

Removal of endosulfan by sal wood charcoal

P.C. Mishra, R.K. Patel *

Department of Chemistry, National Institute of Technology, Rourkela 769008, Orissa, India

Abstract

The removal efficiency of endosulfan from water by two low cost adsorbents viz. sal wood (*Shorea robusta*, family—Diptero carpaceae) charcoal and sand along with activated charcoal as the reference was investigated. For the selection of the suitable adsorbent for endosulfan uptake, the maximum adsorption capacity (Q_{\max}) was chosen as the main parameter. Using linearized forms of equilibrium models like Langmuir, BET, Freundlich, the maximum adsorptive capacities were determined. It was observed that the efficiency for removal of pesticide is higher in activated charcoal with 94% followed by sand 90%. The efficiency of sal wood charcoal is moderately high with 87% which can be regenerated after treatment with dilute HCl and HNO₃. Though the efficiency of sand is better than sal wood charcoal, it cannot be regenerated.

Keywords: Endosulfan; Sal wood charcoal; Langmuir model; Freundlich model; BET model; Time-decay curves

1. Introduction

Indiscriminate use of pesticides in the modern agricultural practices leads to several environmental problems. One of such problems is the contamination of surface and ground water by pesticide. Numerous cases of pesticide residue have been reported in the literature [1,2]. Moreover, it has also been reported that the ground water, surface water and drinking water are contaminated with pesticide [3,4]. In the year 2002, it has been reported by Pollution Monitoring Laboratory, New Delhi that the cold drinks and packaged water bottle also contain pesticide. The sources of water used for the above are ground water in the agricultural rich state of India. Natural waters like lakes, rivers, streams and oceans have been contaminated with residue of various pesticides [2,5–12]. The contamination of surface water and ground water sources with various pesticides is posing a direct threat to human health. Pesticides losses from cultivated fields may be a significant source of pollution for surface and ground water [13]. Although many treatment processes have been proposed for the removal of environmental contaminants from an aqueous solution, adsorption is considered to be one of

the important purification and separation process [14]. Activated carbon due to its high surface area and porosity is very efficient in removing varieties of pesticides from water and wastewater. The efficiency of activated carbon in removing many pesticides from aqueous phase has been documented in the literature [15–21]. Adsorption by activated carbon was found to be most promising method for removal of pesticides but this process is not cost effective particularly in developing countries [21,22]. In the present research work, two low cost adsorbents were investigated as an alternative to activated carbon to abate endosulfan from drinking water.

2. Experimental methods

2.1. Preparation of adsorbents

Two low cost adsorbents viz. sal wood charcoal and sand were tested against a reference charcoal. The reference charcoal was purchased from the retail outlet of Eureka Forbes Limited which is used in water purifier brand name Aquaguard. Sand was collected from bed of river Koel. The sand was taken without crushing. Sand was kept in distilled water for 24 h with intermittent shaking. Finally, it was tested for any heavy metals like lead, iron, chromium and found to be below detectable limit. Sal wood charcoal was prepared in the laboratory by heating small pieces of sal wood in an electric furnace at 900 °C for 2 h. All the

* Corresponding author. Tel.: +91 661 2463652; fax: +91 661 2472926.

E-mail addresses: prakashsivaji@yahoo.co.in (P.C. Mishra), rkpatelnitr@rediffmail.com (R.K. Patel).

adsorbent materials were washed thoroughly with distilled water to avoid the presence of foreign impurities and dried at 110 °C for 10 h followed by cooling down to room temperature. The charcoal was pulverized to the mean size of 200 µm using standard sieves. The pulverized materials were washed thoroughly with distilled water to remove any fine particles. After drying for 10 h at 110 °C in a hot air oven, they were stored in airtight plastic bottles.

2.2. Reagents

All the reagents used were of analytical grade. All glassware used was of Borosil. Distilled water was used for making synthetic samples. All the glassware were cleaned with dilute hydrochloric acid and repeatedly with distilled water followed by drying at 110 °C for 5 h. Technical grade endosulfan of 95% purity was obtained from Ispat Market, Rourkela, India. *n*-Hexane (Merck) of 99.9% purity was used.

