Functionalized Nanoparticles as Sorbents for Removal of Toxic Species

Jerina Majeed, Jayshree Ramkumar, S. Chandramouleeswaran, A. K. Tyagi

Abstract—Removal of various toxic species from aqueous streams is of great importance. Sorption is one of the important remediation procedures as it involves the use of cheap and easily available materials. Also the advantage of regeneration of the sorbent involves the possibility of using novel sorbents. Nanosorbents are very important as the removal is based on the surface phenomena and this is greatly affected by surface charge and area. Functionalization has been very important to bring about the removal of metal ions with greater selectivity.

Keywords—Mercury, lead, thiol functionalization, ZnO NPs.

I. INTRODUCTION

HEAVY metal ions like lead and mercury are known to be toxic and there are stringent specifications for these metal ions in drinking water imposed by the WHO [1]. Hence it is of great interest remove these ions from water stream. A large number of procedures are available for removal of toxic species [2]-[7]. However, sorption using cheap and simple for the removal of these ions from water streams. Nanosorbents are class of sorbents which become useful due to their high surface area and activity. The nanomaterials can be synthesized using simple protocols and the surface charge can be fine tuned by simple experimental conditions. Moreover, the protocols adopted for synthesis is very simple and does need expensive reagents and thus the scale-up if possible can also add to the advantages of nanosorbents [8]. Also many of the nanomaterials are multifunctional and therefore when used for sorption or removal of toxic species can also result in other treatment procedures like antibacterial treatments.

In the present work, the sorption behavior of thiol functionalized ZnO nanoparticles have been evaluated with respect to uptake of toxic heavy metal ions like mercury and lead.

II. EXPERIMENTAL

ZnO@SH NPs was prepared by simple precipitation of Zn (II) in basic medium followed by *in situ* coating of Thiol group.

Jerina Majeed is with the Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India, (Tel: +91 22 25592327; Fax: +91-22-25505151; e-mail: jerina@barc.gov.in)

Jayshree Ramkumar and S. Chandramouleeswaran are with Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India, (e-mail: jrk@barc.gov.in, chandru@barc.gov.in)

A. K. Tyagi is with Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India,(Tel: +91 22 25595330; Fax: +91-22-25505151; email: aktyagi@barc.gov.in)

In a typical synthesis, desired amount of Zn $(NO_3)_2$ was dissolved in 25ml double distilled water in a round bottom flask to get a 2M solution. The reaction mixture was heated to 70°C under vigorous stirring. 50ml of NaOH (2M) was added drop by drop to the mixture till the pH of the medium is 11-12. Further, the reaction was continued at 70°C for 2hr. In order to get thiol coating, 1g of thiourea was added to the above mixture and reacted for 1h at same conditions. The obtained white precipitate was centrifuged and washed with distilled water and acetone to remove the unreacted particles.

X-ray diffraction (XRD) pattern was recorded on a PANalytical's X'Pert PRO diffractometer with Cu Kα radiation. The crystallite size was determined from the X-ray line broadening using Scherrer equation. The surface area and porosity of the samples was obtained from physical adsorption of N_2 at 77K, using a Micromeritics ASAP 2020 analyzer. Prior to N_2 physisorption data collection, the samples were degassed at 150^0C under vacuum for 12h.

Sorption studies were carried out in batch mode wherein 10mL of the solution containing a known amount of the solute at near neutral pH was equilibrated for a known period. After equilibration, the amount left behind in solution was determined by ICP-AES. From these studies the amount taken up by the sorbent was calculated.

III. RESULTS AND DISCUSSION

XRD analysis (Fig. 1 (a)) confirms the formation of highly crystalline single phasic hexagonal wurzite structure of ZnO with an average crystallite size of ~9nm. The surface modification by the thiol moieties on to the ZnO surface was suceesfull as can be seen from the IR spectra (Fig. 1 (b)).The presence of a band at 2557cm^{-1} is attributed to the S-H vibration and a broad peak around 490cm^{-1} is assigned to the Zn-O vibration. From SEM images (Fig. 1 (c)) confirmed the formation of spherical shaped (well defined and discrete) structures of very small size. Furthermore to investigate the porous nature of the ZnO sample, we measured the N_2 adsorption- desorption isotherm. The N_2 isotherm (Fig. 1 (d)) displays the typical type IV curve accompanied by a type H_3 hysteresis loop, which is usually attributed to the predominance of 3D network of mesopores.

