

**RESEARCH ARTICLE****REMOVAL OF LINDANE ( $\Gamma$ -HCH) BY USING NATURAL ZEOLITE IN INDUSTRIAL WASTEWATER****Manohar Kata, Ramana G.V\***

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**ABSTRACT**

Lindane ( $\Gamma$ -HCH) is an organochlorine insecticide that has been widely used in developing countries. It is known to persist in the environment and can cause serious health problems. One of the strategies adopted to remove lindane from the environment is remediation using adsorption technique. Zeolite has been used for the removal of lindane from an aqueous solution in batch sorption technique. The present Thomsonite zeolite is characterized by scanning electron microscopy (SEM) with EDX. Adsorption of lindane on natural zeolite is studied as a function of contact time, adsorbent dose, initial concentration and pH. Lindane concentration can be reduced down to the lower level of  $0.001 \text{ mg L}^{-1}$  under the optimum condition (with solid/liquid ratio of 1:100 and the contact time 3 h and pH 6.8) when initial lindane concentration  $10 \text{ mg L}^{-1}$  is employed, and the maximum lindane adsorption capacity is  $2.31 \text{ mg g}^{-1}$ .

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**INTRODUCTION**

The gamma isomer of hexachlorocyclohexane ( $\Gamma$ -HCH), commercially known as lindane, is a highly chlorinated, recalcitrant pesticide, which has been used worldwide as a broad spectrum insecticide for a variety of crops [1]. It has also been applied to human health as scabicide and pediculocide, in the form of lotions and shampoos [2]. Lindane is a liposoluble compound, which tends to accumulate in fat tissues and as a result biomagnifies in the food chain [3]. Chronic exposure to this xenobiotic has been linked to a range of health effects in humans, including immunosuppression and neurological problems, and it has shown to cause liver cancer in rats and mice [4]. Although nowadays it has been prohibited in most countries, lindane is still used because of economic reasons and, consequently, new sites are being contaminated. Its residues persist in the environment and have been found in water, sediments, soil, plants and animals [5-7].

Natural zeolites are hydrated crystalline aluminium-silicate materials with a framework structure where micro-and mesopores located by water and alkaline cations. Recently natural zeolites and their modified forms have been widely used as effective adsorbents in remediation of water according to their mechanical and thermal properties, capability of cation – exchange and significant worldwide occurrence [8, 9]. However, these minerals have no or little selectivity for anionic contaminants due to the constant negative charge on their surface [10]. Therefore, studies have focused on preparation new anion-selective zeolite especially using metal oxides or surfactants. Among these modification agents; iron and aluminum oxides are the most widespread and excellent candidates for arsenic adsorption in aqueous solution [11-14]. Utilization of these oxides in the treatment processes could cause difficulties in separation owing to their small sizes although they have high sorption capacities. To overcome this

separation difficulty the effective method is to support particles into/onto porous matrix of larger size. Some of the most common support materials reported by researchers are activated carbon, polymers and sands and clay minerals. In addition to these materials, natural zeolites have been recognized as an alternative carrier.

In this present study, natural zeolite (Thomsonite) is used as a lindane adsorbent, and its adsorption behaviour in removing lindane from industrial wastewater is investigated.

**MATERIALS AND METHOD****Reagent**

All chemicals used in this study are analytical grade reagents. Ammonium chloride (99.5%), hydrochloric acid (36%) sodium chloride (99 %), sodium hydroxide (99%), are supplied by Merck, India. While sample of natural zeolite (Thomsonite) with a Si/Al ratio of 5/1 is collected from Hyderabad. Deionized water is produced by Milli-Q system (Millipore Co., India). Rotary evaporator is used for pre-concentrated of sample extracts.

**Table 1** Chemical composition of Natural zeolite (Thomsonite) (wt. %)

Component	Content (%)
CaCO <sub>3</sub>	2.29
SiO <sub>2</sub>	69.22
Al <sub>2</sub> O <sub>3</sub>	13.95
Cu	0.49
Pd	0
Au	2.04
Albite	0
Wollastonite	12.01

**Materials**

The natural zeolite sample of Thomsonite is collected from the southern part of Hyderabad city, India. The natural zeolite sample of Thomsonite is crushed up and sieved to the particle

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size fraction 50–100  $\mu\text{m}$ . The parent zeolite is treated three times with deionized water at 95 °C for 2 h with a solid/solution ratio of 1:10 under stirring. After washing, filtering and drying procedures, adsorption sample of Thomsonite is obtained. The zeolite sample is calcined from room temperature to 550 °C at a rate of 10 K min<sup>-1</sup> under N<sub>2</sub> flow to obtain a sample of H-Thomsonite (Table 1).

