



Utilization of organic by-products for the removal of organophosphorous pesticide from aqueous media

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ABSTRACT

Sorption potential of rice (*Oryza sativa*) bran and rice husk for the removal of triazophos (TAP), an organophosphate pesticide, has been studied. The specific surface area were found to be $19 \pm 0.7 \text{ m}^2 \text{ g}^{-1}$ and $11 \pm 0.8 \text{ m}^2 \text{ g}^{-1}$ for rice bran and rice husk, respectively. Rice bran exhibited higher removal efficiency ($98 \pm 1.3\%$) than rice husk ($94 \pm 1.2\%$) by employing triazophos solution concentration of $3 \times 10^{-5} \text{ M}$ onto 0.2 g of each sorbent for 120 min agitation time at pH 6 and 303 K. The concentration range $(3.2\text{--}32) \times 10^{-5} \text{ M}$ was screened and sorption capacities of rice bran and rice husk for triazophos were computed by different sorption isotherms. The energy of sorption for rice bran and rice husk was assessed as 14 ± 0.1 and $11 \pm 0.2 \text{ kJ mol}^{-1}$ and kinetics of the sorption is estimated to be 0.016 ± 0.002 and $0.013 \pm 0.002 \text{ min}^{-1}$, respectively. Intraparticle diffusion rate was computed to be 4 ± 0.8 and $4 \pm 0.9 \text{ nmol g}^{-1} \text{ min}^{-1/2}$. Thermodynamic constants ΔH , ΔS and ΔG at varying temperatures (283–323 K) were also calculated.

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1. Introduction

The increasing use of synthetic chemical pesticides is causing world-wide pollution. In Pakistan, water resources are interconnected with industrial and agricultural discharge and pollution at one point can spread widely. The quality of the water being supplied to the people is also posing serious problems. Almost 30% of all illnesses, *i.e.* diarrhoea, cholera and hepatitis of all categories, and 60% of infant mortality, in Pakistan, are directly because of water contamination [1]. Excessive use of organophosphorous pesticides (OPPs), untreated industrial waste and discharge from tanneries can lead to toxic chemicals seeping deep into the soil and polluting the subsoil water [2]. The presence of pesticides in the aquatic environment represents a potential threat to water quality and human health due to their toxicity and carcinogenic nature [3]. The OPPs are bioaccumulative and relatively stable, as well as toxic or carcinogenic, they are used frequently in Pakistan for agricultural, forestry and domestic activities [4]. They are transported into ground water or leached to the surface water. Maximum permissible limit of $0.1 \mu\text{g L}^{-1}$ for individual pesticides and related products, $0.5 \mu\text{g L}^{-1}$ for total pesticides in drinking

water and $1\text{--}3 \mu\text{g L}^{-1}$ for surface waters has been recommended [5–7].

Among the newly developed organophosphorous pesticides (OPPs), TAP is the most commonly used in Sindh, Pakistan, for cotton, wheat, rice, soybean and vegetable crops. Triazophos (*O,O*-diethyl-*O*-1-phenyl-1*H*-1,2,4-triazol-3-yl phosphorothioate) trade name hostathion [8] is an important broad-spectrum insecticide, which is derivative of phosphoric acid and contains phosphorous, carbon, hydrogen, oxygen and sulphur in its structure. It is inhibitor of acetylcholinesterase enzyme in the human body and can therefore prevent neural signals being transmitted from the brain to various parts of the body. It causes cancer, and may damage reproductive, endocrine and nervous systems of the body [9].

Increasingly stringent drinking water quality directives focus on the need for efficient pesticide removal processes. Adsorption from aqueous solution to solid surfaces (using natural sorbents) is one of the key processes determining the concentration and rate of transport of pesticides in aquifers.

