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Ultrasound Enhanced Eviction of Lead Ions from Waste Water using Ionic Liquid Modified Silica Gel

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ABSTRACT

Heavy metal ions such as Zinc, Cadmium, Lead, Copper and Nickel are menacing to both human life and the environment. In the present effort, investigation aimed to enhance the removal of Pb(II) from waste water by ultrasound promoted adsorption using Methyltrio ctylammonium Chloride modified Silica gel was carried out. The synthesized materials were characterized by Fourier Transform Infrared (FTIR) spectroscopy and X-Ray Diffraction (XRD). To analyse the adsorption of Lead ions from aqueous solutions batch adsorption studies were carried out. The factors which influence the % adsorption of Pb(II) on IL-Silica gel such as adsorbent dose, contact time, pH value of Pb(II) solution, temperature and adsorbate concentration had been investigated. Adsorption of Pb(II) on the IL-Silica gel was correlated well with the Langmuir model. It has been established that IL-Silica gel has the aptitude to be used for large scale separation of Lead from wastewater under ultrasound irradiations.

Key words: *Adsorption, Lead, Methyltrioctylammonium Chloride, Silica gel, Ultrasound irradiations*

Introduction

Water is polluting day by day due to addition of heavy metal ions from various industries and factories. It also gets polluted by addition of Pesticides to farm runoff water (Mittal and Sharma, 2008; Rani *et al*., 2022). Several studies have been done to remove heavy metal ions and pesticides from water (Bhullar *et al.*, 2021). Heavy metal ions like that of Cadmium, Lead, Mercury make the water toxic for both flora and fauna (Rani. 2019). 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). In developing countries, the heavy metal contamination is a major cause of health risks and environmental problems (Suzuki *et al.*, 1997). Consumption of Heavy metals causes very serious health effects in human beings. With scarce public recognition for the harm they cause, these heavy metals do untold damage to people's lives in terms of heart disease, cancer, skin disorder, neurological disease, brain fog and depression (Borba *et al.*, 2006; Naseem *et al.*, 2001). Lead occurs naturally mainly as PbS and it is widely distributed all over the world. It is used in accumulators, to produce tetraethyl lead, guns, solders and X-ray equipment, among other uses (Arce *et al.*, 2007). This metal inhibits biosynthesis and affects the kidneys, brain cells and liver membrane permeability, reducing some of their functions (Forstner *et al.*, 1983). It can be accumulated in the body and can promote disturbances such as nausea, vomiting, diarrhea, convulsions, coma and death. The inefcient transformations, non-planned progress and non-sustainable processes have polluted the soils, water and air utterly. As a result, a lot of wastewater is disposed to the environment without any prior treatment. Therefore, its treatment is necessary to lower the hazards and specially to minimize the concentration of heavy metals in water samples (Lertlapwasin *et al.,* 2010). There are ongoing attempts to sought more active, selective and environmentally benign protocols for wastewater treatment (Hagiwara, *et al.,* 2011). Many remediation techniques have been implemented to remove the heavy-metal from polluted water and prevent negative eects on the environment, human health and eco-system (Tang *et al.,* 2017). The conventional remediation methods such as chemical precipitation and occulation are unsuitable due to the producing secondary pollution and do not remove metal traces which, despite low concentration, have signicant cumulative eects (Fayazi *et al.,* 2016; Bahrami *et al.,* 2019). The ion exchange, solvent extraction, reverse osmosis, solar distillation and adsorption are also indicated for the metal ion removal from water (Awual *et al.,* 2019; Tiwari *et al.* 2022). However, the adsorption method incorporated with ultrasound irradiations is comparatively suitable due to the specic selectivity by the functional groups of the adsorbent material with several recycles adsorption uses (Rahaman *et al.,* 2008) as well as the acoustic cavitation phenomenon including formation, growth and collapse of microbubbles in a liquid irradiated with ultrasonic waves. That is, the cavitation bubble formed by ultrasonic waves eventually collapses, resulting in high-speed microjets of solution, intense localized heating, and high-pressure shock waves. Which enhances mass transfer rates and could cause the formation of many micro-cracks on the solid surface increasing the surface area between solid–liquid in separation operations such as extraction and adsorption/desorption (Breitbach *et al.* 2003; Sayan 2006; Korkut *et al.* 2010; Liu *et al.* 2013; Dankova *et al.* 2014). Ultrasound irradiation assisted adsorption is well entrenched method for the removal of heavy metal from waste water (Kaur *et al.* 2023). Several natural and synthetic adsorbents have been used to remove heavy metals from water sources. In the present investigation, Lead had been removed from waste water using Methyltrioctylammonium Chloride modified Silica gel as adsorbent under Ultrasound irradiation. The adsorption data were analyzed using Langmuir isotherm. Langmuir isotherm adsorption equations describe judiciously the adsorption isotherm within the metal ion concentration range.