The BET surface area plot of ZnO-SH corresponds to the well known BET equation (Inset of Fig. 1 (d)). In the current case, the BET specific surface area was calculated at 38m^{2}g^{-1} with micropore volume of 0.002557cm³/g, mesopore volume of 0.3557cm³/g and total pore volume of 0.4086cm³/g. In general, porous materials can have more than one class of pores like micropores and mesopores. The N_2 adsorption data

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:8, No:6, 2014

can be plotted as a t-plot, in which the quantity of N_2 adsorbed is ploted as a function of the statistical thickness, (t), of an adsorbed layer on a non-porous surface. If mesopores are present in the adsorbent, capillary condensation will occur in each pore when the relative pressure reaches a value which is related to the pore radius by the Kelvin equation, the t-plot will therefore show an upward deviation commencing at the relative pressure at which the finest pores are just being filled and the extrapolated plot will pass through the origin. On the other hand, if microporosity exists, the uptake is enhanced at the low pressure region and a positive intercept will be observed which can be assigned to micropore volume.
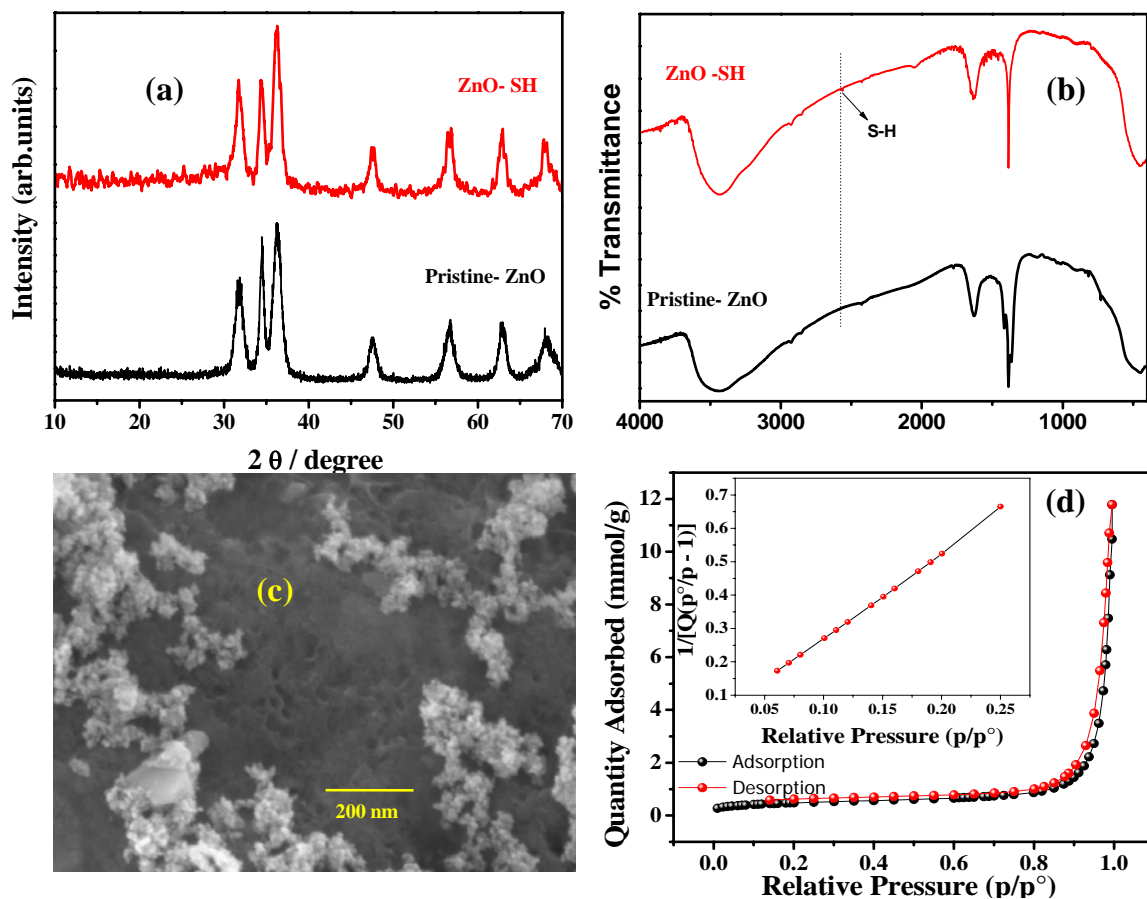
Fig. 1 (a) XRD pattern, (b) IR spectra, (c) SEM micrograph and (d) N_2 adsorption-desorption isotherm of ZnO-SH nanoparticles. (Inset of Fig. 1 (d) shows the BET surface area plot of ZnO-SH nanoparticles)