#### Physical and chemical characterization

The surface morphology of the Thomsonite natural zeolite is observed using scanning electron microscope (SEM, Philips XL30) with an energy dispersive X-ray (EDX) (Fig. 1). The residual lindane concentration is analyzed by Gas Chromatography (GC-q MS) (Thermo Scientific Trace GC Ultra with DSQ II model) coupled with mass spectrometer detector using TR-5MS fused silica capillary column, 30m x 0.25mm i.d.0.25 $\mu\text{m}$  film thickness (J&W Scientific, CA, USA).

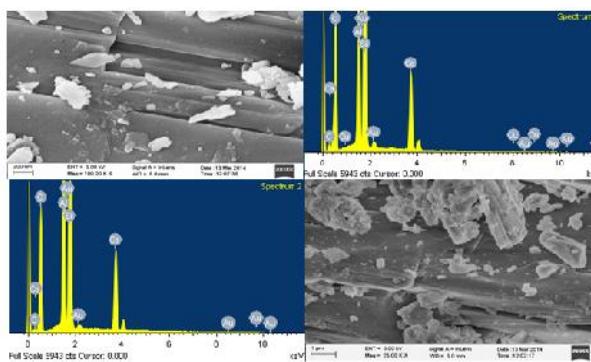


Fig. 1 SEM & EDX images of the natural zeolite (Thomsonite)

#### Batch adsorption studies

Stock solution (5 mg L<sup>-1</sup>) is prepared by dissolving 2.5 mL of 2000 mg L<sup>-1</sup> lindane standard (CRM) to 1 L of deionized water. This is further diluted to the desired concentration for practical use. The known weight of the adsorbent is added to 50 mL of the desired lindane solution in an amber color glass bottle and then stirred thoroughly at room temperature. After continuous stirring in magnetic stirrer for a fixed time interval, the samples are filtered and the lindane concentration in the residual solution is analyzed by GC-qMS. Similar procedures are followed to investigate the effect of contact time, adsorbent dose, initial concentration, pH and coexisting ions.

## RESULTS AND DISCUSSION

#### Effect of contact time

The removal of lindane from industrial waste water with the time is shown in Fig. 2. It is observed that lindane uptake increases with contact time and reaches equilibrium within 3 h. At this time the maximum efficiency of lindane concentration removal is about 94%, so 3 h is fixed as the period of contact time for further studies.

#### Effect of the adsorbent dose

The effect of adsorbent doses is investigated as shown in Fig. 3. As the dosage of adsorbent is increased from 2 to 10g L<sup>-1</sup>, there is an obvious ascending in the percentage of lindane removal. This indicates that the number of active adsorption sites at higher dosage is much enough to accommodate

lindane molecules. However, there is only a slight improvement in the lindane removal when the dosage of adsorbent is above 10g L<sup>-1</sup>. This suggests that adsorption reaction is likely to reach to a dynamic equilibrium. In order to achieve the minimum dosage for maximum lindane removal, 10g L<sup>-1</sup> is chosen as the optimum dosage.

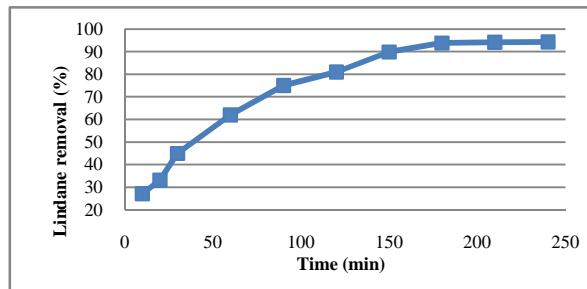


Fig. 2 Effect of contact time (particle size 50–100  $\mu\text{m}$  adsorbent dose 10 g L<sup>-1</sup> lindane concentration of 5.0 mg L<sup>-1</sup> and pH = 6.8)

