# Ultrasound Promoted Expulsion of Lead Ions from Wastewater using Ionic Liquid Modified Aluminium Isopropoxide 

A. Kaur*, A. Pathak** and B. Kaur*<br>*Department of Chemistry, Akal Degree College, Mastuana, Sangrur 148 001, Punjab, India<br>**Department of Chemistry, Guru Kashi University, Talwandi Sabo, Punjab, India

(Received 7 January, 2022; Accepted 2 March, 2022)


#### Abstract

In the present investigation Methyltrioctylammonium Chloride modified Aluminium isopropoxide was prepared under ultrasonicator. The IL-Aluminium isopropoxide was characterized using FTIR and X-ray diffractometer (XRD). The Prepared IL-Aluminium isopropoxide was tested for the adsorption of $\mathrm{Pb}^{2+}$ from aqueous solution and isotherms were determined. The $\mathrm{Pb}^{2+}$ adsorption performance of the prepared samples was studied by Atomic Adsorption Spectroscopy (AAS) method. Adsorption of $\mathrm{Pb}^{2+}$ on the chemically modified Aluminium isopropoxide was correlated well with the Langmuir model. Correlation coefficients $\left(R^{2}\right)$ of Langmuir adsorption isotherms was 0.9994 . Efficient synthesis strategy and high adsorption efficiency of IL-Aluminium isopropoxide showed a best ability to remove $\mathrm{Pb}^{2+}$ metal ions from water.


Keywords: Methyltrioctylammonium Chloride, Adsorption, Ultrasonication, Aluminium isopropoxide.

## Introduction

Lead ions commonly exist in industrial and agricultural wastewater and acidic leachate from landfill sites in relatively high concentration. They are quite harmful to human and living things (Machida et al., 2006). The maximum allowable level of lead in drinking water has been set at a concentration of 100 ppb by the World Health Organization (Orumwense, 1996). Lead contamination of drinking water is often a result from corrosion of lead-containing plumbing (Halttunen et al., 2007). Long-term drinking water containing high level of lead ion would cause serious disorders, such as nausea, convulsions, coma, renal failure, cancer, and subtle effects on metabolism and intelligence (Li et al., 2005). Up to now, many techniques have been applied to remove Pb (II) ion from wastewater, such as ion ex-
change, coprecipitation, cloud point extraction, membrane filtration, flocculation, reverse osmosis, adsorption (Rao et al., 2007; Ghaedi et al., 2009; Uluozlu et al., 2010; Karbassi and Nadjafpour, 1996; Soylak, 2010; Gupta and Ali, 2004) and so forth. Among these methods, adsorption-based methodology is highly efficiency, cost-effectiveness, simple operation, and environmental friendliness (Huang et al., 2011). Normally, adsorption is strongly dependent on the pore structure and surface area of the adsorbents whereas metal ion uptake is largely ascribed to ion exchange or chemical adsorption on specific adsorption sites (Kuchta et al.,
2005). Thus, modification of the surface chemistry strongly influences the metal ion adsorption process (Hyung et al., 2007). Several kinds of adsorbents have been used to remove Pb (II) ion from wastewater. Some of the adsorbents are natural and the oth-
ers are synthetic. In this paper, we report a novel ionic liquid modified Aluminium isopropoxide adsorbent used to adsorb Lead ions from wastewater. Methyltrioctylammonium Chloride was used as an ionic liquid to modify the adsorption properties of Aluminium isopropoxide under ultrasonicator.

## Materials and Methods

## Chemicals and Instruments

Chemicals used in the work were obtained from various companies, such as Methyl trioctylammonium Chloride was procured from Sigma Aldrich, Aluminium isopropoxide and Ethanol were purchased from MERCK.

