroscopy for the estimation of Pb^{2+} ions. The reduction in the amount of lead after adsorption was estimated to be around 50% in case of complex composite adsorbent and around 15% in case of the γ-Fe_2O_3 adsorbents. Orthorhombic $PbSO_4$ precipitated out from the eluent and is reported with a model reaction. Adsorption of lead onto the complex composite is explained through the formation of a surface tertiary complex. The advantage of employing a thiourea–γ-Fe_2O_3 complex composite as solid adsorbent for the adsorption of heavy metal pollutants is envisaged in the present investigation.
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Keywords: Nanosized γ-Fe_2O_3; Ligand complexation; Heavy metal pollutant

1. Introduction

It is a well-known fact that decrease in particle size up to a nanoscale, increases the surface area and hence, increases the number of adsorption sites. It is reported that porous alumina when prepared employing different synthetic routes [1–4], show excellent adsorption behaviour. One of

the possible explanations given is that the octahedral aluminum sites are fully occupied while vacant sites are randomly disturbed at the tetrahedral positions. These vacant sites in the structure are mainly responsible for the adsorption behaviour on γ-Al_2O_3. In contrast to γ-Al_2O_3, which adopts a normal spinel structure, γ-Fe_2O_3 (an important ferrite and a magnetic tape recording material), possess inverse spinel structure with vacancies in the octahedral sites. A critical review on understanding the adsorption behaviour of nanomaterials and nanocomposites is reported [5,6]. Some of the uses of γ-Fe_2O_3 as adsorbents

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include, as an agent for making the halogen containing waste gases harmless [7], removal of phosphate from water [8] and removal of oil from water [9]. Some reports on the selective adsorption of γ-Fe$_2$O$_3$, irradiated γ-Fe$_2$O$_3$, γ-Fe$_2$O$_3$-Al$_2$O$_3$ and γ-Fe$_2$O$_3$-polymer composites as adsorbents is also reported to some extent [10–15]. In our earlier work we have reported the understanding of the adsorption behaviour of Ca^{2+} ions on rubber-α-Fe$_2$O$_3$ composite [16]. However to date the use of γ-Fe$_2$O$_3$ or its complex composites or the composites with polymer matrix as adsorbents for adsorption of heavy metal ions is not reported in detail. The aim of the present work is to understand the removal of a highly hazardous environmental pollutant, lead, employing γ-Fe$_2$O$_3$ and a complexed γ-Fe$_2$O$_3$ (i.e., γ-Fe$_2$O$_3$–thiourea complex composite) as solid adsorbents.

In many environmental settings, the presence of organic ligands that form stable complexes with metal cations can strongly influence their adsorption behaviour on metal oxides, including those of Al and Fe. For example, Co^{2+} forms strong complexes with ligands such as ethylenediaminetetraacetic acid (EDTA) and nitrolotriacetic acid (NTA), and complexes of this type sorb to oxide surfaces in a fashion analogous to that of bare ligands (e.g. EDTA, NTA) rather than the metal cation [17,18]. The adsorption of these complexes increases with decreasing pH, until a pH is reached where the proton-promoted dissolution of the solid releases sufficient structural metal to induce competitive complex dissociation. Fe and Al oxide surfaces show high affinity for natural organic molecules containing carboxylate functional groups [19]. These surfaces may be coated with a veneer of sorbed organic molecules in soils and aquatic sediments. Adsorption of Co^{+2} on both γ-Al-(OH)$_3$ (gibbsite) and α-FeO[OH] (goethite), as well as on natural materials containing these oxides, is enhanced by the presence of sorbed or complexed organic matter which appears to function as a co-complexant along with the oxide surface [20]. However the studies on the morphology of the adsorbate after adsorption was not reported in detail. There are numerous examples where organic ligands can inhibit or enhance metal ion sorption, usually resulting in the formation of ternary complexes, but very little is known about the reasons for these effects at the molecular level or how the metal-organic complex bonds to an oxide surface. Thiourea is commonly known as one such ligand, which shows excellent complexation property with various metals [21]. The use of γ-Fe$_2$O$_3$–thiourea complex composite in the present investigation is employed in this contest and also used to understand the efficiency this composite a valuable adsorbent.