2.3. Analytical methods

Standard methods [23] were adopted for the analysis of various water quality parameters. Gas Chromatograph (GC-14 A Shimazdu, Japan) was used for the measurement of endosulfan. Electron Capture Detector ^{63}Ni with 5% OV 17 – stainless steel poropak packed column was used. The column was of 3 m length and 3.18 mm diameter. The temperature for column, injector and detector was maintained at 230, 250 and 300 °C, respectively. Nitrogen gas with 99.9% purity was used as carrier gas. The flow rate was maintained at 50–60 ml/min. Before the actual measurements, the GC was conditioned for 48 h to avoid column bleeding and soiling of sample and to maintain ideal conditions for every GC run. The detection time required for endosulfan peak using gas chromatograph was found out by injecting a pure sample of endosulfan. A calibration curve was made between known concentration of endosulfan and the corresponding peak areas. A calibration curve for very wide range (0–50 mg/l) would lead to appreciable deviation from the data points. To avoid these, two calibration curves in the range 0–5 mg/l and 5–50 mg/l, respectively, were made for accurate measurements of endosulfan. To avoid any deviation in measurement of endosulfan due to instrumental errors, a standard sample as control was tested for every run of gas chromatography analysis.

2.4. Sample preparation

Stock solution of endosulfan was made according to the standard methods. Working samples were made by adding required stock solution to the predetermined quantity of distilled water. All experiments were performed with a stock solution of 200 mg/l which was prepared as fresh after every 10 days.

2.5. Extraction of endosulfan

Extraction of endosulfan from water was done by liquid–liquid partition method. Representative sample in the range of 30–90 ml based on concentration of pesticide of aque-

ous solution spiked with endosulfan was extracted in a 125 ml separating funnel using *n*-hexane. Extraction was done three times with 15, 10 and 5 ml of *n*-hexane, respectively. During the extraction process the sample–*n*-hexane mixture was shaken for 5 min and then allowed to settle for 5 min. The separated layer of *n*-hexane was passed through a 60 mm bed of sodium sulphate to absorb any trace of moisture present in the extracted sample. *n*-Hexane extract was collected in a volumetric flask and made to 25 ml with *n*-hexane. 5 ml extracted sample was used for analysis. For very low concentrations of pesticides, the *n*-hexane extract was condensed using roto evaporator and then from condensed extract 5 µl of sample was used for analysis using gas chromatographic method with the chromatopac recorder. The extraction efficiency of *n*-hexane was found to be 95%.

2.6. Kinetic studies

Polyethylene bottles (Tarson Co. Ltd., India) of 125 ml capacity were used in the kinetic experiments. Endosulfan spiked synthetic water sample (100 ml) of a particular concentration were taken in the bottle and 20 g/l adsorbent was added to it. The sample bottles were stirred on a mechanical stirrer at 150 rpm. The experiments were carried out at 28 °C. After required contact time the samples were withdrawn and the adsorbents from the sample bottles were separated by gravity. The experiments were carried out for a duration of 24 h with 10 mg/l of endosulfan concentration. Samples were collected at 30 min interval up to first 3 h, every 1 h interval up to 10 h, every 2 h interval up to 14 h and 4 h afterwards. The samples were analyzed for endosulfan after solvent extraction. pH was maintained at the beginning and end of every experiments.

2.7. Equilibrium studies

Batch experiments were conducted for the development of adsorption isotherms for different materials under the same experimental conditions. Polyethylene bottles of 125 ml capacities were used in all the experiments. Endosulfan spiked synthetic water sample (100 ml) of 5–50 mg/l concentration, respectively, were taken in different bottles and adsorbate was added to it at a specified dose. The sample bottles were stirred on a mechanical stirrer at 150 rpm and at 28 °C. After required equilibrium time, the samples were withdrawn from the stirrer and the adsorbent from sample bottle was separated by gravity.

2.8. Desorption experiment

The reusability of used sal wood charcoal sample mainly depends on the ease with which endosulfan gets desorbed from loaded salwood charcoal. For this 100 ml solution of endosulfan of 50 mg/l concentration was treated with 20 g/l of sal wood charcoal and was kept for a contact time of 24 h. The contents of the flask was then filtered and separated. The filtered adsorbent was then retreated with 100 ml of distilled water and was kept for contact time of 24 h. The residual endosulfan concentration was measured.