With the increased safety concerns about surface and ground-water with organophosphorous pesticides, it is the focus of research to exploit some cheaper, rapid and indigenous materials-based adsorbents for the removal of TAP from aqueous solutions. Rice bran and rice husk are the waste materials of rice milling industry, and are abundantly available in Pakistan. Disposal of these agricultural by-products is also a major economical and ecological issue in the country. These materials are either burnt or used as low value

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products (flooring in poultry farms) and their utilization as adsorbents for water decontamination is an outlet towards the solution of this problem, by producing a versatile value-added product, suggesting rice bran and rice husk to be potent sorbents for pesticidal polluted water.

2. Materials and methods

2.1. Reagents/buffer solutions and materials

Triazophos of 99% purity was obtained from Sigma–Aldrich Co. (Seelze, Germany). Methanol (HPLC grade 99.99% purity) was obtained from Fisher Scientific Ltd., UK. All glassware used were of Pyrex, Germany.

Stock solution of pesticide and buffer solutions of pH 1–10 have been prepared by earlier reported methods [10–12].

2.2. Development of sorbents

Rice bran (RB) and rice husk (RH) from an indigenous variety “super kernel basmati” were obtained from local rice milling plant, Hyderabad. These materials were then sieved in the range of 100–1000 μm and were then subjected to chemical and thermal treatment in order to increase the surface area of sorbents [10,13]. The treated materials were then placed in desiccators to be used as sorbents.

2.3. Instrumentation

The concentration of TAP was determined by using liquid chromatograph Hitachi model 6200, equipped with CSW32 software (Data Apex) for data acquisition and integration [11].

Redistilled methanol and doubly distilled deionised water (80:20, v/v) with $0.8 \mu\text{S cm}^{-1}$ conductance and pH 5.8 were used as mobile phase at a flow rate of 1 mL min^{-1} throughout the analysis. The wavelength 246 nm and arbitrary unit full-scale deflection (AUFs) 0.005 were also selected. The limit of detection derived by use of signal to noise ratio 1:3 was observed to be 0.1 mg L^{-1} . The pH measurements were made on digital (inolab level 1) pH meter, Germany.

2.4. Surface area analysis

The surface area measurement of sorbents was carried out on a surface area analyzer (Quanta Sorb Model QS-7) by BET (Brunauer, Emmett and Teller) method (measurement of specific surface area of solids by gas adsorption) using nitrogen as a standard [14].

2.5. Sorption method

The preliminary assessments of the performance of the sorbent materials were carried out as per procedure reported [10]. The removal efficiency or percentage sorption is calculated as

$$\% \text{ sorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of TP expressed in mol dm^{-3} .

All experiments were performed at least in triplicate at pH 6 and 303 K unless stated otherwise. The results are the average of three independent measurements along with standard deviation (S.D.) showing 95% confidence level with the precision in most cases being $\pm 2\%$.

3. Results and discussion

3.1. BET surface area analysis of the sorbents

Study of surface area analysis reveal total pore area 19 ± 0.7 and $11 \pm 0.8 \text{ m}^2 \text{ g}^{-1}$, average pore diameter 78 ± 2.4 and $61 \pm 1.8 \text{ nm}$ from total intrusion volume 0.723 and 0.695 mL g^{-1} for RB and RH, respectively. The activation of sorbents with nitric acid (0.1 M) increases the surface area and pore volume of sorbents. The treatment of the sorbents at 373 K for 8 h also may be attributed to the formation of microporous materials with many additional pores on the surface of sorbents.

3.2. Optimization of sorption parameters

Sorption is a surface phenomenon and is affected significantly by the particle size of sorbent, amount of sorbent and sorbate, equilibration time between the two phases, pH and temperature, so these have to be optimized one by one, keeping others constant at the chosen amount of sorbents ($0.1 \text{ g}/25 \text{ cm}^3$ of $3.2 \times 10^{-5} \text{ mol dm}^{-3}$ sorbate concentration), 60 min agitation time, pH 6, 100 rpm shaker speed and at temperature of 303 K. Particle size of $100 \mu\text{m}$, 120 min agitation time, pH 6, 0.2 g of each sorbent dose gave maximum performances, so these were selected as optimized parameters. The effect of concentration over a 10-fold range ($3.2\text{--}32 \times 10^{-5} \text{ mol dm}^{-3}$ of TAP on its own uptake by 0.2 g RB, and RH was monitored under selected optimized conditions. With the increase in concentration of sorbate, a corresponding decrease in distribution coefficient (R_d) was observed as indicated in Fig. 1, suggesting limiting number of sorption sites available for sorption at higher concentration of sorbate molecules [13].