Lead is found in trace quantities as pollutant in petrol, gasoline oil and in paints and pigments. In urban atmosphere the main source of lead pollution is automobile. It creates urban concentration of inorganic lead of about $1-3$ μg m^{-3}, Inorganic lead acts as a agent causing variety of human disorders [22,23] with high values in areas of heavy traffic. A detailed study on the use of solid adsorbents for this metal is not reported in the literature. In our recent communication we have given a preliminary treatment for the use of γ-Fe$_2$O$_3$ (synthesised from ferrous oxalate precursor) and its complex composite as adsorbents for lead and other metals [23]. The present paper is an investigation to determine the feasibility of lead adsorption on γ-Fe$_2$O$_3$ and its complex composite and to understand the detailed morphological transitions of the Pb^{2+} ions adsorbed onto γ-Fe$_2$O$_3$ (prepared from ferrous acetylacetonate precursor) and its thiourea complex composite forming a surface ternary complex along with other important studies. However the detailed quantitative treatment to the subject will be our future course of study.

Characterisation of adsorbent was undertaken by employing X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX) techniques. The changes in the surface morphology, structure and bonding upon adsorption of lead is also understood from these studies. The amount of Pb^{2+} ions unadsorbed on to the γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$–thiourea complex composite surfaces (γ-Fe$_2$O$_3$ and thiourea are complexed together and hence the called complex composite) were estimated employing atomic absorption spectrometer (AAS).

2. Experimental

All the chemicals used in the present study were of A R grade. The temperature for the adsorption study was controlled by placing the glass columns in a thermostat, maintained at 25 ± 0.5 °C for 12 h.

2.1. Synthesis of nanosized γ-Fe$_2$O$_3$ through combustion route

The ferric acetylacetonate precursor was mixed with polyethylene glycol in the weight ratio 1:5 and ground well in a pestle and mortar. The resultant solid was placed in a crucible and heated in the air. It was observed that initially polyethylene glycol melted, then frothed and finally ignites to form γ-Fe$_2$O$_3$. On cooling to room temperature no traces of carbon impurities was observed in the final residue of γ-Fe$_2$O$_3$ [24]. The detailed synthetic procedure and characterisation employing thermal (TGA/DTA), SEM, TEM, infrared spectra (IR) and other techniques is reported elsewhere [24,25]. The as synthesised γ-Fe$_2$O$_3$ is then employed for the adsorption study.

2.2. Preparation of γ-Fe$_2$O$_3$–thiourea complex composite

A known weight of thiourea was dissolved in acetone and to this solution equimolar quantity of γ-Fe$_2$O$_3$ (the above synthesised) was added. The resulting γ-Fe$_2$O$_3$ dispersed solution was taken in a round bottom flask and was refluxed on a hot water bath for 6 h. After 6 h, the solvent was slowly evaporated on a temperature-controlled hotplate. The final dried powder product was characterised employing IR, EDX and XRD, analyses and this complex composite is then used for adsorption study.

2.3. Preparation of columns

Two glass columns of equal length and diameter were taken. The bottoms of the empty columns were packed with glass wool for about 1 cm height. One gram each of pure γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$–thiourea complex composite were poured onto the columns and packed uniformly by gentle tapping.

2.4. Adsorption studies

To the above said columns, a 50 ml of known concentration (containing 300 ppm of lead ions) of lead acetate solution was added and kept aside for adsorption (under static and isothermal conditions). After 12 h the solution was eluted and was preserved for atomic absorption studies. The solid product i.e., adsorbent was washed with water and air-dried. This solid adsorbent was characterised employing XRD, IR, EDX and SEM techniques.