Sonicator used in this study was of Microsil model no. GB2500B ultrasonic bath cleaner (with a frequency of 40 KHz and capacity of 2500 ml ) and FTIR spectra of the samples were obtained by using FT-IR Spectrometer (FTLA2000 spectrophotometer using KBr disc method). The phases of the synthesized adsorbent were determined by an X-Ray diffractometer (XRD) (Maker: Broker, Model: D8 Advance. Adsorption was analysed by UV-260 (UV260, Shimadzu)

## Results and Discussion

## Synthesis of Methyltrioctylammonium chloride modified Aluminium isopropoxide

4 mmol of Methyltrioctylammonium Chloride was added in 15 ml of Ethanol and was sonicated for 30 min . at room temperature. Then 10 ml of Ethanol
was added to 10 mmol of Aluminium isopropoxide and sonicated for 30 min . at room temperature. After this both solutions of ionic liquid and Aluminium isopropoxide were mixed and sonicated for 4 hr at $40^{\circ} \mathrm{C}$ to form a colloid. Temperature is wellordered by adding cold water in ultrasonicator bath after every 15 minutes. Then, colloid was put into oven to endure solvent evaporation process. The final product will be gained after grinding with pestle mortar.

## Characterization

To study the functional groups and bonds characteristic of the IL-Aluminium isopropoxide, Fouriertransform infrared spectroscopy (FTIR) and X-Ray diffraction was carried out on specimens.

## FTIR Analysis

The FT-IR spectra of the activated Aluminium isopropoxide was recorded by Perkin Elmer 100 spectrometer using potassium bromide ( KBr ) disc method.

Peak at $1461.484 \mathrm{~cm}^{-1}$ due to $C=C$ stretch. Peak at $3043.451 \mathrm{~cm}^{-1}$ due to OH stretch. Peak at 1378.304 $\mathrm{cm}^{-1}$ due to aromatic overtones. Peaks falling in the range of $1088.565 \mathrm{~cm}^{-1}$ and $722.229 \mathrm{~cm}^{-1}$ are due to C H wags of alkenes.

## XRD Analysis

XRD spectra of Aluminium isopropoxide and ILAluminium isopropoxide were recorded. The different phases of the Aluminium isopropoxide and ILAluminium isopropoxide were examined by an X Ray diffractometer (XRD). Comparison of both spec-


Fig. 1. FT-IR spectra of Methyltrioctylammonium Chloride modified Aluminium isopropoxide
tra was done, and it was investigated that no characteristic peak of unmodified Aluminium isopropoxide appeared. The crystalline phase appeared in the IL-Aluminium isopropoxide from the three peaks at position $12^{\circ}, 16^{\circ}$ and $24^{\circ}$. Other peaks were broad expressing amorphous nature of synthesized compound.

## Adsorption Essay

Stock solutions of $1000 \mathrm{mg} \mathrm{l}^{-1}$ of lead Pb (II) in distilled water was prepared from the salt precursor $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}$. By diluting the stock solutions, the working solutions for adsorption test was prepared. The adsorption isotherms were performed under favourable conditions for the Lead, as previously determined: initial pH of Lead solution was 3 at room temperature (approximately $35^{\circ} \mathrm{C}$ ). The concentration of metal ion varied from 10 to $500 \mathrm{mg} \mathrm{l}^{-1}$. The initial pH of the metal solutions was adjusted by adding $0.1 \mathrm{M} \mathrm{HNO}_{3}$ or 0.1 M NaOH . After reaching equilibrium, the mixture was filtered through Whatman filter paper. The content of $\mathrm{Pb}(\mathrm{II})$ in the filtrate were analysed with Atomic Absorption Spectrophotometer (Perkin Elmer 3100) provided with hollow cathode lamps for lead ( $=217.0 \mathrm{~nm}$ ).

The adsorption capacity of Aluminium Isopropoxide was calculated as follows:

$$
\mathrm{qe}=\mathrm{V}(\mathrm{Ci}-\mathrm{Ce}) / \mathrm{m}
$$

qe is the adsorption capacity $\left(\mathrm{mg} \mathrm{g}^{-1}\right)$ at equilibrium, V is the volume of solution in litres, Ci is the initial concentration of the metal in solution (in mg $1^{-1}$ ), and Ce its concentration at equilibrium. In liq-uid-solid systems, the isotherm models most used is Langmuir isotherm. The linearized form Langmuir of this isotherm is represented by the following equation:

$$
\mathrm{C}_{\mathrm{e}} / \mathrm{q}_{\mathrm{e}}=\frac{1}{\mathrm{bq}_{\max }}+\frac{\mathrm{C}_{\mathrm{e}}}{\mathrm{q}_{\max }}
$$

Where Ce is the concentration of adsorbate ( $\mathrm{mg} \mathrm{l}^{-}$ ${ }^{1}$ ) at equilibrium, qe is the amount of adsorbate retained per gram of adsorbent $\left(\mathrm{mg} \mathrm{g}^{-1}\right)$, qmax ( $\mathrm{mg} \mathrm{g}^{-}$ ${ }^{1}$ ) is Langmuir constants related to the maximum adsorption capacity and $\mathrm{b}\left(\mathrm{mg}^{-1}\right)$ is Langmuir constants related to the maximum adsorption energy.

