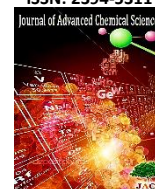




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Nano Sized Cobalt Oxide as Adsorbent for Pb(II) Ions

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ABSTRACT

Metal oxide nanomaterials are synthesized by combustion route is attracted by researcher due to its simple experimentation, which integrates the materials chemistry. Nanosized cobalt oxide is prepared by combustion route using polymer as a fuel. Adsorption studies of lead ions on as prepared cobalt oxide sample is undertaken. Dynamic method is adopted for the adsorption study of lead ions on the cobalt oxide sample. The results obtained show that, the cobalt oxide acts as a very good adsorbent for heavy lead ions. Lead adsorbed cobalt oxide sample was well characterized for its structure by employing powder X-ray diffraction (XRD) tool. The morphology of adsorbate material was studied by Scanning Electron Micrograph (SEM) tool. Fourier Transform infrared (FTIR) spectral study was undertaken to know the bonding nature in the cobalt oxide sample. EDX analysis is undertaken to know the presence of adsorbed lead on cobalt oxide adsorbent. Solution conductivity study and Atomic absorption study is also undertaken for better confirmation of the adsorption behaviour.

1. Introduction

The surface area of crystalline materials increase with decrease in particle size, which increases the adsorption sites on the materials. Many metal oxides prepared by employing different synthetic routes [1-4], show excellent adsorption behavior. The octahedral aluminum sites are fully occupied while vacant sites are randomly disturbed at the tetrahedral positions of the alumina. These vacant sites in the structure are mainly responsible for the adsorption behavior on alumina material. In general many of the organic legands forms a metal complexes during its adsorption and complexes of this type sorb to oxide surfaces [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. Cobalt oxide surfaces show high affinity towards organic molecules containing functional groups [7]. These surfaces may be coated with a veneer of sorbed organic molecules in soils and aquatic sediments. Metal ions adsorption on cobalt oxide is enhanced by the presence of its high surface area [8].

A recent study by Cheah et al. [9] illustrates the significant effect that some organic ligands can have metal adsorption at metal oxide-water interfaces. Cu(II) sorbs on γ -Al₂O₃ more strongly at low pH ~ 4 than an amorphous silica [10-11]. However, pyridine enhances Cu(II) sorption on amorphous SiO₂ but inhibits uptake of Cu(II) on γ -Al₂O₃ relative to the bipyridine free system. Based on Cu(II) K-edge XAFS spectra, EPR and UV-vis spectra, Cheah et al. concluded that Cu(II) sorbs predominately as dimeric complexes on the amorphous SiO₂ surface and as monomeric complexes on the γ -Al₂O₃ surface. 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. The particle morphology of the adsorbent upon adsorption is also not reported in detail. Lead is found in trace quantities as pollutant in petrol, gasoline oil and in environment. A detailed study on the use of solid adsorbents for this metal is not reported much in the literature.

The present work reports the possible application cobalt oxide (Co₃O₄) as a potential adsorbent for heavy lead ions. Dynamic method is adopted

for the adsorption study. The adsorbent was characterized by employing XRD, IR, SEM and EDX techniques. The amount of Pb⁺² adsorbed on to the Co₃O₄ was estimated from atomic absorption spectroscopy and further confirmed by solution conductivity and AAS study.

2. Experimental Methods

2.1 Adsorption Studies

Exactly 0.1 M lead acetate solution is prepared in 100 mL volumetric flask. A nozzle based glass column with well cap is used for adsorption study in which its bottom is packed with glass wool for about 1 cm height. Our earlier study reports the synthesis of cobalt oxide by combustion route and is well characterized [12]. One gram of as prepared Co₃O₄ sample was poured into the glass columns and is packed uniformly by shaking the column slowly. 50 mL of 0.1 M lead acetate solution was added in to the column and kept aside for adsorption for about 12 h. After 12 h the solution was eluted and preserved for atomic absorption study and solution conductivity study. The solid product i.e. cobalt oxide adsorbent was air-dried. The adsorption column is as shown in Fig. 1. This adsorbent was characterized by employing XRD, IR, EDX and SEM studies.