Methodology

Chemicals utilized in the work were obtained from various companies, such as Methyltrioctyl-ammonium Chloride was persuaded from MERCK. Silica gel, Toluene, $Pb(NO_3)_2$, HCl, NaOH were purchased from Sigma Aldrich. Methyltrioctylammonium Chloride was used after purification. Silica gel was used without any purification. Solvents used for the chemical synthesis, obtained from pecuniary sources and used without any further purification.

Exact 83.22 mmol of Silica gel was dissolved in 25 ml of conc. H_2SO_4. The solution was sonicated for 9 hrs at room temperature. Then sample washed with distilled water to make it acid free. Then the sample was dried in oven at 100 ^{0}C for 10 hrs. After this a suspension was made by adding Toluene in above mixture. Then 5 g of Methyltrioctylammonium Chloride was added to suspension. The mixture was sonicated for 7 hrs at 35 ^{0}C. Temperature of the

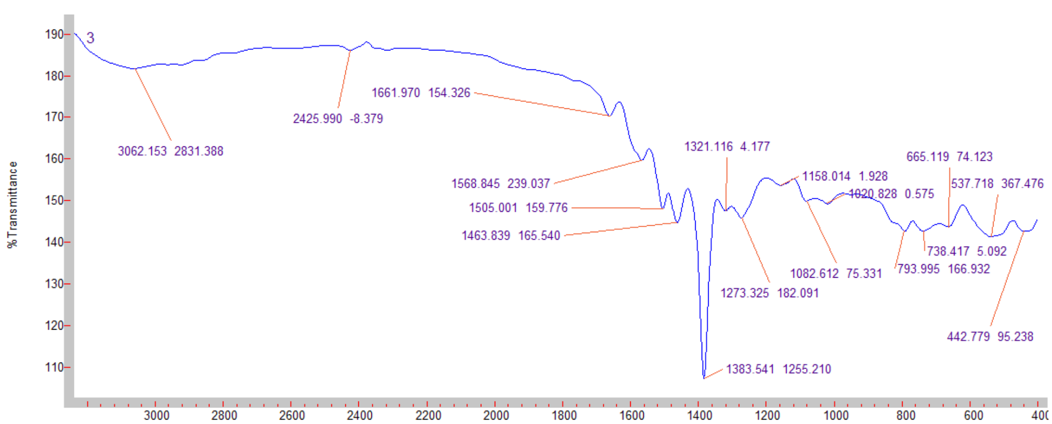

Fig. 1. FTIR of Methyltrioctylammonium Chloride modified Silica

ultrasonicator bath was maintained by adding cold water after every 15 min. After sonication the reaction mixture was filtered and washed with ethanol and Diethyl ether, then placed in oven at 60 ^{0}C for 1 hr.

FT-IR analysis of adsorbent was performed to detect the functional groups present in the IL-Silica gel. The FT-IR spectra of the IL-Silica gel was recorded by Perkin Elmer 100 spectrometer using Potassium bromide (KBr) disc method.

Peak at 793.995 cm^{-1} was attributed to Si-H in plane bending. Peaks at 1321.116 cm^{-1} and 1383.541 cm^{-1} were due to C-N stretch. Peak at 1568.845 cm^{-1} belongs to C=N stretch. Peak at 1463.839 cm^{-1} attributed to C=C stretching. Peak at 1661.970 cm^{-1} attributed to C=N stretching or O-H bending. Peak at 3062.153 cm^{-1} belongs to Si-OH bond. New peaks appear at wavelength 2425.990 cm^{-1} and 1568.845cm^{-1} which confirms the modification of Silica by ionic liquid. The XRD spectra of Silica gel and the IL-Silica gel have also performed. The different phases of the Silica and IL- Silica were examined by an X-Ray diffractometer (XRD). Comparison of both spectra was done and it was observed that characteristic peak of unmodified Silica appeared at 22.5^0 and crystalline phase appeared in the IL-Silica from the two peaks at position 42.6^0 and 43.6^0, rest of peaks were broad showing amorphous nature of synthesized compound.