3. Results and discussion

3.1. Infrared studies

The adsorbents have been investigated for the adsorption behaviour of Pb^{2+} ions on pure γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$–thiourea complex composite surfaces from infrared spectra. The IR spectrum of pure γ-Fe$_2$O$_3$ shows the characteristic lines of a typical ferrite at 545 and 455 cm^{-1} [26,27]. Though the IR spectrum of γ-Fe$_2$O$_3$ after Pb^{2+} ions adsorption is similar to that of the pure γ-Fe$_2$O$_3$ in the region below 600 cm^{-1}, however, some additional features above 600 cm^{-1} are observed as given in Table 1. The IR bands at around 1560, 1408 and 1370 cm^{-1} are characteristics of the acetate groups. The band at 1015 cm^{-1} could be assigned to inplane bending of CH$_3$ group. The other two bands at around 1164 and 1095 cm^{-1} are overtones arising out of pure γ-Fe$_2$O$_3$. A careful examination of the IR spectra of pure γ-Fe$_2$O$_3$ with the lead adsorbed γ-Fe$_2$O$_3$ shows that the new bands are weak in nature in the later case which indicates a weak interactions of the adsorbed Pb^{2+} ions on the γ-Fe$_2$O$_3$, The weak interactions are possibly due to the less amount of Pb^{2+} ions adsorbed.

The IR data for γ-Fe$_2$O$_3$–thiourea complex composite is given in Table 1. The finger print region for pure γ-Fe$_2$O$_3$ (below 600 cm^{-1}) hardly shows any change. Little shifts in the stretching frequencies, which are observed, are due to inter-

Table 1
Various vibrational bands observed in the IR spectra

Pure γ-Fe$_2$O$_3$	Pb adsorbed γ-Fe$_2$O$_3$	Pb–thiourea complex composite	Pb–thio–γ-Fe$_2$O$_3$ ternary complex
448	1015	450	320–310
552	1095	540	455
1080	1164	1124	542
	1370	1337	1071
	1408	1449	1150
	1560	1620	1410
		3195	1520
		3200	

All the values are in cm^{-1}.

action of surface oxygen with thiourea. There is a chance of ambiguity that the surface oxygen of γ-Fe$_2$O$_3$ could interact with the amine hydrogen of thiourea or the Fe-atoms of Fe$_2$O$_3$ could interact with the sulphur atoms of thiourea, however the IR spectrum clearly indicates the first possibility. The presence of N–H stretching frequency around 3195 cm^{-1} indicates the presence of bound NH$_2$ group. The bands in the range 1600–700 cm^{-1} are characteristics of free C=S group, where the C is bound to S.

Table 1 gives the IR spectrum of the γ-Fe$_2$O$_3$–thiourea complex composite after adsorption of Pb^{2+} ions. Complexation of metal ions with thiourea shows down shift indicating 'S' bonding [21]. The occurrence of a new peak in our adsorbed sample below 400 cm^{-1} and in the region 320–310 cm^{-1} is then understood to be due to the complexation of Pb^{2+} ions with the 'S' of thiourea.

3.2. X-ray diffraction

The XRD pattern of the pure γ-Fe$_2$O$_3$ adsorbed with Pb^{2+} ions is shown in Fig. 1(a). The presence of additional reflections along with those corresponding to pure γ-Fe$_2$O$_3$ indicates the adsorption of Pb^{2+} ions on γ-Fe$_2$O$_3$. We also report here the XRD pattern of the adsorption nature of Pb^{2+} ions on γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$–thiourea complex composites. The XRD pattern of the composite after eluting with Pb^{2+} ions is shown in Fig. 1(b).
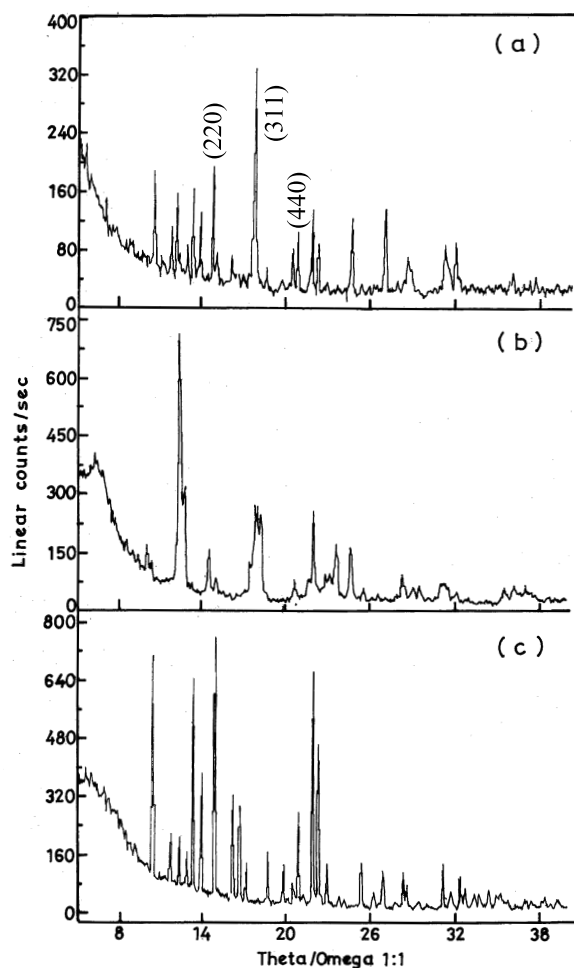
Fig. 1. XRD pattern of (a) Pb-adsorbed γ-Fe$_2$O$_3$, (b) Pb adsorbed γ-Fe$_2$O$_3$–thiourea complex composite and (c) Pb precipitated as PbSO$_4$.