3. Results and discussion

3.1. Kinetic studies

Kinetic profiles of removal were generated for all the materials to assess the equilibrium time. Fig. 1 shows the typical kinetic profile of different adsorbents. It was observed that for all adsorbents, the equilibrium was reached after 6 h as there was not much removal of endosulfan after that time. Major part of the adsorption took place within the first 1–2 h after which the removal rate decreased. Because of complex structure (Fig. 2) and high molecular weight, the endosulfan takes long time to attain equilibrium in adsorption. Activated charcoal removes 94% of endosulfan from water in 24 h of study because of its larger surface area.

Sand exhibited a removal efficiency of 90% followed by sal wood charcoal which exhibited a removal efficiency of 87% which is moderately lower. The removal efficiency of sand is due to more affinity of pesticide towards sand particle (Francis and Lee, 1972) but it will be exhausted quickly. The composition of sand is same as that of big boulders from which they have been formed, but the main constituent of sand is silica (93–94%) and rest 6–7% contains oxides of various other metals like sodium, potassium, etc.

The sal wood charcoal shows moderate efficiency, but it is definitely cost effective. Moreover, the pores of sal wood charcoal can be corroded easily to enhance the surface area by the acid treatment which is an inexpensive activation process.

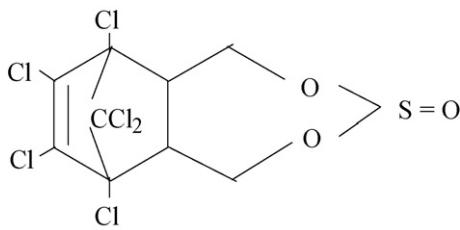


Fig. 1. Chemical structure of endosulfan.

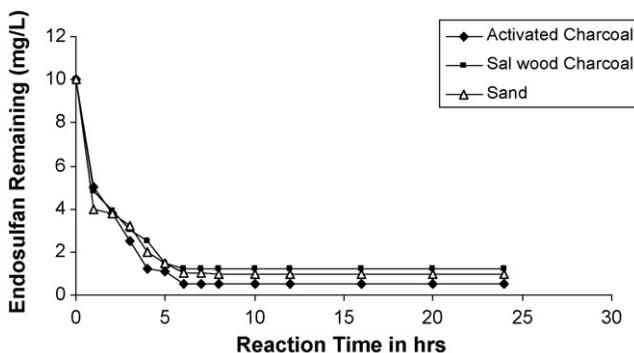


Fig. 2. Time decay curves for different adsorbents used for removal of endosulfan from water. NB: initial endosulfan concentration 10 mg/l, adsorbent size 0.2 mm, adsorbent dose 20 g/l, agitation speed 150 rpm, pH 6.6–5.4, temperature 30 °C.

3.2. Equilibrium studies

Equilibrium studies were carried out for all the materials to assess the adsorption equilibrium model that they followed. Langmuir, BET and Freundlich models were considered. From a set of experimental data, the model which gave the best correlation coefficient by linear regression method was adopted for the calculation of Q_{\max} of the corresponding adsorbent material. So, to estimate Q_{\max} the linearized forms of Langmuir, BET and Freundlich isotherms as given below were used.

$$Q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (\text{Langmuir model})$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{b Q_{\max}} \quad (\text{BET model})$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (\text{Freundlich model})$$

where C_e is solute concentration at equilibrium in aqueous phase in mg/l, C_s is saturation concentration of solute in mg/l, Q_e is solute adsorbed per unit weight of adsorbent in mg/g, Q_{\max} is maximum solute adsorbed per unit weight of adsorbent in mg/g and b , n , K_f and B are constant. The isotherms were developed for all the adsorbents which are shown in Figs. 3–5. To determine Q_{\max} , linear plots were made with the corresponding parameters of various models. Linear regression analysis was carried out for all the adsorbents for all the three adsorption equilibrium models. The correlation of data with various models for different materials with Q_{\max} values are represented in Table 1.