3.3. Sorption isotherms

In order to evaluate the maximum saturation capacities of sorbents, data shown in Fig. 1 was subjected to Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models.

3.3.1. Freundlich sorption isotherm

Fig. 2 shows Freundlich sorption isotherm of TAP onto RB, and RH. This isotherm [15] assumes that the uptake of sorbate occurs on a heterogeneous surface by multilayer sorption and can be described by the following equation:

$$\log C_{\text{ads}} = \log C_m + \frac{1}{n} \log C_e \quad (2)$$

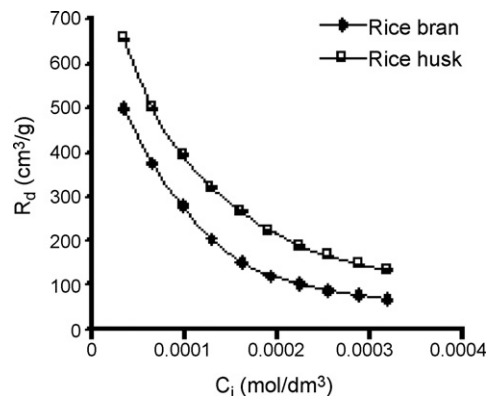


Fig. 1. Effect of concentration ($3.2\text{--}32 \times 10^{-5} \text{ M}$) of TAP onto 0.2 g of RB, and RH, 120 min agitation time at pH 6 and 303 K.

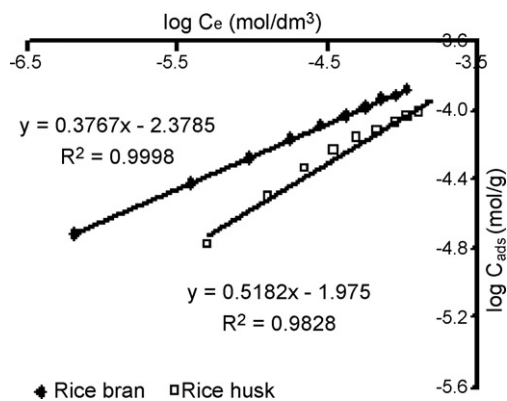


Fig. 2. Freundlich sorption isotherms of TAP onto RB, and RH.

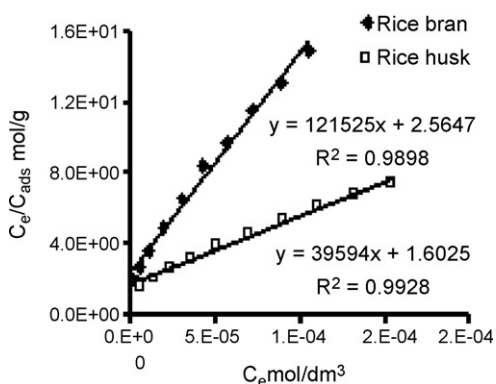


Fig. 3. Langmuir sorption isotherms of TAP onto RB, and RH.

where $1/n$ is a characteristic constant, C_{ads} and C_e are sorbed and equilibrium concentrations, respectively, of sorbate onto sorbent surface (mol g^{-1}) and in solution at equilibrium (mol dm^{-3}) and C_m is the multilayer sorption capacity (mmol g^{-1}). Logarithmic plot of sorbed and equilibrium concentration gives straight lines and the slopes of the straight lines exhibit the value of $1/n$ which is a measure of intensity of sorption and the intercept yields the value of C_m mmol g^{-1} indicating multilayer sorption capacity. The results are recorded in Table 1.

