

Adsorption studies of lead ions on γ -Fe₂O₃-thiourea complex composite

Arunkumar Lagashetty, N N Mallikarjuna & A Venkataraman*

Department of Chemistry, Gulbarga University, Gulbarga 585 106, India

Received 1 May 2002; revised received 9 August 2002; accepted 5 October 2002

Adsorption of lead ions in aqueous solution on γ -Fe₂O₃-thiourea complex composite is reported. The adsorbent was characterised by X-ray diffraction (XRD), infrared (IR) and scanning electron micrograph (SEM) studies. The eluent was subjected to atomic absorption spectroscopy to determine the percentage of the adsorbed lead ions onto the complex composite. IR studies of the complex composite showed that the formation of hydrogen bond from the amine group of the thiourea to the surface hydroxyl groups, and lead ions adsorbed on adsorbent shows shift in frequencies and with appearance of some new peaks. SEM studies for pure γ -Fe₂O₃ show particles in the range of 100-200 nm with varying shape and size. The adsorbent shows foam net like structure on the surface of the complex composite. Atomic absorption studies showed the decrease of lead ions to 50% after adsorption with the complex composite. Solution conductivity of the eluent is increased to double that of pure lead solution after adsorption. The potential use of γ -Fe₂O₃-thiourea complex composite in adsorption study is explained.

It is a well-known fact that the decrease in particle sizes upto a nano scale, increases the surface area and hence, the number of adsorption sites. It is reported that porous alumina when prepared employing different synthetic routes, show excellent adsorption behaviour¹⁻⁴. One of the possible explanations given is that the octahedral alumina 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 -Al₂O₃.

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(II) forms strong complexes with ligands such as ethylenediaminetetraacetic acid (EDTA) and nitrolotriactic acid (NTA), and complexes of this type absorb to oxide surfaces in a fashion analogous to that of bare ligands (e.g. EDTA, NTA) rather than the metal cation^{5,6}. 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 con-

taining carboxylate functional groups⁷. These surfaces may be coated with a veneer of sorbed organic molecules in soils and aquatic sediments. Adsorption of Co(II) 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 surface⁸.

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 surface⁹. The particle morphology of the adsorbent upon adsorption is also not studied in detail by them⁹.

Lead is found in trace quantities as pollutant in petrol, gasoline oil and in environment and is a hazardous pollutant. A detailed study on the use of solid adsorbents for this metal is not reported anywhere in the literature. The present paper describes one of the first attempt on adsorption of low concentrations of lead ions on a solid adsorbent contributing to much needed pollution abatement literature. The adsorption study of Pb²⁺ ions is carried out on γ -Fe₂O₃-thiourea complex composite. Thiourea is a well-known organic ligand having C=S group and can bind strongly with the metal ions to form metal complexes. In the present study thiourea bonded to γ -Fe₂O₃ (i.e., γ -Fe₂O₃-

*For correspondence(E-mail: raman_chem@reddifmail.com;
Fax: 08472-421632)

thiourea complex composite) is used as an adsorbent. Our earlier studies¹⁰ have shown that pure $\gamma\text{-Fe}_2\text{O}_3$ could not achieve the desirable results of adsorption. Hence, the present treatment of employing a complex composite ($\gamma\text{-Fe}_2\text{O}_3$ -thiourea) is undertaken. The adsorbent and eluent are both characterised and the solid state changes occurring on adsorption are discussed with the help of XRD, IR and SEM techniques. The amount of Pb^{2+} adsorbed on to the $\gamma\text{-Fe}_2\text{O}_3$ -thiourea complex composite was estimated from atomic absorption spectroscopy. The advantage of employing a complex composite is presented in this paper.

Experimental Procedure

Preparation of ferrous oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)

A mixture of equimolar solutions of ferrous ammonium sulphate heptahydrate and oxalic acid was stirred well. The yellow precipitate of ferrous oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) obtained was filtered through sintered glass crucible and was washed with cold, oxygen-free distilled water till it was free from sulphate ion and oxalic acid, finally with dry acetone and then dried under vacuum¹¹.

Synthesis of nanosized $\gamma\text{-Fe}_2\text{O}_3$

The ferrous oxalate dihydrate 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 ignite to form $\gamma\text{-Fe}_2\text{O}_3$. On cooling to room temperature no trace of carbon impurities was observed in the final residue of $\gamma\text{-Fe}_2\text{O}_3$.