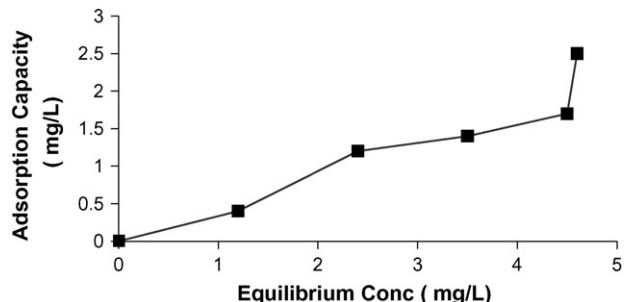


Fig. 3. Isotherm developed (BET) using equilibrium data for activated charcoal. NB: initial endosulfan concentration 5–50 mg/l, adsorbent—activated charcoal, adsorbent size 0.2 mm, adsorbent dose 20 g/l, agitation speed 150 rpm, pH 6.6–5.8, contact time 6 h, temperature 30 °C.

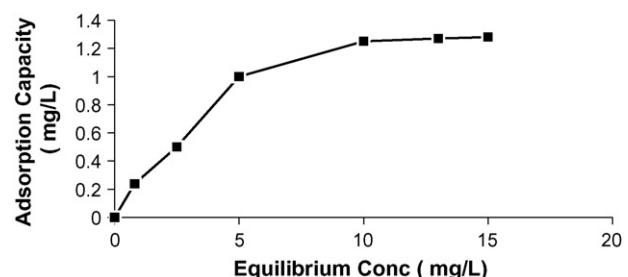


Fig. 4. Isotherm developed (Langmuir) using equilibrium data for wood charcoal. NB: initial endosulfan concentration 5–50 mg/l, adsorbent—sal wood charcoal, adsorbent size 0.2 mm, adsorbent dose 20 g/l, agitation speed 150 rpm, pH 6.6–5.4, contact time 6 h, temperature 30 °C.

Table 1
Correlation coefficients and values of Q_{\max} ($\mu\text{g/g}$) for the adsorbents with respect to different adsorption equilibrium models

Sl. no.	Adsorbents	Langmuir	BET model	Freundlich model	Q_{\max} ($\mu\text{g/g}$)	Model chosen
1.	Activated charcoal	0.783	0.855	0.556	2145.0	BET
2.	Sal Wood charcoal	0.990	0.541	0.541	1773.9	Langmuir
3.	Sand	0.996	0.587	0.834	323.1	Langmuir

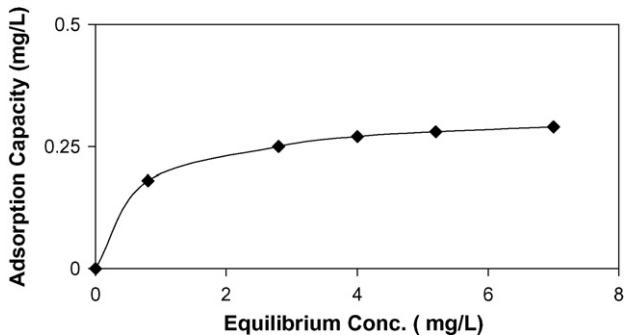


Fig. 5. Isotherm developed (Langmuir) using equilibrium data for sand. NB: initial endosulfan concentration 5–50 mg/l, adsorbent—sand, adsorbent size 0.2 mm, adsorbent dose 20 g/l, agitation speed 150 rpm, pH 6.6–5.4, contact time 6 h, temperature 30 °C.

To determine Q_{\max} , the model that showed best correlation with data was selected. The correlation between data and the model was estimated. Linearised isotherms used for calculation of saturation adsorption capacity for various adsorbents are represented in Figs. 6–8.