3.3.2. Langmuir isotherm

Fig. 3 shows the simplest theoretical model for monolayer adsorption, *i.e.* Langmuir isotherm [16] of TAP onto RB, and RH. This isotherm assumes that sorption takes place at specific homogeneous sites within the sorbent. The saturated monolayer coverage of the sorbate on the sorbent surface can be written in the linearized form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (3)$$

where Q is the monolayer sorption capacity and b is the constant related to the free energy of sorption, independent of temperature. In Fig. 3 plots of C_e/C_{ads} versus C_e yield straight lines indicating that Langmuir sorption is followed by the sorption data very well. The value of Q (mmol g^{-1}) are calculated from the slopes of the linear

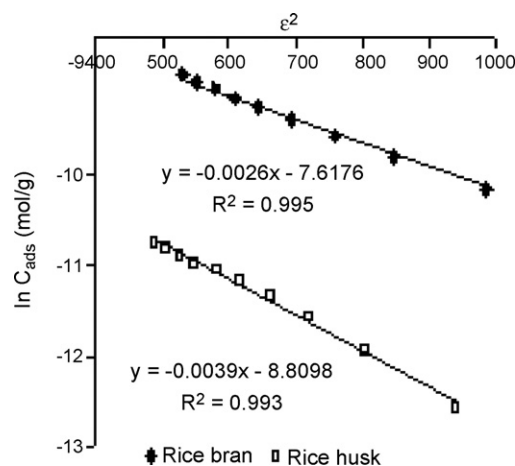


Fig. 4. D–R sorption isotherms of TAP onto RB, and RH.

plots whereas, the values of b ($\text{dm}^3 \text{mol}^{-1}$) are calculated from the intercepts [17]. The results are exhibited in Table 1. From the values of b , the Langmuir constant r (dimensionless constant, separation factor) is estimated in the concentration range $(3.2\text{--}32) \times 10^{-5}$ M by using the relationship $r = 1/1 + bC_i$ where b and C_i are discussed earlier. The results of r in the range 0.06–0.4 for rice bran and 0.1–0.6 for rice husk indicate favorable sorption at low concentration.

3.3.3. Dubinin–Radushkevich (D–R) isotherm

Fig. 4 shows the Dubinin–Radushkevich (D–R) isotherm model [18], which postulates a fixed volume or ‘sorption space’ close to the sorbent surface where sorption takes place and is tested in the following linearized form:

$$\ln C_{ads} = \ln X_m - \beta \epsilon^2 \quad (4)$$

where C_{ads} is the amount of sorbate sorbed onto sorbent surface (mol g^{-1}), X_m represents maximum sorption capacity of sorbent (mmol g^{-1}) and β is constant with dimension of energy. This model assumes the heterogeneity of sorption energies within this space. The polanyi adsorption potential ϵ , the amount of energy required to pull a sorbed molecule from its sorption site to infinity is independent of temperature, which is equal to

$$\epsilon = RT \ln \left(\frac{1 + 1}{C_e} \right) \quad (5)$$

where R is a gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), T is the temperature (K), C_e is the equilibrium concentration of sorbate in solution (mol dm^{-3}). The plots of $\ln C_{ads}$ versus ϵ^2 follow linearity with coefficient of determinations close to unity. The computed values of β and X_m from the slopes and intercepts of respective plots are scheduled in Table 1. The values of sorption energy, E (kJ mol^{-1}), can be calculated using the following relationship [19],

$$E = \frac{1}{\sqrt{-2\beta}} \quad (6)$$

The values of E for TAP calculated from Eq. (6) are enlisted in Table 1 and its results suggest ion-exchange mechanism of the sorption process.