Stock solutions of 1000 μg/l Lead Pb(II) in distilled water was prepared from the salt precursor $Pb(NO_3)_2{\cdot}4H_2O$**.** The adsorbent was exposed to metal ion solutions after an optimum contact time, i.e. 30 min, the filtrate was analysed by ICP-OES

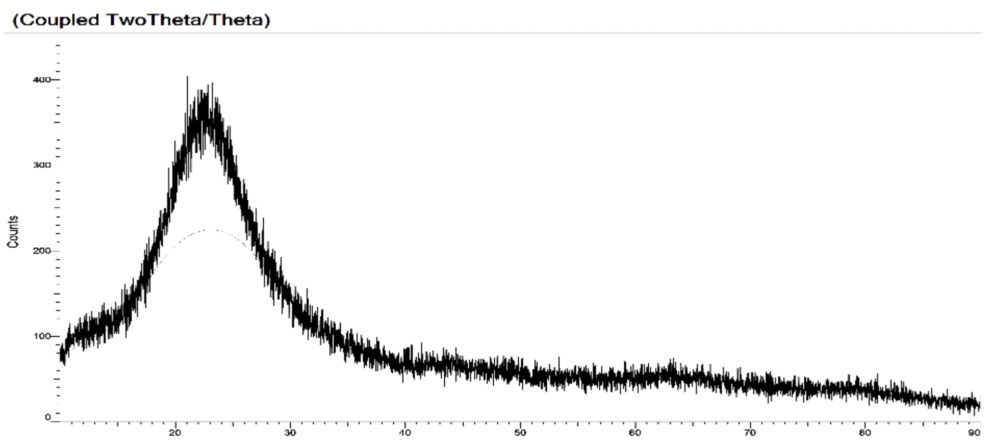

Fig. 2. XRD of unmodified Silica

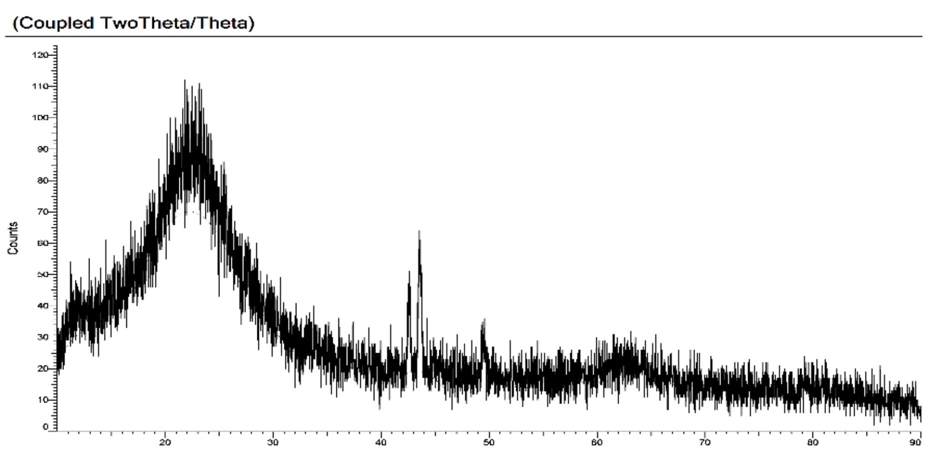

Fig. 3. XRD of ionic liquid modified Silica

(Perkin Elmer) for the determination of residual metal ions concentration. Effects of various parameters that influence adsorption process such as adsorbent dose, contact time, pH, and temperature and adsorbate concentration were investigated to optimize conditions.

The percent of adsorption by the adsorbent was calculated using the following Eq. (1).

$$\%Adsorption = \frac{C_i - C_e}{C_i} * 100 \quad .. (1)$$

where C_i and C_e are the initial and final concentrations, respectively, of metal ions expressed in ìg/l.

In order to investigate the effect of adsorbent dosage, different amounts of IL-Silica gel ranging from 5 to 50 mg were added in separate beakers. Each beaker had 10 ml of Pb(II) solution with a concentration of 1,000 µg/l. Beakers containing solution were ultrasonicated for 30 min. The solutions were filtered and filtrates were subjected to analysis. In 10 ml Pb(II) solution of concentration 1000 µg/l,30 mg of IL-Silica gel was added and ultrasonicated for different time intervals, i.e. from 15 to 90min.