Comparison between Fig. 1(a and b) give the following: presence of lead peaks with indices (2 2 0), (3 1 1), and (4 4 0) is clearly visible along with other less intensity peaks in Fig. 1(a). However in case of thiourea–Fe_2O_3 complex composite, though the amount of lead present is higher than in earlier case (due to more lead adsorption), cannot be clearly indexed. Some of the possible reasons for this feature of XRD pattern include: (i) thiourea peaks mask the crystalline lead peaks, (ii). The splitting of (3 1 1) peak and broadening of other peaks indicate the complexation of lead with thiourea.

Furthermore, an interesting observation was made, a colourless solid got precipitated out from the eluent of γ-Fe_2O_3–thiourea composite. The XRD pattern of this solid product is shown in Fig. 1(c). On comparison of the XRD pattern of this solid product with that of the literature (JCPDS 36-1461) it is found to be pure orthorhombic $PbSO_4$ crystals having anglesite structure. Unit cell parameters were obtained by least square refinement of the powder XRD data using the PROSZKI program and is given in Table 2. The formation of $PbSO_4$ crystals could be due to the hydrolysis of γ-Fe_2O_3–thiourea composite after the addition of lead solution with partial retention of the complex structure and adsorption of Pb^{2+} ions onto the complex composite surface. Formation of this surface ternary structure is shown in Fig. 2. The possible mechanism for this reaction can be represented as follows;

1) Formation of ternary complex;

Table 2
Comparison of *d*-spacing values with calculated $PbSO_4$

h k l	*d* observed (Å)	*d* calculated[a] (Å)	Delta
1 0 1	4.261	4.263	0.007
1 1 1	3.802	3.809	0.042
1 2 0	3.619	3.622	0.019
2 0 0	3.473	3.479	0.043
0 2 1	3.339	3.334	−0.041
2 1 0	3.215	3.219	0.034
1 2 1	3.008	3.007	−0.015
2 1 1	2.764	2.764	0.005
0 0 2	2.697	2.696	−0.010
1 3 0	2.622	2.620	−0.029
1 1 2	2.408	2.411	0.046
0 2 2	2.277	2.276	−0.027
2 3 0	2.196	2.195	−0.036
1 2 2	2.166	2.163	−0.055
2 1 2	2.067	2.067	0.002
2 1 3	2.033	2.033	0.001
0 4 1	1.976	1.974	−0.042
3 3 0	1.794	1.793	−0.030
1 0 3	1.742	1.741	−0.044
4 1 0	1.703	1.704	0.036
4 1 1	1.623	1.625	0.074
1 2 3	1.609	1.610	0.038
3 3 2	1.494	1.493	−0.044
2 5 1	1.468	1.468	−0.040
4 1 2	1.441	1.441	−0.040
4 3 1	1.430	1.429	−0.050
1 5 2	1.404	1.407	0.132
2 3 3	1.392	1.391	−0.076
0 4 3	1.370	1.371	0.098