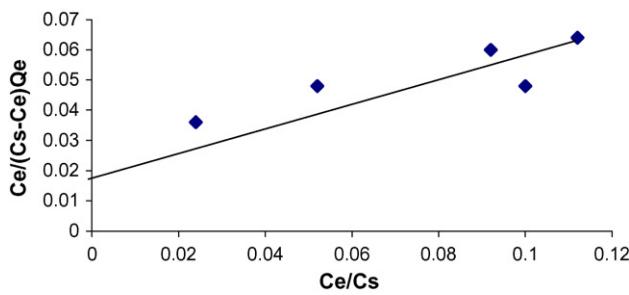


Fig. 6. Linearised form of BET isotherm for activated charcoal. NB: initial endosulfan concentration 5–50 mg/l, adsorbent—activated charcoal, adsorbent size 0.2 mm, adsorbent dose 20 g/l, agitation speed 150 rpm, pH 6.6–5.4, contact time 6 h, temperature 30 °C.

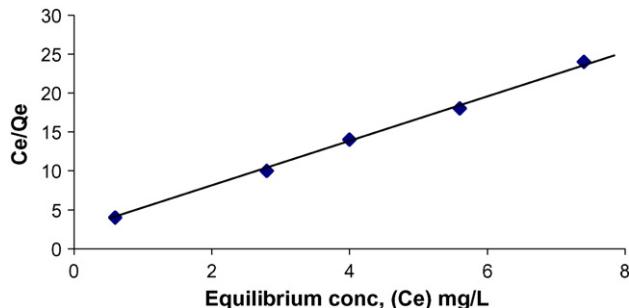


Fig. 7. Linearised form of Langmuir isotherm for sand. NB: initial endosulfan concentration 5–50 mg/l, adsorbent—sand, adsorbent size 0.2 mm, adsorbent dose 20 g/l, agitation speed 150 rpm, pH 6.6–5.4, contact time 6 h, temperature 30 °C.

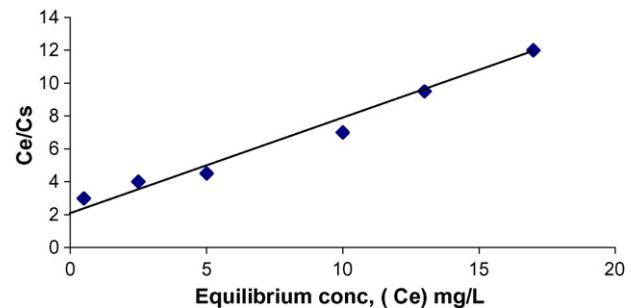


Fig. 8. Linearised form of Langmuir isotherm for sal wood charcoal. NB: initial endosulfan concentration 5–50 mg/l, adsorbent—sal wood charcoal, adsorbent size 0.2 mm, adsorbent dose 20 g/l, agitation speed 150 rpm, pH 6.6–5.4, contact time 6 h, temperature 30 °C.

It is observed from the data that sand which was behaving better in the kinetic study has a poor saturation adsorption capacity. Sal wood charcoal even without any activation showed the best adsorptive capacity with reference to activated charcoal. From this it indicates sal wood charcoal is the best material for the removal of endosulfan from water environment. Moreover, the material is very soft and the adsorptive capacity can be enhanced by improving the surface area with a treatment by acid.

3.3. Effect of acid treatments on the removal efficiency of sal wood charcoal

Treatment of sal wood charcoal with HCl and HNO₃ at different normalities was carried out. Both acids were tried at five different normalities 0, 0.5, 1.0, 1.5 and 2N. The samples were kept under agitation for 3 h and the samples after solvent extraction were analyzed for endosulfan. The percentage removal efficiency of sal wood charcoal after treatment improved from 45 to 74% for 2N HCl. In case of HNO₃, the efficiency improved from 45 to 73% at 1N HNO₃. But from 1 to 2N the efficiency came down from 73 to 55%. The effect of acid treatment on removal efficiency is represented in Fig. 9.

The improvement in percentage removal efficiency may be due to the corroding effect of acid in sal wood charcoal pore wall surface which enhances the surface area. But for normalities larger than 1N HNO₃ the inner walls of the pores were corroded completely and resulted in a decrease in surface area. So, 1N HNO₃ treatment is preferred to 2N HCl.

The effect of 1N HNO₃ treatment on sal wood charcoal to remove endosulfan from water was studied by plotting the time decay curves for both treated and untreated sal wood charcoal samples. The kinetic profiles developed are presented in Fig. 10. It is observed that the acid treatment has influenced the adsorptive capacity of sal wood charcoal to 90% in 24 h time.