For determining pH effect, 30 mg of IL- Silica gel was taken in beaker. A 5ml Pb(II) solution of 1,000 µg/l was then added, followed by addition of 5 ml buffer solutions of pH 1 to 7 and ultrasonicate it for 60 min. Maximum removal efficiency of Pb(II) was determined at respective pH by ICP-OES. 30 mg of IL-Silica gel were added to 10 ml Pb(II) solution (1,000 µg/l, pH 6). The beaker containing solution was sonicated for 60 min, at different temperatures, i.e. 10–50 °C. These samples were then filtered and filtrate was analysed to determine the effect of temperature on extraction efficiency. Pb(II) solutions of different concentrations i.e. 500, 750, 1000, 1250, and 1500 µg/l were prepared. 10 ml of these solution (pH 6), was added to 30mg IL- Silica gel. The mixture was then ultrasonicated for 60min before subjecting the samples to filtration. The filtrate was analysed to determine the amount of Pb(II)extracted by the sorbents.

Results and Discussion

The study exposed that the adsorbent dosage had a direct effect on Pb(II) removal efficiency since the removal of Pb(II) increases with an increase in the mass of adsorbent. Maximum removal efficiency was 90% of Pb(II) was achieved by IL-Silica gel at an adsorbent dose of 30 mg (Fig. 4(a)). Further increase in the amount of adsorbent did not result in sizable increase in the removal efficiency. The reason behind this is that after a certain concentration of adsorbent, the quantity of adsorbed and free metal ions remains constant in the solution.

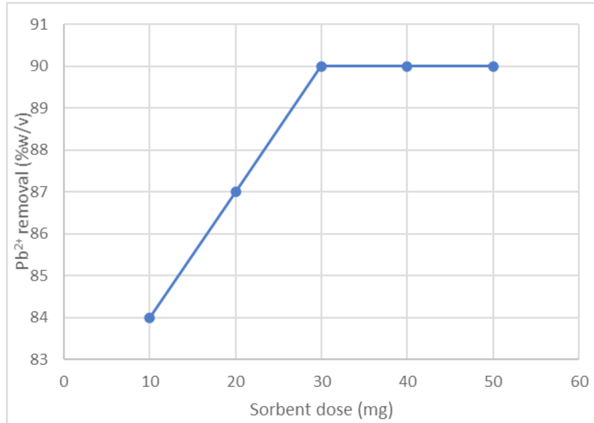

Fig. 4(a). Effect of adsorbent dose on adsorption

The maximum adsorption (90%) was observed for contact times of 60 min for IL-Silica gel. Further increase in contact time had no effect on the removal efficiency of IL-Silica gel as indicated in Fig. 4(b). This rapid adsorption process shows the availability of large number of available active sites and high surface area.

The pH of solution plays a major role in the removal of metal ions through adsorption. Batch studies were performed in the pH range from pH 1 to 7. Adsorption capacity increased with an increase in the pH with maximum adsorption efficiency observed at pH 6. At low pH values, the extraction ef-

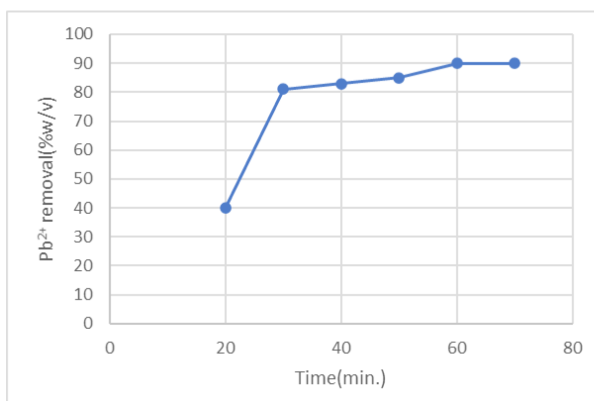

Fig. 4(b). Effect of contact time on adsorption of Pb(II) by IL-Silica gel ficiency of IL-Silica gel is low due to the protonation of functional groups containing lone pairs.

The adsorption efficiency is significantly affected by disparity in temperature. The ideal temperature range was found to be 20-40 °C for IL-Silica gel. The maximum uptake capacity for IL-Silica gel was observed at 40 °C. Binding forces of IL-Silica gel with the adsorbent may become weak with an increase in temperature above 50 °C therefore; an increase in temperature above 50 °C does not favour the adsorption process.