[a] $a = 6.95856$, $b = 8.48414$ and $c = 5.39298$ Å, calculated using the PROSZKI program and the position parameter for $PbSO_4$ reported in literature (JCPDS for $PbSO_4$ system).
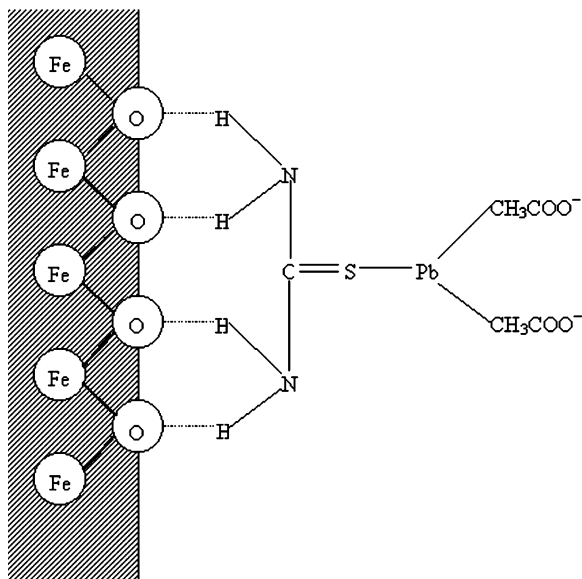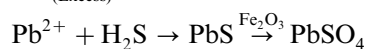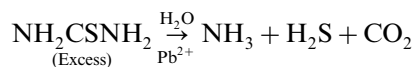

$$Fe_2O_3 + NH_2 = \overset{\overset{\displaystyle S}{\|}}{C} = NH_2 \longrightarrow Fe_2O_3\text{---}NH_2 = \overset{\overset{\displaystyle S}{\|}}{C} = NH_2$$

$Pb(CH_3COOH)_2$

Ternary complex (shown in Figure 2)

Fig. 2. Possible ternary complex in γ-Fe$_2$O$_3$–thiourea–Pb system.

2)   Precipitation of PbSO$_4$

$$\underset{\text{(Excess)}}{NH_2CSNH_2} \overset{H_2O}{\underset{Pb^{2+}}{\rightarrow}} NH_3 + H_2S + CO_2$$

$$Pb^{2+} + H_2S \rightarrow PbS \overset{Fe_2O_3}{\rightarrow} PbSO_4$$

Liberation of NH$_3$ and H$_2$S gases from thiourea is also understood from the literature [28].

3.3. Atomic absorption spectroscopy

Atomic absorption spectroscopic characterisation was carried out for the (blank) lead acetate solution and the eluent solution (after passing through the columns in both the cases, i.e., for pure γ-Fe$_2$O$_3$ and for γ-Fe$_2$O$_3$–thiourea complex composite). In case of pure γ-Fe$_2$O$_3$ the concentration of Pb^{2+} ions did not reduce to consider-

Table 3
Atomic absorption results

|	
Initial concentration of Pb(II)-ions	280
After passing through γ-Fe$_2$O$_3$	220
After passing through γ-Fe$_2$O$_3$–thiourea complex composite	140

All the values are in ppm.

able extent. This result is in agreement with the XRD and IR results discussed earlier, however in case of γ-Fe$_2$O$_3$–thiourea complex composite there is a considerable decrease in the concentration of Pb^{+2} ions ($\sim 50\%$). The results are given in Table 3. This result indicates that a considerable amount of Pb^{2+} ions gets adsorbed on the γ-Fe$_2$O$_3$–thiourea complex composite when compared with that of the pure γ-Fe$_2$O$_3$.