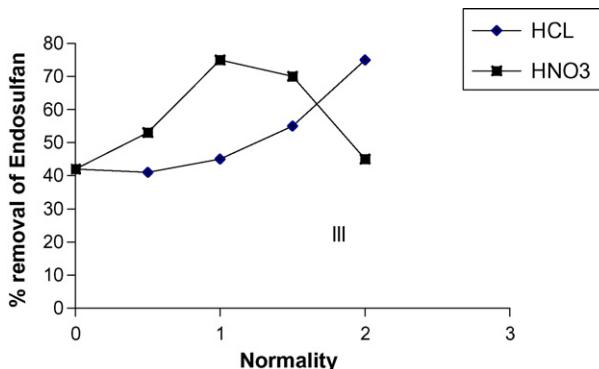


Fig. 9. Effect of acid treatment on removal efficiency of sal wood charcoal. NB: initial endosulfan concentration 10 mg/l, adsorbent size 0.2 mm, adsorbent dose 10 g/l, agitation rate 150 rpm, pH 6.4–5.8, temperature 28 °C, contact time 4 h.

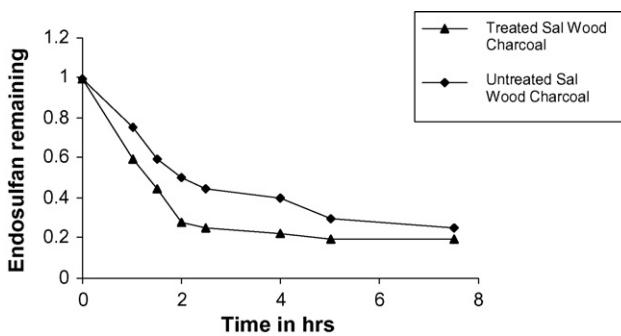


Fig. 10. Kinetic profiles for both sal wood charcoal and sal wood charcoal (treated) for the removal of endosulfan from water. NB: initial endosulfan concentration 1 mg/l, adsorbent—sal wood charcoal, adsorbent size 0.2 mm, adsorbent dose 10 g/l, agitation rate 150 rpm, pH 6.4–5.8, temperature 28 °C.

3.4. Determination of adsorption rate constants

The adsorption rate constants were also determined. The sorption of endosulfan from liquid phase to the solid phase can be considered as a reversible reaction with equilibrium established between two phases. So, a simple first order reaction model was used to establish the rates of reaction, which can be expressed as



So, the rate equation for the reaction is expressed as

$$\begin{aligned} \frac{dC_s}{dt} &= -\frac{dC_L}{dt} = C_{L_0} \frac{dX_A}{dt} k_f C_L - k_r C_s \\ &= k_f (C_{L_0} - C_{L_0} X_A) - k_r (C_{s_0} + C_{L_0} X_A) \end{aligned} \quad (1)$$

where C_s is concentration of endosulfan on the sorbent in mg/g, C_L is concentration of endosulfan in the solution in mg/l, C_{s_0} is initial concentration of endosulfan on the sorbent in mg/g, C_{L_0} is initial concentration of endosulfan in solution in mg/l, X_A is fractional conversion of endosulfan, K_f is rate constant for forward reaction and K_r is rate constant for backward reaction.

At equilibrium

$$\begin{aligned} \frac{dC_s}{dt} &= \frac{dC_L}{dt} = 0 \\ \text{or, } X_{A_e} &= \frac{k_e - (C_{s_0}/C_{L_0})}{k_e + 1} \end{aligned} \quad (2)$$

where K_e is equilibrium rate constant and X_{A_e} is fractional conversion at equilibrium

$$k_e = \frac{C_{s_e}}{C_{L_e}} = \frac{C_{s_e} - C_{L_0} X_{A_e}}{C_{L_e} - C_{L_0} X_{A_e}} = \frac{k_f}{k_r} \quad (3)$$

where C_{s_e} is equilibrium concentration of endosulfan on sorbent in mg/g and C_{L_e} is equilibrium concentration of endosulfan in solution in mg/l. So,

