Kinetic Approach for the Adsorption of Organophosphorous Pesticides from Aqueous Solution Using “Waste” Jute Fiber Carbon

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Abstract: Chemically activated “Waste” Jute Fiber carbon has been effectively used for the removal of five organophosphorous pesticides (malathion, monocrotophos, methylparathion, phosphamidon and dimethoate) from aqueous solutions. The prepared activated jute fiber carbon was characterized by using Elemental analyzer and proximate analysis methods. The adsorption equilibrium was examined at 28 °C. Three different kinetic models, the pseudo first order, pseudo second order and Elovich kinetic models were selected to analyses the adsorption process. To compare the fitness of pseudo first order and pseudo second order, sum of the squares of the errors and correlation coefficient, r^2 values were calculated. The Elovich model was used to confirm the chemisorptions.

Keywords: Pesticides, Waste jute fiber carbon, Characterization, Adsorption, Kinetics.

Introduction

A pesticide gives potential hazards to animals, humans and aquatic life¹. They also cause deleterious effect on soil fertility and crop productivity. They enter into cyclic environment process such as absorption by soil, leaching by water². Pesticides are very dangerous and harmful because of their toxic and carcinogenic in nature³. Organophosphorous pesticides (OPPs) are frequently used to control the pest in the agricultural field. Common members of the family are methylparathion, malathion, dimethoate, phosphamidon, phorate, fenitrothion, monocrotophos *etc.* Therefore, the removal of OPPs from water is one of the major environmental concerns. Some treatment methods such as biodegradation⁴, extraction⁵, solid-phase extraction⁶, photocatalysis⁷, photo-fenton⁸, flocculation⁹, ion-exchange¹⁰, chlorination and ozonisation¹¹ and adsorption have been used to remove toxic materials from aqueous solutions.

In the recent years, adsorption has become one of the most important processes for the removal of organic pollutant from water¹²⁻¹⁸. Currently, the use of new low cost agricultural by product materials such as tea leaves¹⁹, biomass¹³, chickpea husk²⁰, olive stones²¹, cotton stalk²², rice bran, rice husk, bagasse fly ash^{23,24}, date stone^{25,26}, biowaste²⁷, coconut tree male flower^{28,29} and Jute fiber^{28,30} is being considered as adsorbent for the removal of toxic chemicals from aqueous solutions. In this study, we prepared sulphuric acid activated “Waste” jute fiber carbon (JFC) was used as a low-cost material for the removal of five OPPs from aqueous solution. Recently, our research group successfully used “waste” jute fiber carbon (JFC) as adsorbent for the dye removal³⁰.

Experimental

Technical grade malathion (CAS No: 121-75-5), methyl parathion (CAS No: 298-00-0), monocrotophos (CAS No: 6923-22- 4), phosphamidon (CAS No: 13171-21-6) and dimethoate (CAS No: 60-51-5) were used as an adsorbate.

Adsorbent

Sun dried “waste” Jute Fiber (JF) was carbonized using sulphuric acid (SA) in the weight ratio 4:3 (JF:SA) and kept in hot air oven, maintained at 160 °C for a period of 12 h. The carbon was then dried for 4 h at 100 °C. The resulting carbons were washed with distilled water until a constant pH of the slurry. The dried materials were used as adsorbent for the removal of OPPs.

Elemental and proximate analysis

Carbon / hydrogen / oxygen / nitrogen / sulfur (C/H/O/N/S) contents of our carbon were analyzed by using elemental analyzer (model CHNO-RAPID, Heraeus Co., Germany). For each analysis, the standard sample was first analyzed for checking the experimental error. All measurements were carried out in duplicate. The proximate analysis was made according to ASTM 3172-3175 standards and the results are given in Table 1.