The IR spectral data, XRD pattern and the AAS results all confirm the adsorption of Pb^{2+} on
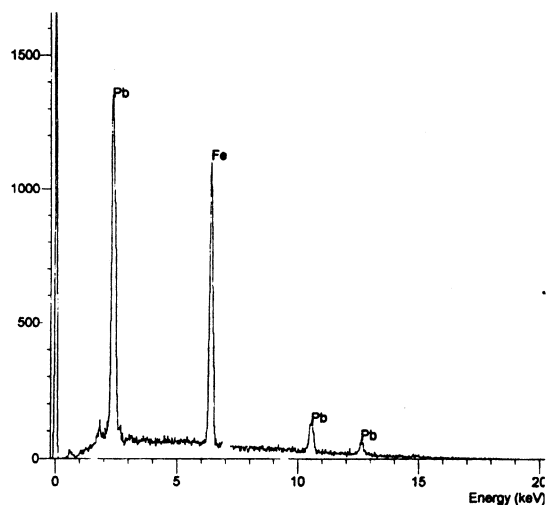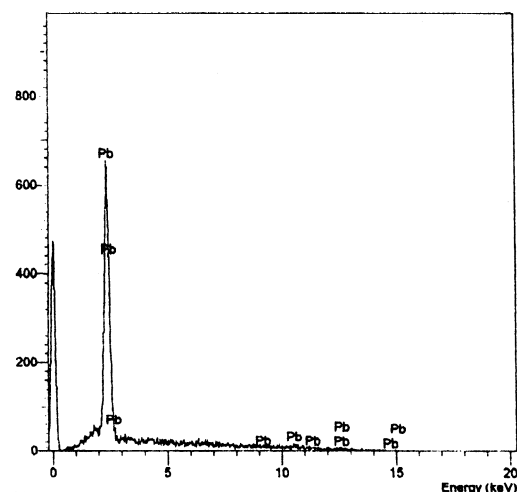
Fig. 3. EDX of (a) γ-Fe$_2$O$_3$–thiourea–Pb ternary complex and (b) as precipitated PbSO$_4$ crystals.

the γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$–thiourea complex composite adsorbents.

3.4. Energy dispersive X-ray microanalysis and scanning electron microscopy studies

The energy dispersive X-ray microanalysis data (Fig. 3(a)) of the γ-Fe$_2$O$_3$–thiourea complex composite adsorbent after the adsorption shows the presence of both Pb^2 and Fe^{3+} ions. This EDX analysis confirms the fact that the γ-Fe$_2$O$_3$–thiourea complex composite adsorbs a consider-

able amount of Pb^{2+} ions. The EDX analysis (Fig. 3(b)) of the precipitate of the eluent which was collected at the bottom after adsorption showed presence of only lead. The precipitate was found to be PbSO$_4$ as was earlier confirmed from XRD pattern (Fig. 1(c), and discussed in Section 3.2).

We have investigated surface morphology of Pb^{2+} ions adsorbed onto γ-Fe$_2$O$_3$ and adsorbed γ-Fe$_2$O$_3$–thiourea complex composite surfaces, employing SEM technique. The scanning electron micrograph images for the γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$–thiourea complex composite samples are shown in Fig. 4(a and b), respectively. In Fig. 4(a), we see beautiful surface adsorbed spherical shaped Pb particles on spherical agglomerates of nanosized γ-Fe$_2$O$_3$. The individual particle agglomerates look like tennis balls with an average size of 1 μm. Pb^{2+} ions sorbs from aqueous solution as inner-sphere complex on both the (0 0 0 1) and (1 1 0 2) surfaces, bonded in a dominantly tridentate fashion above tetrahedral interstices to surface OH groups at pH values near to 8. Pb^{2+} is also known to form a weakly bonded outer-sphere complex on the (0 0 0 1) surface at pH 7. Further investigation like, EXAFS is required to understand whether Pb^{2+} is forming weakly bonded outer-sphere complex or a strongly bonded inner-sphere complex in these samples.

Fig. 4(b) shows the surface morphology of γ-Fe$_2$O$_3$–thiourea–Pb ternary complex composite. Here, we see two different types of structures. One bundle like self-assembled structures and others are spherical like structure attached to bundles. One kind of structures could be due to the existence of complex between γ-Fe$_2$O$_3$–thiourea, and the later kind could be due to adsorption of Pb^{2+} ions on γ-Fe$_2$O$_3$–thiourea complex composite forming a ternary surface complex. The surface morphology of the ternary system is completely different from the surface morphology of Pb^{+2} adsorbed γ-Fe$_2$O$_3$. The giant like (bundles) structures could be due to the complex composite system.

Fig. 5(a) and (b) shows the SEM images of the colourless PbSO$_4$ crystals, which was precipitated from the eluent. The micrograph images show fine orthorhombic crystals of PbSO$_4$ with an average size of 3–4 μm.