$$\frac{dX_A}{dt} = (k_f + k_r)(X_{A_e} - X_A) \quad (4)$$

Integrating Eq. (4) and substituting K_f from Eq. (3) the equation will be

$$-\ln \left(1 - \frac{X_A}{X_{A_e}} \right) = K_f \left(1 + \frac{1}{K_e} \right) t \quad (5)$$

$$\ln[1 - U(t)] = -K^I t \quad (6)$$

where K^I is rate constant and $U(t)$ is fractional attainment of equilibrium

$$K^I = K_f \left(1 + \frac{1}{K_e} \right) = K_f + K_r \quad (7)$$

$$U(t) = \frac{C_{L_0} - C_L}{C_{s_0} - C_s} = \frac{X_A}{X_{A_e}} \quad (8)$$

By using the Eq. (6) a graph was made between $\ln[1 - U(t)]$ and t , which is shown in Fig. 11.

A near straight line was observed for all concentrations indicating that sorption reaction can be approximated to first order reversible kinetics (Snoeyink and Jenkins, 1980). The initial part of the curve was not linear and it was neglected to avoid error in rate calculation. So, only the linear portion was considered to calculate overall rate constant K^I . For different initial concentrations the constants were calculated by using Eqs. (3) and (7). The results of the calculation are represented in Table 2.

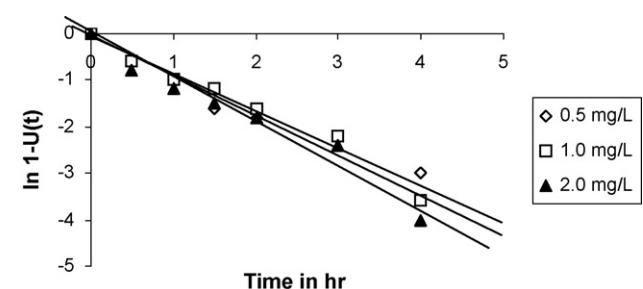


Fig. 11. 1st order reversible kinetics for the removal of endosulfan using sal wood charcoal. NB: adsorbent size 0.2 mm, adsorbent dose 10 g/l, agitation rate 150 rpm, pH 6.4–5.8, temperature 28 °C.

Table 2

Values of 1st order kinetic rate constants (K^I , K_f , and K_r) for sal wood charcoal

Initial endosulfan concentration (mg/l)	K^I (h ⁻¹)	K_f (h ⁻¹)	K_r (h ⁻¹)
0.5	0.757	0.622	0.132
1.0	0.920	0.854	0.052
2.0	0.990	0.956	0.024

3.5. Determination of equilibrium time by different approaches

The adsorption kinetic curves were developed for different initial adsorbate concentrations, different adsorbent sizes and different adsorbent doses. The magnitude of endosulfan removal by sal wood charcoal at different initial concentration of endosulfan is presented in Fig. 12. The removal was found to be 84, 90 and 94% in 24 h at 0.5, 1 and 2 mg/l initial concentrations, respectively. For the first 2.5–3 h the removal was faster and then it was slowed down. After 5 h the removal rate was reduced to about 5, 3 and 4.8%, respectively, for 19 h and further contact time.

Rough judgment was made using various kinetic profiles for different adsorbent doses and sizes, as shown in Figs. 13 and 14.

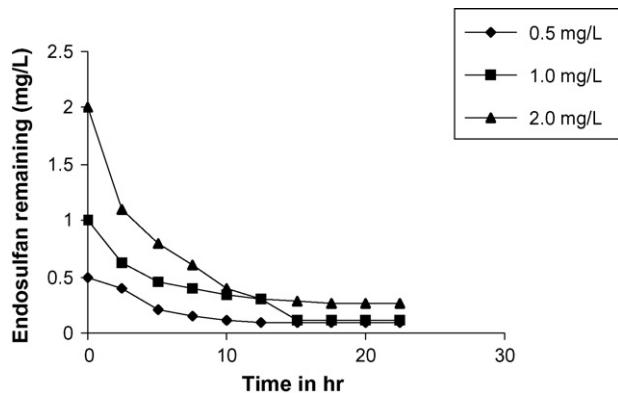


Fig. 12. Kinetic curves for the removal of endosulfan at different initial concentration. NB: adsorbent size 0.2 mm, adsorbent dose 10 g/l, agitation rate 150 rpm, pH 6.4–5.8, temperature 28 °C.