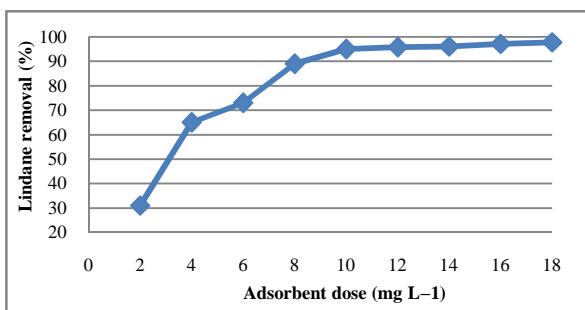


Fig. 3 Effect of adsorbent dose (particle size 50–100  $\mu\text{m}$  adsorbent dose 10 g L<sup>-1</sup> lindane concentration of 5.0 mg L<sup>-1</sup>, contact time 3 h and pH = 6.8)

#### Effect of initial concentration

The specific amount adsorbed is calculated from the following equation.

$$q_e = \left( \frac{C_o - C_e}{W} \cdot V \right) \quad (1)$$

Where  $q_e$  is the adsorption capacity ( $\text{mg g}^{-1}$ ) at the equilibrium;  $C_o$  and  $C_e$  are the initial and equilibrium concentrations of lindane ( $\text{mg L}^{-1}$ ) respectively;  $V$  is the volume of the aqueous solution (L) and  $W$  is the mass (g) of adsorbent used in the experiments.

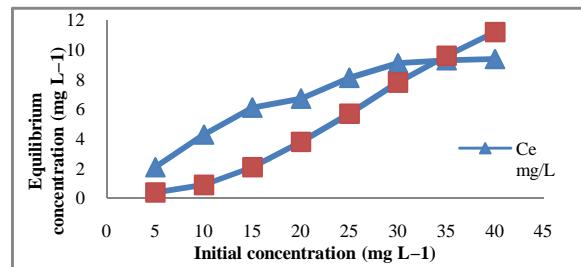


Fig. 4 Effect of initial concentration (particle size 50–100  $\mu\text{m}$  initial lindane concentration in the of 5.0–40 mg L<sup>-1</sup>, contact time 3 h, adsorbent dose 10 g L<sup>-1</sup> and pH = 6.8)

The effect of initial concentration on lindane removal is shown in Fig. 4. It is noticed that the adsorption capacity reaches stable at high initial concentration. This plateau represents saturation of the active adsorption sites available at

the high initial concentration. Additionally, the equilibrium concentration of the lindane increases with increasing in initial lindane concentration. When the initial lindane concentration is  $1 \text{ mg L}^{-1}$ , the equilibrium concentration of lindane can be reduced down to the level of  $0.01 \text{ mg L}^{-1}$  under the current experimental conditions, which approaches to the Indian Drinking water Standards of pesticide concentration ( $0.001 \text{ mg L}^{-1}$ ).

### Effect of pH

The removal of lindane from aqueous solution is highly dependent on the pH. Lindan removal is studied over the pH range of 3 to 11 as shown in Fig. 5. It is evident from Fig. 5 that the adsorption capacity of lindane increases with increasing the pH. The adsorption capacity reaches to a maximum of  $0.54 \text{ mg g}^{-1}$  at pH 6.8 and then slightly decreases to  $0.43 \text{ mg g}^{-1}$  at pH 8.0. After that, the adsorption capacity dramatically decrease and the adsorbent exhibits negligible adsorption  $0.08 \text{ mg g}^{-1}$  at pH 11.0. The quick reduction of the amount of lindane adsorbed in alkaline pH range should be accredited to competitive.

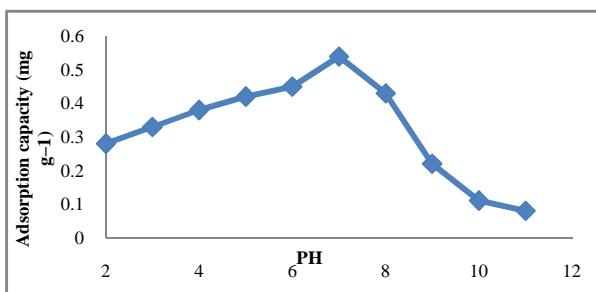


Fig. 5 Effect of pH on lindane removal (particle size  $50-100 \mu\text{m}$  initial lindane concentration in the of  $5.0 \text{ mg L}^{-1}$ , contact time 3 h, adsorbent dose  $10 \text{ g L}^{-1}$ )

### Application

In a sorption study, efficiency of a developed sorbent material should be examined on the industrial wastewater. The blank analysis for wastewater showed that it is free of lindane contamination. The industrial wastewater samples have  $0.38 \text{ mg/L}$  of lindane and the sorption process is carried out under optimum conditions (pH of solution: 6.8, natural zeolite dosage:  $10 \text{ g/L}$ , contact time: 3 h, shaking speed: 220 rpm, temperature:  $27^\circ\text{C}$ ). The removal of lindane from wastewater by using natural zeolite was above 92%. This result showed that natural zeolite can be efficiently used for the removal of lindane from industrial wastewater.