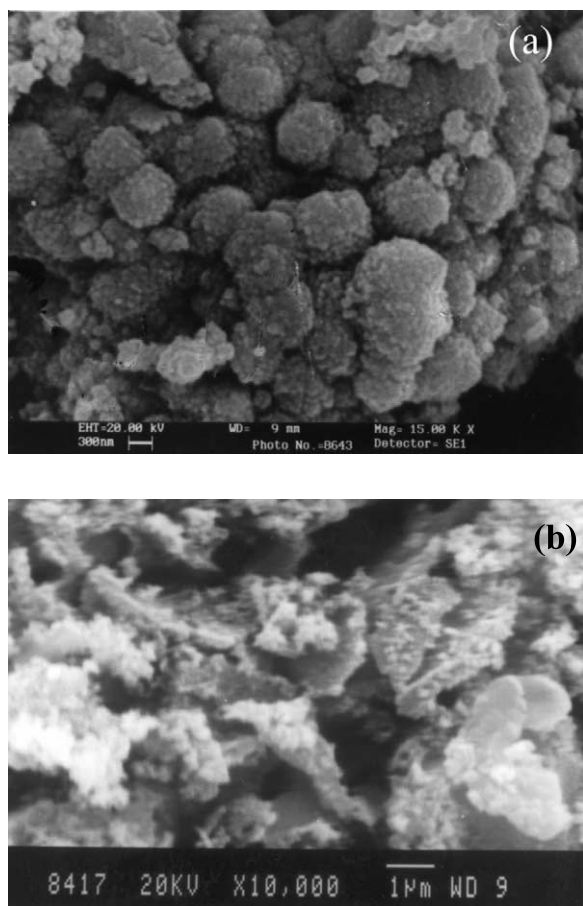Fig. 4. SEM images of (a) Pb adsorbed γ-Fe$_2$O$_3$ and (b) γ-Fe$_2$O$_3$–thiourea–Pb ternary complex.
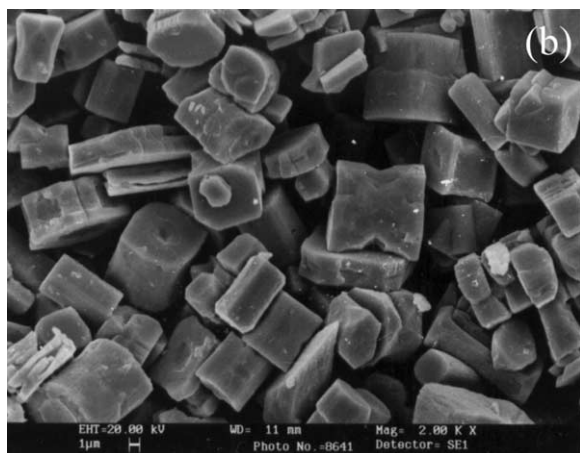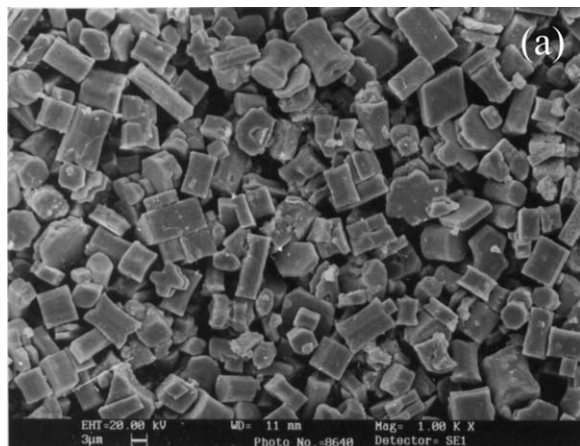
Fig. 5. SEM images of (a) low and (b) high resolution of as precipitated PbSO$_4$.

4. Conclusions

Following are the conclusions made from the above study:

- The γ-Fe$_2$O$_3$ adsorbent shows some adsorption. However, the thiourea complexed γ-Fe$_2$O$_3$ shows higher adsorption, which indicates that the complexed γ-Fe$_2$O$_3$ can act as a better solid adsorbent.
- The possible mechanism for the formation of Pb ternary complex is explained and the formation of fine orthorhombic PbSO$_4$ crystals and its precipitation is also understood on the basis of hydrolysis of thiourea.
- From these studies it may be envisaged that γ-Fe$_2$O$_3$ and complexed γ-Fe$_2$O$_3$ can act as valuable adsorbents for controlling environmental pollutants viz., lead and other heavy metals.
- The detailed understanding about the quantitative aspects and the structural transformations is the future direction of our work.

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