Preparation of $\gamma\text{-Fe}_2\text{O}_3$ -thiourea complex composite

First, a known weight of thiourea was dissolved in acetone and to this solution equimolar quantity of $\gamma\text{-Fe}_2\text{O}_3$ prepared by above method was added. The resulting $\gamma\text{-Fe}_2\text{O}_3$ dispersed solution was taken in a round bottom flask and was refluxed on a water bath for 6 h. After refluxing the solvent was slowly evaporated on a temperature-controlled hotplate. The final powdered product was characterised employing IR and X-ray analysis and used for adsorption studies.

Preparation of column

A glass column of equal length and diameter was taken. The bottom of the empty column was packed

with glasswool for about 1 cm height. 1g of $\gamma\text{-Fe}_2\text{O}_3$ -thiourea complex composite was poured onto the column and packed uniformly by shaking the column.

Adsorption studies

To the above prepared column, 50 mL of known concentration of lead acetate solution was added and kept aside for adsorption. After 12 h the solution was eluted and preserved for atomic absorption studies. The solid product i.e., adsorbent was washed with water and air-dried. This solid was characterised employing XRD, IR and SEM studies.

The structure of the powder was examined by a Seimens diffractometer using $\text{Cu K}\alpha$ ($\lambda=1.54 \text{ \AA}$) at 30 kV. The IR spectra were recorded using Perkin Elmer (Model-1000) spectrometer. The scanning electron micrographs were obtained from Leica-Cambridge (440).

Results and Discussion

Infrared studies

Figure 1(a) shows the IR spectra for $\gamma\text{-Fe}_2\text{O}_3$ -thiourea complex composite. The finger print region for pure $\gamma\text{-Fe}_2\text{O}_3$ (below 600 cm^{-1}) hardly shows any change when compared with pure $\gamma\text{-Fe}_2\text{O}_3$. Little shifts in the stretching frequencies, which are observed, are due to interaction of surface oxygen with thiourea. There is a chance of ambiguity that the surface oxygen of $\gamma\text{-Fe}_2\text{O}_3$ could interact with the amine hydrogen of thiourea or the Fe-atoms could interact with the sulphur atoms of thiourea, but the IR spectrum clearly indicates the first possibility. The presence of N-H stretching frequency at around 3195 cm^{-1} indicates the presence of bound NH_2 group. The bands in the range $1600\text{-}700 \text{ cm}^{-1}$ are characteristics of free C=S group where the C is bound to N.

Figure 1(b) shows the IR spectra of lead ions adsorbed onto the complex composite. The spectrum shows some shifts in frequencies in the region $1600\text{-}700 \text{ cm}^{-1}$. Some new peaks appeared below 400 cm^{-1} (354 and 376 cm^{-1}) due to the Pb-O vibrations. The N-H stretching frequency shifted to 3392 cm^{-1} as compared to Fig. 1 (a). This shift and appearance of new peaks directly indicate the adsorption of lead ions onto the complex composite through free C=S groups.

X-ray diffraction studies

X-ray diffraction studies were carried out to see the phase changes during the adsorption. Fig. 2(a) shows