The pore size distribution analysis of ZnO nanoparticles were performed on desorption branch of the isotherm by Barrett-Joiner- Halenda (BJH) method. The BJH desorption dV/dD pore volume versus pore diameter plot of ZnO nanoparticles show a broad distribution of mesopres with average pore diameter of 46nm. The surface area of pores (S^P_{BJH}) and pore volume (V^P_{BJH}) of ZnO were found to be 35m²/g and 0.4048cm³/g respectively.

The sorption studies were carried out at room temperature and near neutral conditions of solution pH. This was carried out with an aim of understanding the sorption properties at conditions of real samples thus leading to a potential application of these sorbents in actual water systems. The studies were carried out using 10mg of the sorbent. Various experimental factors were varied to get optimum conditions to achieve maximum uptake.

The time of equilibration is one of the experimental conditions which were varied in the range of 10-60mins. It was seen from Fig. 2, the uptake was complete within the first 10mins. Therefore further studies were carried out by equilibration for 10mins.
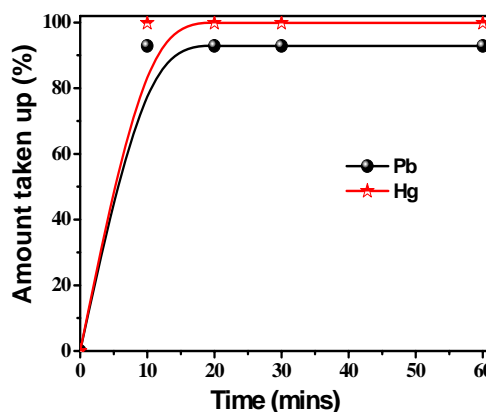

Fig. 2 Effect of equilibrium time on the amount of Pb^{2+} taken up

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:8, No:6, 2014

The effect of initial metal ion concentration on the uptake was studied by varying the concentration between 1-10mg/L. Fig. 3 shows the adsorption efficiency of ZnO-SH nanoparticles as a function of time. The sorbent was found to be efficient in removing the toxic metal ions within 10min of equilibration. More interestingly, at a period of 10min ZnO-SH showed almost 100% removal efficiency for Hg^{2+} and about 90% for $Pb^{2+.}$
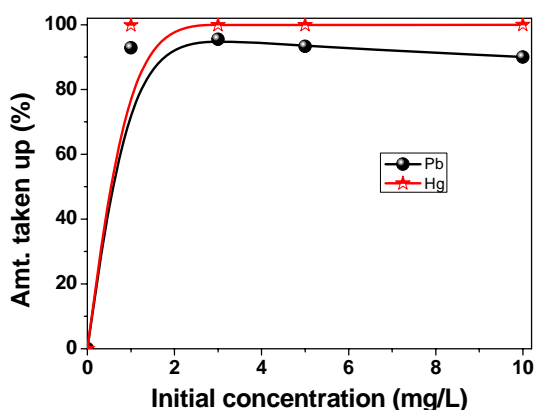

Fig. 3 Effect of initial concentration of metal ion on the uptake

It was seen that for the entire concentration range the amount taken up was nearly 99.9% for mercury. The amount of lead taken up was around 90% and it decreased with increase in concentration.