Table 1
Freundlich, Langmuir and D–R parameters for TAP onto RB and RH

Sorbents	$1/n$	C_m (mmol g^{-1})	Q (mmol g^{-1})	b ($\text{dm}^3 \text{mol}^{-1}$)	X_m (mmol g^{-1})	E (kJ mol^{-1})
Rice bran	0.52 ± 0.024	10.6 ± 0.52	0.0082 ± 0.1	47384 ± 37	0.49 ± 1.2	14 ± 0.12
Rice husk	0.38 ± 0.002	4.2 ± 0.02	0.025 ± 0.1	24707 ± 20	0.15 ± 1.3	11 ± 0.2

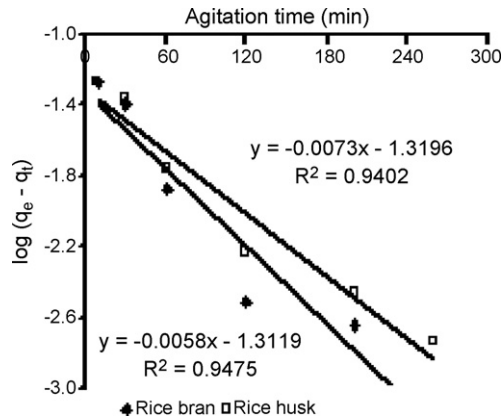


Fig. 5. Lagergren plots of TAP onto 0.2 g of RB, and RH in the contact time range of 10–120 min using 25 cm³ of 3.2 × 10⁻⁵ M sorbate concentration at pH 6, 100 rpm shaking speed and 303 K.

3.4. Kinetic studies

The kinetics of sorption of TAP onto RB, and RH was examined at 120 min agitation time by using Lagergren and Morris–Weber equations. The rate constant of the sorption of TAP onto sorbents is evaluated by using the linear form of Lagergren equation [20]:

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \quad (7)$$

where k is the first-order rate constant of sorption while q_e and q_t are the maximum sorbed concentrations at equilibrium and at time t . In Fig. 5 $\log(q_e - q_t)$ are plotted versus t , and the values of k computed from the slopes of the linear plots are presented in Table 2. During the sorption processes, the possibility of intraparticle pore diffusion of sorbate cannot be ignored, which is often the rate-controlling step. Thus the rate constant of intraparticle diffusion is determined by using following form of Morris–Weber relationship [21].

$$q_t = \frac{R_{id}}{\sqrt{t}} \quad (8)$$

where q_t is the sorbed concentration ($\mu\text{mol g}^{-1}$) at time t , and R_{id} is the rate constant of intraparticle transport. The q_t is plotted against $t^{1/2}$ as designated in Fig. 6. The values of R_{id} calculated from the slopes of linear plots are enlisted in Table 2.

3.5. Thermodynamic considerations

Temperature dependence of adsorption was monitored in the range of 283–323 K under the optimized conditions chosen. Thermodynamic parameters, like heat of adsorption ΔH , entropy ΔS and energy of activation ΔG play an important role in predicting the adsorption behavior as these are strongly dependent on temperature. The equilibration constant K_c is determined by using the following relation:

$$K_c = \frac{F_e}{1 - F_e}$$

Table 2
Lagergren, Morris–Weber and thermodynamic constants for TAP onto RB and RH

Sorbents	k (min ⁻¹)	R_{id} (nmol g ⁻¹ min ^{-1/2})	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG_{303K} (kJ mol ⁻¹)
Rice bran	0.016 ± 0.002	4 ± 0.8	-26 ± 2.1	-64 ± 7	-6.5 ± 1.4
Rice husk	0.013 ± 0.002	4 ± 0.9	-12 ± 0.6	-27 ± 2	-3.5 ± 0.8

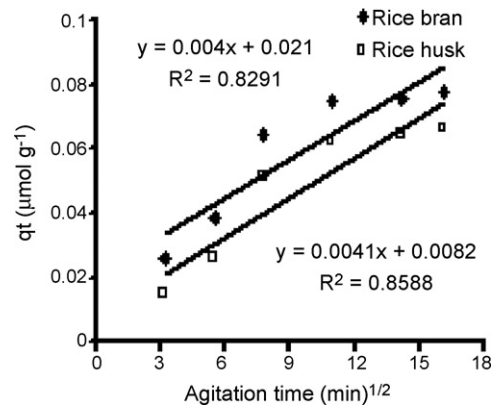


Fig. 6. Morris–Weber plots of TAP onto 0.2 g of RB, and RH in the contact time range of 10–120 min using 25 cm³ of 3.2 × 10⁻⁵ M sorbate concentration at pH 6, 100 rpm shaking speed and 303 K.