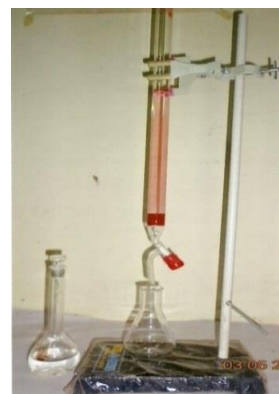


Fig. 1 Adsorption column

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2.2 Characterization

The structure of lead adsorbed cobalt oxide sample was studied by X-ray diffraction using Phillips X-ray diffractometer (PW3710) with Cu K α as source of radiation. Morphology of the cobalt oxide sample was investigated using a field-emission scanning electron microscope (FE-SEM model: FEI-200NXL, Hillsboro, OR, USA), equipped with an energy-dispersive X-ray (EDX) spectrometer for elemental analysis. Bonding nature of the sample was studied by Perkin–Elmer 1600 spectrophotometer in KBr medium tool.

3. Result and Discussion

3.1 X-ray Diffraction Studies

Fig. 2 shows XRD pattern of lead adsorbed Co₃O₄. The pattern shows highly intense Bragg's reflections show the crystalline nature. Co₃O₄ reflections are observed on comparison with our earlier study [13]. It also shows some additional Bragg's reflections corresponding to lead ions, which is adsorbed on the surface of Co₃O₄ particles. Adsorbed lead peaks in the lead adsorbed pattern are identified by JCPDS file no. 44-0872. These additional lead peaks in adsorbed pattern confirms the lead adsorption on the Co₃O₄ surface.

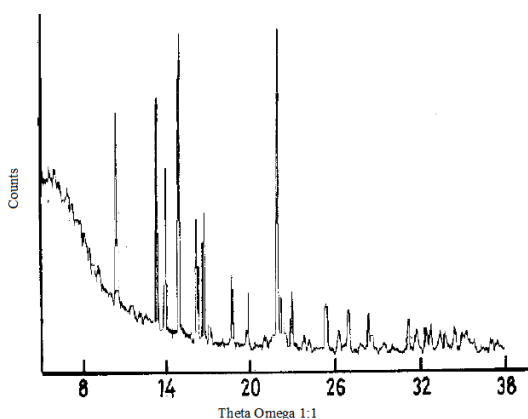


Fig. 2 XRD pattern of lead adsorbed Co₃O₄

3.2 Scanning Electron Micrograph

Fig. 3 shows SEM image of lead adsorbed Co₃O₄. The image shows fine spherical particles agglomerated each other. Close compact structure of these particles are also observed in the image. Self-assembled spherical lead particle on the surface of the oxide can also be viewed.

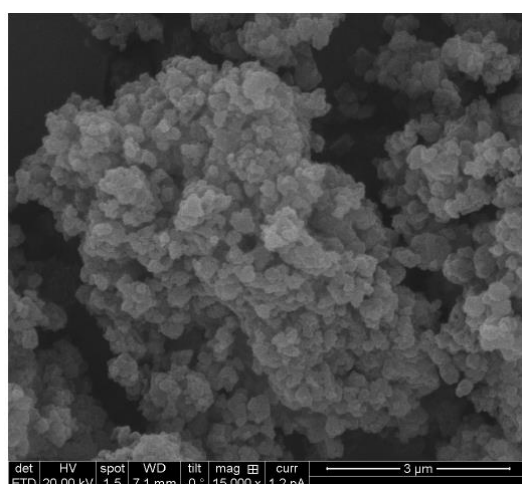


Fig. 3 SEM image of lead adsorbed Co₃O₄

3.3 Infrared Studies

Table 1 shows the vibrational frequencies of lead adsorbed Co₃O₄ sample. The bands at 440, 480 and 550 cm⁻¹ are due to the presence of metal-Oxygen vibrational frequency i.e. below 100 cm⁻¹ [14]. The IR bands at 1300 cm⁻¹ is the characteristic of acetate group. Bands at 1025 in lead adsorbed Co₃O₄ is assigned to in plane bending of CH₃ group. The other peaks at around 1090, 1025 and 1270 cm⁻¹ corresponds to overtones.