The system was then applied to a synthetic mixture containing 10mg/L of each of the metal ion. The results are given in Fig. 4. The removal efficiency of metal ions with 100mg of ZnO-SH nanoparticles are found to be about 7%, 9%, 27%, 90% and 99% for Co^{2+}, $Ni^{2+,}$ Cu^{2+}, Pb^{2+} and Hg^{2+} respectively
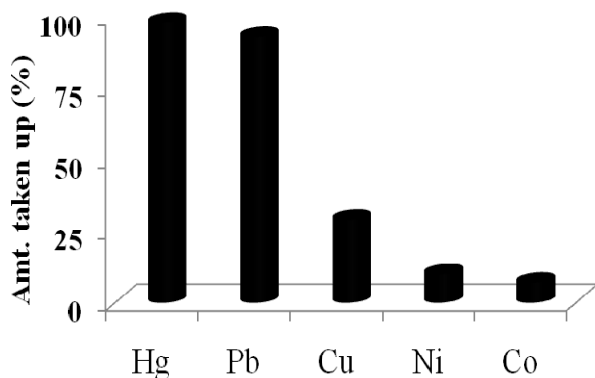

Fig. 4 Removal efficiency of different toxic metal ions by ZnO-SH nanoparticles

Though the exact mechanism is not clear, we assume that the combination of porous structure of the nanosorbent, electronegativity of metal ions and the high affinity between –SH groups on the nanosorbent and ions like Pb^{2+} and Hg^{2+} ions attribute to their rapid and selective sorption as compared to the other metal ions. The electronegativity values of Co^{2+},

Ni^{2+}, Cu^{2+}, Hg^{2+} and Pb^{2+} are 1.88, 1.91, 1.95, 2.00 and 2.33 respectively. Due to the high electronegativity Hg and Pb have stronger attraction toward the ZnO-SH nano structure and hence exhibit better removal efficiency.

IV. CONCLUSION

A simple synthesis procedure is followed for the preparation of thiol coated ZnO nanoparticles. The thiol coating on to the surface of the nanoparticles is confirmed via IR spectra and the mesopores nature from porosity measurement. Our preliminary studies on removal of toxic metal ions suggested that functionalization of nanoparticles surface with thiol group makes it highly efficient for sorptive removal of Pb^{2+} and Hg^{2+} from waste water.

REFERENCES

[1] F.W. Pontius, *J. Am. Water Works Assoc.,* 1996, 88:22-27, 30-33.
[2] J. Y. Choi, D. S. Kim, J. Y. Lim, J. *Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 2006, 41, 1155-1172.
[3] S. Pacheco, R. Rodriguez, *J. Sol-Gel Sci. Technol.* 2001, 20, 263–273.
[4] F. M. Koehler, M. Rossier, M. Waelle, E. K. Athanassiou, L. K. Limbach, R. N. Grass, D. Günther, W. J. Stark, *Chem. Commun.* (Cambridge), 2009, 4862–4864.
[5] S. Singh, K. C. Barick, D. Bahadur, *J. Mater. Chem. A.* 2013, 1, 3325 - 3333.
[6] B. R. White, B. T. Stackhouse, J. A. Holcombe, *J. Hazard. Mater.* 2009, 161, 848–853.
[7] S. Singh, K. C. Barick, D. Bahadur, *J.Hazard. Mater.* 2011, 192, 1539-1547.
[8] Jerina Majeed, Jayshree R, S. Chandramouleeswaran, O. D. Jayakumar, A. K. Tyagi , *RSC Adv.* 2013, 3, 3365-3373.