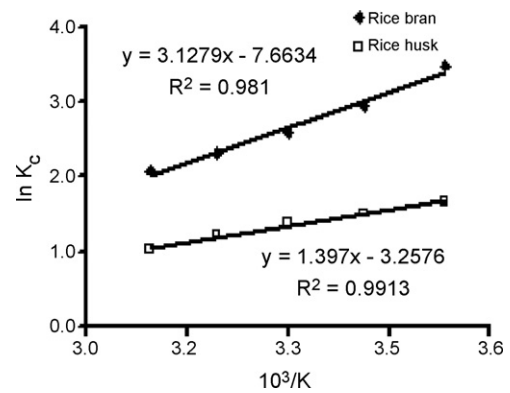


Fig. 7. Variation of sorption equilibrium of TAP with temperature (283–323 K) onto 0.2 g of RB, and RH using 25 cm³ of 3.2 × 10⁻⁵ M sorbate concentration, 120 min agitation time and at pH 6.

where F_e is the fraction of percent sorption at equilibrium and dependence of the equilibration constant with temperature is indicated by the relationship [17]:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (9)$$

where ΔH is the enthalpy (kJ mol⁻¹) and ΔS the entropy (J mol⁻¹ K⁻¹). The plots of $\ln K_c$ versus $1/T$ (K⁻¹) in Fig. 7 are linear and the values of ΔH and ΔS computed from the respective slopes and intercepts of the plots are documented in Table 2. Another thermodynamic parameter ΔG (kJ mol⁻¹) Gibbs free energy was estimated using following equation:

$$\Delta G = -RT \ln k_c \quad (10)$$

where R is a gas constant in kJ mol⁻¹ K⁻¹ and T is temperature in K. The negative values of ΔH , ΔS and ΔG (Table 2) exhibit the exothermic, stable and spontaneous nature of the sorption process respectively.

3.6. Application to real water samples

Amount of TAP in surface and groundwater samples collected from the agricultural area of Taluka, Hyderabad was determined [22] to be 4.5 and $3.2 \mu\text{g L}^{-1}$. By employing sorption method described earlier RB ($98 \pm 1.3\%$ and 99 ± 0.2) and RH ($94 \pm 1.2\%$ and 96 ± 0.5) effectively remove TAP from surface and groundwater samples. The sorbed amounts of TAP (in surface and groundwater samples) were successfully recovered from RB ($97 \pm 0.5\%$ and 98 ± 0.4) and RH ($96 \pm 0.7\%$ and $96 \pm 0.9\%$) with 5 cm^3 of methanol by sonication on an ultrasonic bath for 10 min.

4. Conclusion

The present study concludes that low-cost agricultural waste, *i.e.* rice bran and rice husk can be effectively used to remove triazophos pesticide from water. The order of removal efficiency is rice bran > rice husk may be due to the presence of surface functional groups, *i.e.* amine, hydroxyl, carboxyl and fibre carbonaceous C_xOH [10]. The sorption data fitted well to linear form of Langmuir, Freundlich and D–R isotherms and sorption capacity of each sorbent for the sorbate has been estimated. Values of rate constant, k , suggest the first-order kinetics of the uptake of TAP by the RB and RH whereas, results of Morris–Weber constants show the partial intra-particle diffusion and have been used successfully to monitor the progress of the sorption. The negative values of the thermodynamic parameters, *i.e.* ΔH , ΔS , and ΔG indicate that sorption is exothermic, feasible, and spontaneous in nature. The developed procedure has been employed successfully to determine TAP concentration in real ground and surface water samples.

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