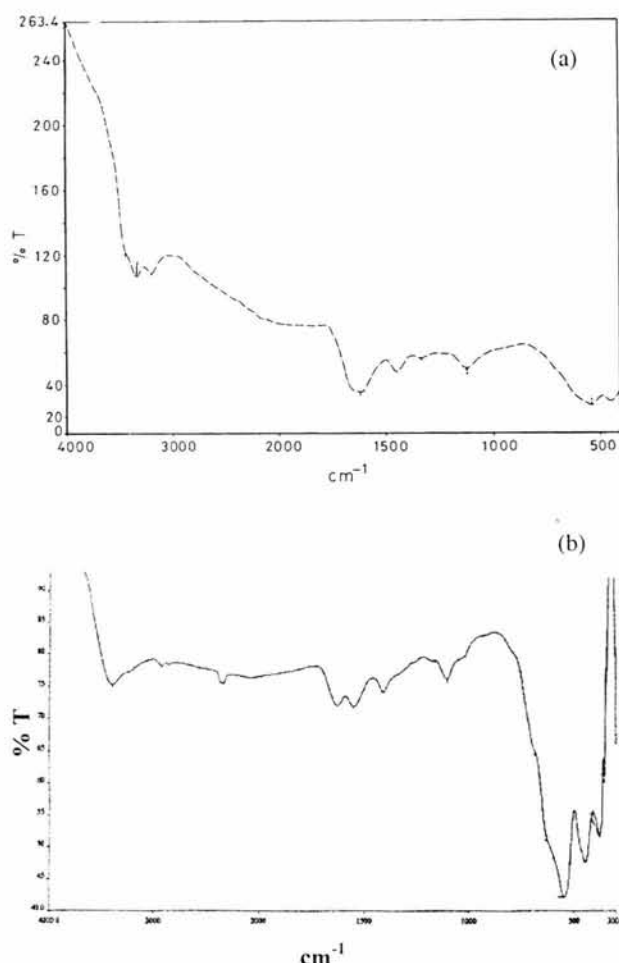


Fig. 1—IR spectra of (a) γ -Fe₂O₃-thiourea complex composite (b) lead ions adsorbed γ -Fe₂O₃-thiourea complex composite

the X-ray diffraction pattern for pure γ -Fe₂O₃. The pattern shows spinel cubic system. Unit cell parameters were calculated using PROSZKI program. Fig. 2(b) shows the X-ray diffraction pattern of lead adsorbed γ -Fe₂O₃ complex composite. The cubic crystal system of the pure γ -Fe₂O₃ retains its structure along with some additional reflections corresponding to lead adsorption on to the complex composite which again is in confirmation with IR studies where the shifting of frequencies are observed.

Scanning election micrograph studies

Particle size plays a very important role in adsorption. When the particle size decreases, higher surface area is achieved and hence high adsorption is expected. Fig. 3(a) shows the SEM image of the synthesised γ -Fe₂O₃. The particles are in the range of 100-200 nm. Two types of particles are observed, one lump type having big giant structure and other of ir-

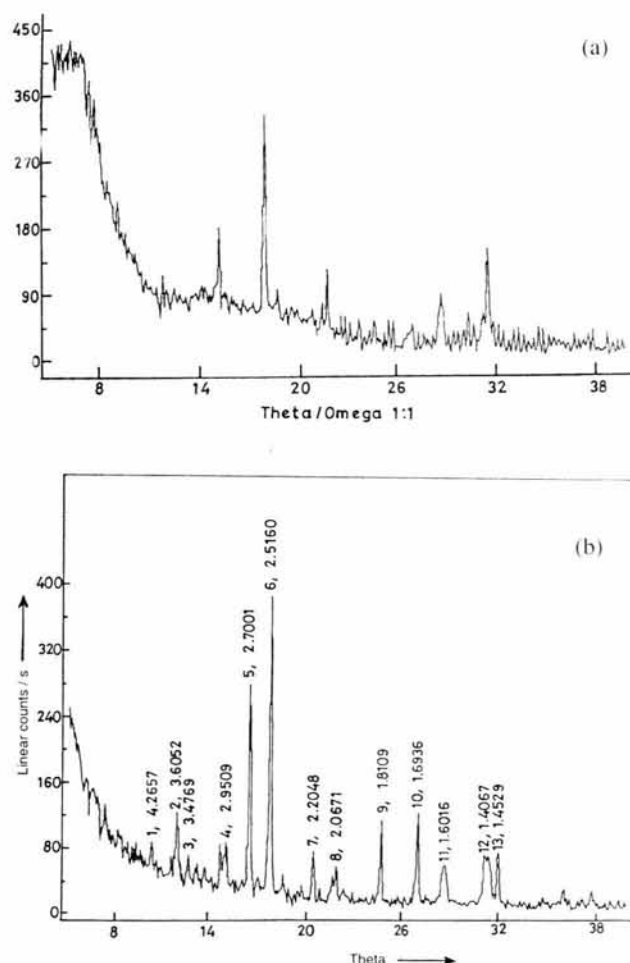


Fig. 2—XRD pattern of (a) Pure γ -Fe₂O₃ (b) lead ions adsorbed γ -Fe₂O₃-thiourea complex composite

regular shape. Fig. 3(b) shows the SEM image of lead adsorbed γ -Fe₂O₃-thiourea complex composite. A foam like net anchored to the surface of the complex corresponding to the adsorbed lead ions onto the surface can be observed. Some lump kind structure back to the foam net can also be observed due to the complex composite.