## Effect of initial concentration

Figure 5 shows the adsorption curves of $\mathrm{Pb}^{2+}$ at different initial concentration and the pH values of the solution was kept original without any treatment ( pH 7 7). It is observed that the adsorption capacity of


Fig. 2. XRD spectra of unmodified Aluminium isopropoxide


Fig. 3. XRD spectra of Methyltrioctylammonium Chloride modified Aluminium isopropoxide


Fig. 4. Langmuir isotherm for the adsorption of $\mathrm{Pb}^{2+}(\mathrm{pH}$ at 7.0, Temperature at $35^{\circ} \mathrm{C}$ )
$\mathrm{Pb}^{2+}$ increases with increasing the initial concentration, while the removal percentage decreases. This may be attributed to the fact that the driving force provided by high initial dye concentration can overcome the mass transfer resistance between the aqueous and solid phases ((Nuengmatcha et al., 2014; Kumar et al., 2013). The ratio of available surfaceactive sites to the dye molecule decreases at higher concentrations, resulting in the decreases of remove percentage. The absorption capacity of $\mathrm{Pb}^{2+}$ increases from $45.4 \mathrm{mg} \mathrm{g}^{-1}$ to $265.6 \mathrm{mg} \mathrm{g}^{-1}$ with the increasing of concentration from $30 \mathrm{mg} \mathrm{l}^{-1}$ to $270 \mathrm{mg} \mathrm{l}^{-}$


Fig. 5. The adsorption curves of $\mathrm{Pb}^{2+}$ at different standard reaction conditions i.e. ( pH :- 7, Time:- 60 min ., Temp:- $35^{\circ} \mathrm{C}$ )
${ }^{1}$. Based on the above discussion, the most favourable adsorption of $\mathrm{Pb}^{2+}$ is seen at concentration of $220 \mathrm{mg} \mathrm{L}^{-1}$. With further increase in concentration of the solution the adsorption capacity becomes constant and no increase in adsorption capacity.

## Effect of pH

The pH of solution is a very vital factor in the adsorption process. The effect of pH was studied in the range of $2-7$ for $\mathrm{Pb}^{2+}$. The adsorption capacities of $\mathrm{Pb}^{2+}$ increase with increasing solution pH . Maximum adsorption capacity $250 \mathrm{mg} / \mathrm{gm}$ obtained at 7 pH .

## Effect of Contact Time

The adsorption capacity of $\mathrm{Pb}^{2+}$ increases sharply at the initial stage, then become slower and gradually reaches the equilibrium. This is probably due to the existence of a large number of absorption sites and the strong driving force for absorption at the initial stage (Cechinel et al., 2014; Pokhrel and Viraraghavan, 2104). As the time prolongs, the more and more absorption sites can be occupied by $\mathrm{Pb}^{2+}$, which leads to the slow rate of absorption, and eventually approaches equilibrium after 1 h .

## Effect of Temperature

The adsorption capacity increases with an increase of temperature from $25^{\circ} \mathrm{C}$ to $40^{\circ} \mathrm{C}$ then declines as the temperature increased further. The maximum adsorption capacity $\left(250 \mathrm{mgg}^{-1}\right)$ can be obtained at $35^{\circ} \mathrm{C}$.

## Acknowledgement

Principal and Management of Akal Degree College

Mastuana is thanked for providing lab facilities.

