ASSESSMENT OF LOW COST SORBENTS FROM AGRICULTURAL WASTE FOR THE REMOVAL OF CHLORPYRIFOS FROM AQUEOUS MEDIA

DEV KUMARI, SIBY JOHN

Abstract: The present study evaluates the sorption potential of rice husk (R H) and rice straw (R S), agriculture waste materials, for removal of Chlorpyrifos from aqueous media. Removal efficiency of the sorbents were investigated using a batch sorption experiment. Rice straw exhibited higher removal efficiency than rice husk. At 0.4 g sorbent quantity, rice husk showed 90% removal whereas, rice straw removed 93% chlorpyrifos. Freundlich isotherm model was used to fit sorption data. The maximum sorption capacity calculated by Freundlich equation were 4.3 ± 0.81mol/g and 5.1 ± 1.04 mol/g for RH and RS, respectively. The calculated R^2 value for RH and RS were 0.97 ± 0.05 and 0.96 ± 0.06, respectively. Based on relative cheapness and field application potential these sorbents could be recommended for the decontamination of pesticide contaminated agricultural runoff.

Keywords: Pesticide, Aqueous Media, Sorption, Low Cost Sorbents.

Introduction: India is primarily an agricultural economy with more than 70% of its population dependent on agriculture [Sachdeva, 2007]. Extensive use of pesticides have been reported for crop protection [Bhardwaj and Sharma, 2013]. The problems of persistence of higher levels of pesticides residue in soil, water and air were also reported [Yadav et al., 2015]. Many studies reported the surface water contamination due to pesticide runoff from agriculture fields [Bhat and Padmaja, 2014; Sangchan et al., 2014; Xing et al., 2012; Marino et al., 2005]. High concentrations of pesticides and its transport from agriculture fields to water bodies is an issue of concern as its presence in water adversely effects human health and aquatic life [Imo et al., 2007]. Chlopyrifos (0,0-ddiethyl 0-3,5,6-trichloropyridin-2-yl phosphorothioate), with a molecular structure as shown in Fig. 1, is an organophosphate pesticide which is used in great extent around the world [Sereno et al., 1997].

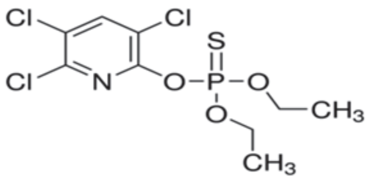

Fig 1: Molecular Structure of Chlorpyrifos

Residual concentrations of chlorpyrifos in range of 0.2 - 10 μg/L have been reported in agricultural drainage [Waghmare et al., 2015; Pujeri et al., 2010; Sangchang et al., 2014]. Ingestion of chlorpyrifos (CP) by living organisms was found to affect functioning of lungs, immune system and central nervous system. It showed fish kill even at parts per trillion concentration [Quezada et al, 2013; Racke, 1993]. Half Life of chlorpyrifos in water was estimated to be 78 days [Kamrin, 1997].

A number of technologies such as photodegradation, anaerobic degradation, ozonation, advanced oxidation processes, nanofiltration, ion exchange and sorption on different activated carbon have been proposed to remove chlorpyrifos from water [Cara et al., 2015]. However, most of these technologies suffer from limitations of high cost and maintenance. Among these available technologies, sorption is preferred due to its relative cheapness, ease of operation and design simplicity [Sharma et al., 2008]. Activated carbon is considered as a universal sorbent for the removal of various types of pollutants from water [Bansal et al., 2005]. However, extensive use of commercially available activated carbon is restricted due to its high cost [Gupta et al., 2009]. Various attempts have been made to develop economic alternative sorbents utilizing agricultural and municipal waste materials [Gupta et al., 2009].

In the present study, an attempt was made to assess the sorption potential of rice husk and rice straw derived from agricultural waste for the removal of chlorpyrifos from aqueous media.

Materials and Methods: Rice husk and Rice straw were collected from the rice cultivation areas of Haryana (India). Reference grade standard of selected pesticide i.e. chlorpyrifos was from Sigma-Aldrich was used for the study. Acetonitrile and ultrapure water analytical (HPLC) grade from Sigma Aldrich were used. Removal of selected pesticide was studied using batch sorption experiments. The studies were conducted with synthetic wastewater prepared by spiking 50 mg of CP in 1 L of distilled water in a dark room to avoid photolysis. In kinetic and sorption studies, the flasks (Borosil glass make, 250 mL capacity) were shaken at 150 rpm in an orbital shaker to provide homogeneous mixing and uniform sorption for 24 h. All experiments were conducted at the optimum sorbent dosage (0.4 g) and pH (6) at room temperature.