Atomic absorption spectroscopy

An atomic absorption spectrum gives an important information regarding the percentage of the metal present in a solution qualitatively and quantitatively. Atomic absorption spectrum was carried out for the quantitative estimation of lead adsorption onto the complex composite. The eluent obtained after adsorption shows the lead to be 140 ppm which is the half of the original lead solution (270 ppm). From this one may conclude that adsorption has accrued extensively by complexing the ligand thiourea.



Fig. 3—SEM images of (a) Pure $\gamma\text{-Fe}_2\text{O}_3$ (b) lead ions adsorbed $\gamma\text{-Fe}_2\text{O}_3$ -thiourea complex composite

Solution state conductivity

Solution state conductivity gives an idea about the conductivity of the solution and hence, helps in understanding qualitatively the amount of ionic species present.

The conductance of pure lead acetate solution (0.1N) in the present study was 3×10^5 , when this solution was subjected to adsorption onto the $\gamma\text{-Fe}_2\text{O}_3$ -thiourea complex composite, conductance further increases to 6.8×10^5 . This increasing value in conductance of the solution shows a definite proof of adsorption of lead ions on $\gamma\text{-Fe}_2\text{O}_3$ -thiourea complex composite.

Conclusions

- Considerable adsorption of lead ions on $\gamma\text{-Fe}_2\text{O}_3$ -thiourea surface is observed, indicating that the

complex composite can act as a potential adsorbent in the treatment of Pb^{2+} pollution.

- X-ray diffraction studies showed that $\gamma\text{-Fe}_2\text{O}_3$ retains its structure after complexing with thiourea and as well as lead ions adsorption onto the surface of complex composite.
- IR studies showed that the formation of hydrogen bonds in complex composite and appearance and or disappearance of peaks after adsorption.
- SEM studies showed different particles with varying shape and size and afterwards lead ions adsorption, along with thiourea showed a foam net like structure.
- From atomic absorption studies it is observed that 50% of the lead ions are adsorbed onto the surface of $\gamma\text{-Fe}_2\text{O}_3$ -thiourea complex composite.
- Solution conductivity increases considerably on adsorption.

Acknowledgements

The authors thank UGC, New Delhi for financial assistance, and The Chairman, Department of Chemistry, Gulbarga University, Gulbarga, for providing laboratory facilities.

References

1. Bargar J R, Towle S T, Brown Jr G E & Parks G A, *Geochim Acta*, 60 (1996) 3541.
2. Bargar J R, Towle S T, Brown Jr G E & Parks G A, *J Colloid Int Sci*, 185 (1997) 473.
3. Bargar J R, Brown Jr G E & Parks G A, *Geochim Acta*, 61 (1997) 2617.
4. Towle S T, Bargar J R, Brown Jr G E & Parks G A, *J Colloid Int Sci*, 187 (1997) 62.
5. Girvin D C & Glassman P L, *Soil Sci Soc Am J*, 57 (1993) 1.
6. Zachara J M, Smith S C & Kuzel L S, *Geochim Cosmochim Acta*, 59 (1995) 4825.
7. Davis J A, *Geochim Cosmochim Acta*, 46 (1982) 2381.
8. Zachara J M, Smith S C & Kuzel L S, *Geochim Cosmochim Acta*, 58 (1994) 553.
9. Toru T, Sadatsuger O & Nabuhiko K, *J Poly Sci. Poly Chem Ed*, 23 (1985) 2109.
10. Arunkumar Lagashetty, Govindaraj B, Vijay Hiremath Mallikarjuna N N & Venkataraman A, *Paper presented at XIXth Indian Council of Chemists Conference (PO 71)* held at Kuvempu University, Shimoga, 2000.
11. Vogel A I, *Quantitative Inorganic Analysis* (ELBS Longman, London), 1979.
12. Mallikarjuna N N, B Govindaraj, Arunkumar Lagashetty & Venkataraman A, *J Therm Anal Calor* (In press).