### CONCLUSION

The natural zeolite (Thomsonite) has a considerable potential for the removal of excess lindane from the industrial wastewater. Batch adsorption studies show that lindane concentration can be reduced down to the very low level  $0.001 \text{ mg L}^{-1}$ under the optimum conditions. Lindane adsorption on Thomsonite is well described by the Langmuir adsorption model, and maximum adsorption capacity is  $2.31 \text{ mg L}^{-1}$ . The kinetic result indicates that the adsorption of lindane on the zeolite follows legergren equation. The natural zeolite is an environment-friendly adsorbent with lower chemical consumption and waste release and operating costs.

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### References

- [1] Bidlan, R., Afsar, M., Manonmani, H.K. 2004: Bioremediation of HCH-contaminated soil: elimination of inhibitory effects of the insecticide on radish and green gram seed generation. Chemosphere. 56: 803 – 811.
- [2] Carvalho, P.N., Rodrigues, P.N.R., Basto, M.C.P., Vasconcelos, M.T.S.D. 2009: Organochlorine pesticides levels in Portuguese coastal areas. Chemosphere. 75: 595 – 600.
- [3] Chutia, P., Kato, S., Kojima, T., Satokawa,S. 2009: Adsorption of As (V) on surfactant-modified natural zeolites.J. Hazard. Mater. 162: 204–211.
- [4] Cid, F.D., Anton, R.S., Caviedes-Vidal, E. 2007: Organochlorine pesticide contamination in three bird species of the Embalse La Florida water reservoir in the semiarid Midwest of Argentina. Sci. Total Environ. 385: 86 – 96.
- [5] Concha-Grana, E., Tumes-Carou, M.I., Muniategui-Lorenzo, S., Lopez-mahia, P., Prada-Rodriguez, D., Fernandez-Fernandez,E. 2006:Evaluation of HCH isomers and metabolites in soils, leachates, river water and sediments of a highly contaminated area. Chemosphere. 588 – 595.
- [6] Doušová, B., Fuitova, L., Grygar, T., Machovic, V., Koloušek, D., Herzogova, L., Lhotka, M. 2009:Modified aluminosilicates as low-cost sorbents of As (III) from anoxic groundwater. J. Hazard. Mater. 165: 134–140.
- [7] Goh, K.H., Lim, T.T., Dong, Z. 2008: Application of layered double hydroxides for removal of oxyanions: a review. Wat.Res. 42: 1343–1368.
- [8] Jimenez-Cedillo, M.J., Olguin, M.T., Fall, Ch., Colin, A. 2011:Adsorption capacity of iron-or iron-manganese-modified zeolite-rich tuffs for As (III) and As (V) water pollutants. Appl. Clay Sci. 54: 206–216.
- [9] Macedo-Miranda, M.G., Olguin, M.T. 2007: Arsenic sorption by modified clinoptilolite-heulandite rich tuffs. Macrocycl. Chem. 59: 131–142.
- [10] Philips, T.M., Seech, A.G., Lee, H., Trevors, J.T. 2005: Biodegradation of hexachlorocyclohexane (HCH) by microorganisms. Biodegradation.16: 363 – 392.
- [11] Pigna, M., Krishnamurti, G.S.R., Violante, A. 2006: Kinetics of Arsenate sorption-desorption from metal oxides. Soil Sci. Soc. Am. J. 70: 2017–2027.
- [12] Silva, J., Mello, J.W.V., Gasparon, M., Abrahao, W.A.P., Ciminelli, V.S.T., Jong, T. 2010: The role of Al-Goethites on arsenate mobility. Wat. Res. 44: 5684–5692.
- [13] Vega, F.A., Covelo, E.F., Andrade, M.L., 2007: Accidental organochlorine pesticide contamination of soil in Porrino, Spain.J. Environ. Qual. 36: 272 – 279.
- [14] Walker, K., Vallero, D.A., Lewis,R.G. 1999:Factors influencing the distribution of lindane and other hexachlorocyclohexanes in the environment. Environ. Sci. Technol. 33: 4373 – 4378.

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