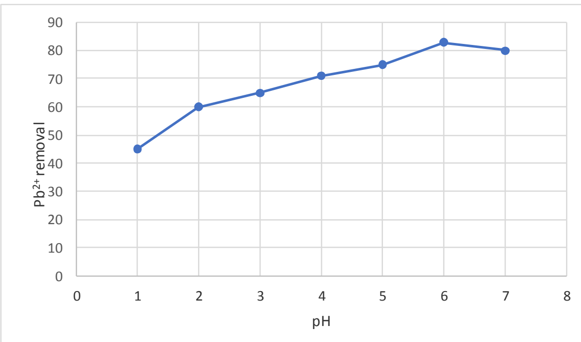

Fig. 4(c). Effect of pH on Pb(II) removal by IL-Silica gel

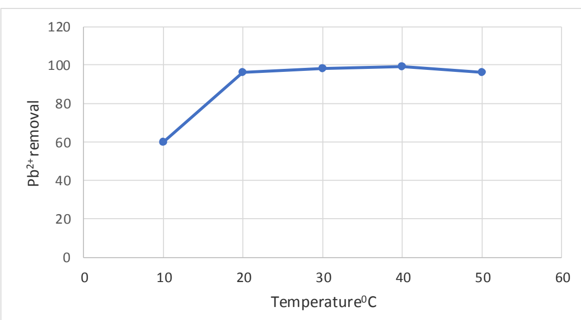

Fig. 4(d). Effect of temperature on adsorption of Pb(II) by IL-Silica gel

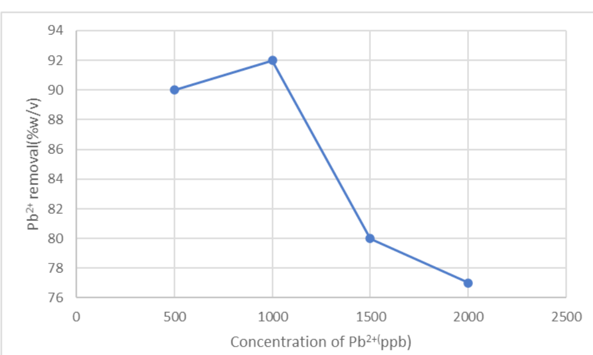

Fig. 4(e). Effect of concentration of Pb(II) (ppb) on adsorption of Pb(II) by IL-Silica gel

The removal efficiency was more than 90% for IL-Silica gel up to a concentration of 1,000 µg/ l. With an increase in adsorbent concentration above 1,000 µg/l, the Pb(II) extraction efficiency decreases continuously down to 75% at 2,000 µg/l. This designates that binding sites of IL-Silica gel are saturated, leading to reduced efficiency at higher concentration of metal ions.

Adsorption isotherms are the mathematical models used for adsorption studies and these isotherms give information about the relative metal ion concentration between liquid phase and adsorbent, amount of sorbate adsorbed by the sorbent, and mechanism of interaction among the adsorbate species and adsorbent (Saqib *et al.*, 2013; Baig *et al.*, 2010). In this study, Langmuir isotherm was applied to the experimental data and the results are shown in Fig. 5. Langmuir isotherm model is based on the assumption that number of active sites is fixed in a monolayer and only one ion can be adsorbed by each active site and the adsorbed ions have no interaction with each other (Bulut *et al.*, 2003). The Langmuir isotherm is given by Eq. (2).

$$\frac{1}{q} = \frac{1}{q_m . k_{ads}} . \frac{1}{C} + \frac{1}{q_m} \quad .. (2)$$

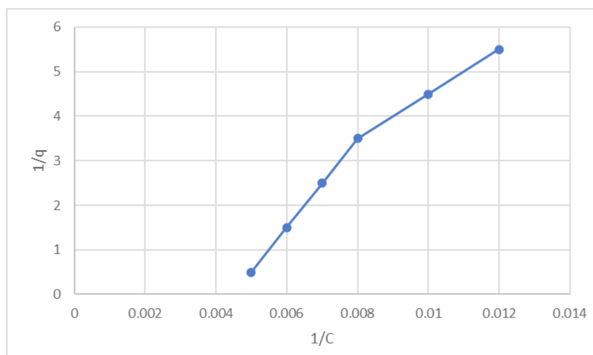

Fig. 5. Langmuir isotherm plot for IL-Silica gel

where q_m and q are monolayer and equilibrium sorption capacities of the sorbents (µg mg^{-1}), respectively, k_{ads} is the energy constant related to heat of adsorption and C is equilibrium concentration (mass per unit volume). A plot of 1/C against 1/q produced a straight line with an r^2 value of 0.98.

Conclusion

Methyltrioctylammonium Chloride modified Silica gel under ultrasound irradiations was used as an adsorbent to remove Pb(II) in polluted water. Ultrasound assisted IL-Silica gel is a low-cost good methodology for the removal of Lead ions form aqueous solution. Batch adsorption kinetic studies show that the maximum adsorption of Pb(II) was 90% at adsorbent dose 30 mg, contact time 60 min., pH 6, temperature 40 ^{0}C and adsorbate concentration 1000 μg /l.

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Conflict of Interest: None

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