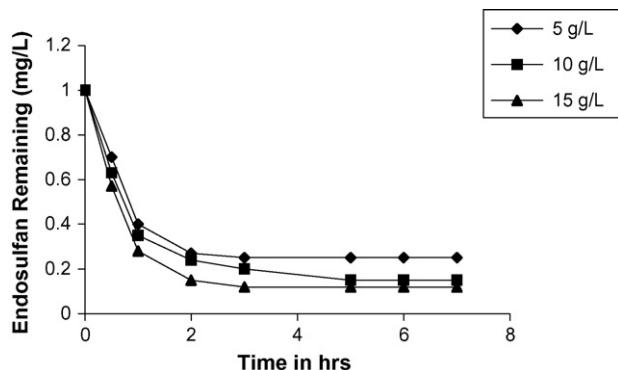


Fig. 13. Kinetic curves for endosulfan removal using sal wood charcoal at different adsorbent doses. NB: initial endosulfan concentration 1 mg/l, adsorbent size 0.2 mm, agitation speed 150 rpm, pH 6.4–5.8, temperature 28 °C.

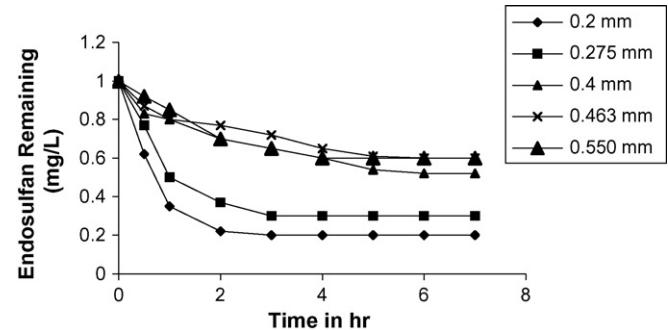


Fig. 14. Kinetic curves for endosulfan removal using sal wood charcoal at different adsorbent sizes. NB: adsorbent size 0.2 mm, adsorbent dose 10 g/l, agitation rate 150 rpm, pH 6.4–5.8, temperature 28 °C.

It is evident that after 3–4 h of contact time, the removal rate was only 2–3%. After 5 h of contact time, the curve became asymptotic to time axis. So, 5 h is the time required for equilibrium.

3.6. Desorption study

In order to know the nature of adsorption, i.e. physical, chemical or both, the desorption study was carried out; the regeneration study at varying pH was studied in a range of pH 2.2–11. Dilute HCl and NaOH were used to adjust the pH of the solution. Change of percentage sorption in acidic environment was insignificant. At pH of 6.3 maximum sorption of endosulfan was observed. As pH increase to 7.6, percentage of sorption decreased from 87 to 79%. The percentage sorption remained unchanged between pH of 7.6 and 10.8 and further decreased to 67.9% at pH of 11. The desorption of adsorbed endosulfan on sal wood charcoal resulted about—amount adsorbed 40.2 mg/l, amount desorbed 2.1 mg/l, percentage desorption 5.3%. Thereby indicating the process of adsorption predominantly physical in nature.

4. Conclusion

The results show that the removal effectiveness of sal wood charcoal for the endosulfan was higher than the one of sand. For the above the maximum adsorptive capacity Q_{\max} was adopted as the screening parameters. Sal wood charcoal was found to be effective and economical, as it can be used by rural people. The removal efficiency of sal wood charcoal is also increased remarkably. The kinetic studies were carried out with all systematic parameters viz. initial endosulfan concentrations, adsorbent doses, adsorbent sizes. From these studies, it was found that the removal rate was found to increase with increasing initial concentration of endosulfan in the range of 5–15 mg/l and the removal efficiency increases with decrease in adsorbent size. From equilibrium time determination it was observed that the removal process was found to be reversible 1st order. Though the sal wood charcoal was used effectively in the laboratory process, it requires further studies to use it for commercial purpose.

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