Kinetic and Equilibrium Studies: Batch sorption experiments were conducted at 0.4 g of sorbent (RH and RS) and 100 mL of 50 mg/L chlorpyrifos solution. The experiments were carried out in triplicate. 5 ml of sample was taken out and analysed at time intervals of 0.25, 0.5, 0.75, 1, 1.5, 2, 3, 4, 6, 8, 10, 14, 18 and 24 h. Sorption equilibrium studies were conducted with concentration of chlorpyrifos ranging from 0 to 20 mg/L. Reaction mixtures were agitated in shaker at 150 rpm for the estimated equilibrium time from kinetics. After estimated equilibrium time samples were taken for the analysis.

Analysis by HPLC: Water samples were filtered using glass fibre filter and extracted using acetonitrile. The samples were analysed in High performance liquid chromatograph (HPLC). Extracts were analysed using 1100 series HPLC (Agilent Co., Sunnyvale, CA) equipped with a UV/Vis detector (UV at 230 nm). C18 analytical column was used (5 mm, 250 mm×4.6 mm i.d.), along with a Phenomenex Security Guard column (4mm × 2 mm, C18). Extracts were chromatographed with a pre-mixed mobile phase comprised 75% acetonitrile/25% ultrapure water (pH 4.5) at room temperature. Prior to the HPLC analysis, the samples were passed through 0.45 µm nylon syringe filters and were manually injected (20 µl) into the HPLC system each time. The identification of the pesticide was performed by comparing peak retention times in samples to those of peaks in the pure analytical standard and quantified according to height / area of chromatograms.

Data Analysis: The equilibrium isotherm constants and the maximum adsorption capacity of the soils were determined by Using Langmuir and Freundlich equilibrium models as shown in (I) and (II).

$$\frac{Q_e}{Q_{ad}} = \frac{1}{K}b + \frac{Q_e}{K} \qquad \text{------(I)}$$

$$Log\,Q_{ad} = LogK + \frac{1}{n}LogQ_e \qquad \text{------(II)}$$

Where Q_e is the equilibrium concentration of chlorpyrifos in solution and Q_{ad} amount sorbed on sorbents (R H and R S). K is the sorption capacity of sorbents, b is Langmuir constant and n is the sorption intensity. The plot of Q_e/Q_{ad} against Q_e from eq (II) gives Langmuir isotherms and the plot of log Q_{ad} and Q_e from eq (II) Freunlich isotherm.

Results and Discussion: Removal of chlorpyrifos was studied with rice husk and rice straw shown in Fig. 2 represents the gradual decline in the concentration of chlorpyrifos using rice husk. 90% and 93% chlorpyrifos was removed by rice husk and rice straw, respectively.

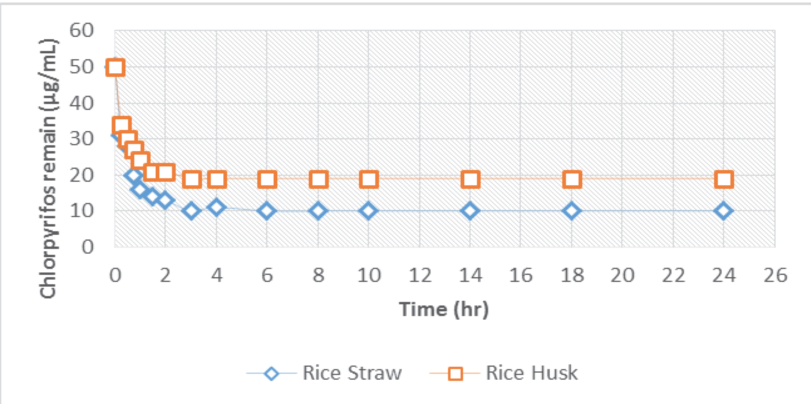

Fig 2: Removal of Chlorpyrifos by Sorption on Rice Husk and Rice Straw

Akhtar et al., (2007) in their comparative study observed higher sorption capacity of rice straw for the removal of Pesticides. Low cost adsorbents especially derived from agricultural wastes were demonstrated to be efficient for the removal of different pesticides from aqueous solution [Memon et al., 2009; Memon et al., 2007; Shrama et al., 2008; Gisi et al., 2016].