Careful observation of IR spectra of pure cobalt oxide and its lead adsorbed sample shows the new bands are weak in nature in the latter case, which indicates a weak interaction of the adsorbed Pb²⁺ ions on the cobalt oxide. The weak interactions are possibly due to the fewer amounts of Pb²⁺ ions adsorbed.

Table 1 Vibrational bands of lead adsorbed Co₃O₄

S.No.	Vibrational frequencies (cm ⁻¹)
1	440
2	480
3	550
4	1025
5	1090
6	1270
7	1300

3.4 Atomic Absorption Study and Conductivity Results

An atomic absorption spectroscopic characterization was carried out for the blank lead acetate solution and the eluent solution after adsorption of Co₃O₄. Table 2 shows the atomic absorption spectroscopy results of blank and eluent lead solutions. The initial concentration of lead acetate solution is 294 ppm, whereas after adsorption, the concentration of lead solution decreases to 190 ppm. This decrease in concentration of eluent solution indicates the absence of some lead ions in the eluent lead solution and confirms the adsorption of lead ions on the metal oxides.

Table 2 AAS and Solution Conductivity results of Co₃O₄

Sl. No	Property	Pure Lead acetate solution	Eluent lead solution
1	Atomic Absorption Spectroscopy (ppm)	294	190
2	Conductivity (mho ⁻¹)	3.2 x 10 ⁻⁵	5.2 x 10 ⁻⁵

Solution conductance gives information about the conducting nature of pure lead acetate as well as eluent lead solutions of Co₃O₄. The concentration goes on decreasing the conductance increases because of rapid movement of the metal ions. Table 2 gives the conductivity results of pure lead solution and eluent lead solutions of Co₃O₄. The conductance of pure lead acetate solution is 3.2 x 10⁻⁵ mho⁻¹, whereas eluent solution of Co₃O₄ is 5.2 x 10⁻⁵ mho⁻¹ respectively. This increase of conductance indicates the absence of some lead ions in the eluent solution and confirms the adsorption of lead ions on the cobalt oxide.

3.5 Energy Dispersive X-Ray Microanalysis Studies (EDX)

The energy dispersive X-ray microanalysis was carried out to know the presence of lead adsorption on cobalt oxide surface. Fig. 4 shows the EDX pattern of lead adsorbed cobalt oxide sample. This pattern shows the presence of both lead and cobalt peaks, confirms the lead adsorption on cobalt oxide surface.

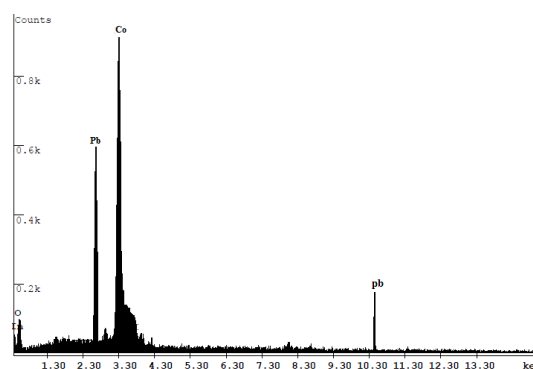


Fig. 4 EDX pattern of lead adsorbed Co₃O₄

4. Conclusion

The characterization study indicates shows considerable adsorption of lead ions on high surface area Co₃O₄ surfaces. This adsorption study of lead ions on Co₃O₄ also reveals that this cobalt oxide acts as valued adsorbents for other heavy metal ions like lead and mercury. Amount of lead ions adsorbed on metal oxide surface depends on the history of the preparative techniques. Dynamic method for the adsorption needs simple equipment; it may be adopted for other metal oxides adsorbent and other metal ions adsorbate.

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