## References

Alves, N. M. and Mano, J.F. 2008. Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications. International Journal of Biological Macromolecules. 43 (5): 401-414.
Cechinel, M.A.P., Ulson De Souza, S.M.A.G. and Ulson De Souza, A.A. 2014. Study of lead (II) adsorption onto activated carbon originating from cow bone. Journal of Cleaner Production. 65 : 342-349.
Crini, G. and Badot, P. M. 2008. Application of chitosan, a natural aminopolysaccharide for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature. Progress in Polymer Science. 33 (4): 399-447.
Ghaedi, M., Shokrollahi, A., Niknam, E., Niknam, A., Najibi, M. and Soylak, 2009. Cloud point extraction and flame atomic absorption spectrometric determination of cadmium (II), lead (II), palladium (II) and silver (I) in environmental samples. Journal of Hazardous Materials. 168 (2-3) :1022-1027.
Gupta, V.K. and Ali, I. 2004. Removal of lead and chromium from wastewater using bagasse fly ash-A sugar industry waste. Journal of Colloid and Interface Colloid Interface Science. 271 (2): 321-328.
Halttunen, T., Salminen, S. and Tahvonen, R. 2007. Rapid removal of lead and cadmium from water by specific lactic acid bacteria. International Journal of Food Microbiology. 114(1) : 30-35.
Huang, Z.H., Zheng, X., Lv, W., Wang, M., Yang, Q.H. and Kang, F. 2011. Adsorption of lead (II) ions from aqueous solution on low-temperature exfoliated graphene nanosheets. Langmuir. 27 (12) : 7558-7562.
Hyung, H., Fortnter, J. D., Hughes, J. B. and Kim, J.H. 2007. Natural organic matter stabilizes carbon nanotubes in the aqueous phase. Environmental. Science and Technology. 41 (1): 179-184.
Karbassi, A. R. and Nadjafpour, S.1996. Flocculation of dissolved $\mathrm{Pb}, \mathrm{Cu}, \mathrm{Zn}$ and Mn during estuarine mixing of river water with the Caspian Sea. Environmental Pollution. 93 (3): 257-260.
Kuchta, B., Firlej, L. and Maurin, G. 2005, Modeling of adsorption in nanopores. Journal of Molecular Modeling. 11 (4-5) : 293-300.
Kumar, K. Y., Muralidhara, H. B., Nayaka, Y.A., Balasubramanyam, J. and Hanumanthappa, H. 2013. Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution. Powder Technol. 246 : 125-136.
Li, Y.H., Di, Z., Ding, J., Wu, D., Luan, Z. and Zhu, Y. 2005. Adsorption thermodynamic, kinetic and desorption studies of $\mathrm{Pb} 2+$ on carbon nanotubes. Water Research. 39 (4): 605-609.

Machida, M., Mochimaru, T. and Tatsumoto, H. 2006. Lead (II) adsorption onto the graphene layer of carbonaceous materials in aqueous solution. Carbon. 44: 2681-2688.
Neill, C.O., Hawkes, F.R., Hawkes, D.L., Lourenco, N.D., Pinheiro, H. M. and Delée, W. 1999. Colour in textile effluents-sources, measurement, discharge consents and simulation: a review. Journal of Chemical Technology and Biotechnology. 74 (11) : 1009-1018.
Nuengmatcha, P., Mahachai, R. and Chanthai, S. 2014. Thermodynamic and kinetic study of the intrinsic adsorption capacity of graphene oxide for malachite green removal from aqueous solution. Oriental Journal of Chemistry. 30 (4) : 1463-1474.
Orumwense, F. 1996. Removal of lead from water by adsorption on a kaolinitic clay. Journal of Chemical Technology \& Biotechnology: International Research in Process. Environmental and Clean Technology. 65(4): 363369.

Pokhrel, D. and Viraraghavan, T. 2004. Treatment of pulp and paper mill wastewater-a review. Science of the

Total Environment. 333 (1-3) : 37-58.
Rao, G.P., Lu, C. and Su, F. 2007. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review. Separation and Purification Technology. 58 (1): 224-231.
Robinson, T., McMullan, G., Marchant, R. and Nigam, P. 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology. 77 (3): 247-255.
Soylak, M., Unsal, Y.E., Kizil, N. and Aydin, A. 2010. Utilization of membrane filtration for preconcentration and determination of Cu (II) and Pb (II) in food, water and geological samples by atomic absorption spectrometry. Food and Chemical Toxicology. 48 (2): 517-521.
Uluozlu, O. D., Tuzen, M., Mendil, D. and Soylak, M. 2010. Coprecipitation of trace elements with Ni2+/2-nitroso-1-naphthol-4-sulfonic acid and their determination by flame atomic absorption spectrometry. Journal of Hazardous Materials. 176 (1-3): 1032-1037.