Kinetic Studies: Kinetic studies showed that sorption of chlorpyrifos best fit to pseudo second order model (Fig. 3). The rate of sorption of chlorpyrifos on sorbents (R H and R S) are shown in Table 1.

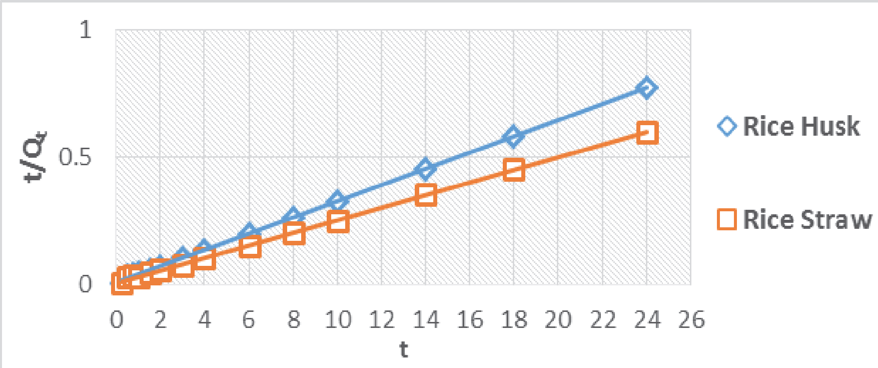

Fig 3: Pseudo Second Order Plot of Sorption of Chlorpyrifos On Rice Husk and Rice Straw

Table 1: Rate of Sorption of Chlorpyrifos on Rice Husk and Rice Straw

Sorbents	Rate of sorption , k (mg/mL/min)	R^2
Rice Husk	0.04± 0.01	0.98± 0.07
Rice Straw	0.03± 0.02	0.97± 0.05

Equilibrium Studies: In order to find the equilibrium constant of sorption of chlorpyrifos on sorbents, isotherm studies were carried out for equilibrium time obtained from kinetics. The results showed that adsorption of chlorpyrifos followed Freundlich isotherm model as shown in Fig 4. Adsorption capacity and adsorption intensity was calculated from equation (II). Sorption capacity of RH was 4.3 ± 0.81 mol/g and that of RS was 5.1 ± 1.04 mol/g. Table 2 represent the sorption constants of rice husk and rice straw.

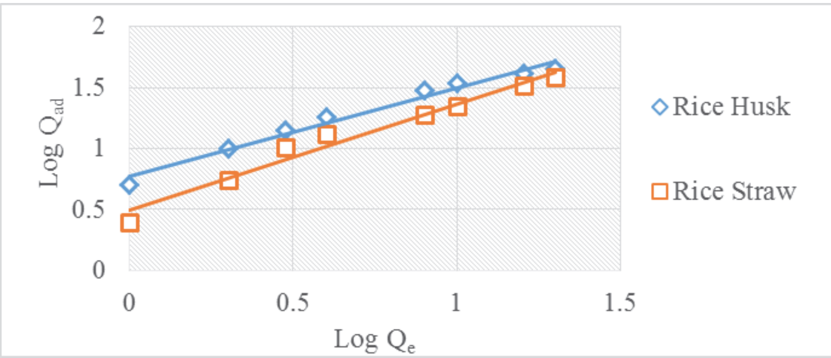

Fig. 4: Freundlich Sorption Isotherm of Chlorpyrifos on Rice Husk and Rice Straw

Table 2: Freundlich Constants for Sorption of Chlorpyrifos on Rice Husk and Rice Straw

Rice Husk			Rice Straw		
K (mol/g)	1/n	R^2	K (mol/g)	1/n	R^2
4.3 ± 0.81	0.41 ± 0.03	0.971± 0.05	5.1 ± 1.04	0.32 ± 0.02	0.964± 0.06

Conclusion: Utilization of waste material is recognized as a sustainable solution for the removal water contaminants and same time it contributing to the waste minimization by recovering and reuse. Rice husk and rice straw show great potential for the removal of chlorpyrifos pesticide from aqueous media and can be applied on the field for decontamination of agricultural drainage contaminated with pesticides
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Dev Kumari, Research Scholar/Environment Engineering/PEC University of Technology
Siby John, Professor and Head of Civil Engineering/PEC University of Technology/Chandigarh (India)
mine.dev@gmail.com ; johnsiby1@gmail.com