Table 1. Elemental and proximate analysis of JFC

Element	Composition, Wt. %
Carbon	52.66
Hydrogen	3.22
Nitrogen	0.14
Oxygen	43.03
Contents	Composition, %
Moisture	12.22
Ash	2.69
Volatile Matter	61.28
Fixed Carbon	23.81
Sulfur	0.98

Batch studies

In equilibrium experiments, a fixed amount of “Waste” Jute Fiber Carbon (JFC) (0.5 g/L) and fifty milliliters of different initial pesticides concentrations (10, 20, 30 and 40 mg/L) were taken in a 100 mL conical flasks. The flasks were agitated at room temperature (28 °C) at 120 rpm for a pre-determined time intervals using thermostatic rotary orbital shaker with an initial pH 6.57. At time $t = 0$ and equilibrium, the concentration of pesticides were measured using Shimadzu UV-Vis spectrophotometer (Shimadzu Model: UV 1601).

Adsorption kinetics

Pseudo first order equation is generally expressed as follows³¹,

$$dq_t / dt = k_1(q_e - q_t) \quad (1)$$

Where, k_1 is the pseudo first order rate constant. After integration by applying conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, then equation (1) becomes

$$\log(q_e - q_t) = \log q_e - (k_1 / 2.303) t \quad (2)$$

Where, q_e is the amount adsorbed at equilibrium of pseudo second order equation. If the rate of adsorption is a second order mechanism, the pseudo second order kinetic rate equation (3) is expressed as³²,

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Where, k_2 is the pseudo second order rate constant. On integrating the equation (3)

$$t / q_t = (1 / k_2 q_e^2) + (1 / q_e) t \quad (4)$$

Elovich model

The most interesting model to describe the activated carbon adsorption³³ is Elovich equation (5),

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (5)$$

Where, 'a' and 'b' are constants. The constant 'a' is considered as the initial adsorption rate (mg/g min) and 'b' is related to the extent of surface coverage and activation energy for adsorptions (g/mg). $(dq_t / dt) \rightarrow a$ as $q_t \rightarrow 0$ and given that $q_t = 0$ at $t = 0$, the integrated form of equation (5) becomes,

$$q_t = (1 / b) \ln(t + t_o) - (1 / b) \ln t_o \quad (6)$$

Where, $t_o = (1 / ab)$. If $t \gg t_o$, equation 6 is simplified as,

$$q = 1 / b \ln ab + 1 / b \ln t \quad (7)$$

Where, 'a' is the initial adsorption rate (mg/g), and the parameter 'b' is related to the extent of surface coverage. Sum of the squares of the errors, SSE are calculated using the expression³⁴

$$SSE = \sqrt{\sum (q_e \exp - q_e \text{ cal})^2 / N} \quad (8)$$

Where, N is the number of data points.

Results and Discussion

Effect of contact time and initial malathion concentration on adsorption

Adsorption of pesticides onto waste JFC at different concentrations (10, 20, 30 and 40 mg/L) with fixed adsorbent dose (0.025 g/50 mL) was carried out at room temperature (28 °C). The effects of pesticide initial concentration with contact time are shown in Figures 1-5, respectively for malathion, monocrotophos, methylparathion, phosphamidon and dimethoate. It shows that, the percent adsorption decrease with increase in the initial pesticide concentration. But the actual amount of pesticides adsorbed per unit mass of carbon increases with increase in pesticides concentration. The curves in the Figures 1-5 are smooth and continuous, suggesting the possible monolayer coverage of pesticides on JFC surface. Similar results were reported by various researchers for the adsorption of pesticides onto different adsorbents^{23,30, 35}.

Effect of contact time and initial concentration.

Figure 1. Malathion,

Figure 2. Monocrotophos,

Figure 3. Methylparathion,

Figure 4. Phosphamidon,

Figure 5. Dimethoate

Conditions: Initial pH = 6.5; JFC dose = 0.5g/L;
Temperature = 28°C.

Kinetic models

For evaluating the adsorption kinetic of OPPs on JFC, the pseudo first order and the pseudo second order kinetic models were used. The Elovich model is used to explain adsorption behaviors that concur with the nature of chemical adsorption.

The pseudo first order and pseudo second order kinetic correlation coefficients, r^2 and SSE values are calculated from the plot of $\log(q_e - q_t)$ vs. t and t/q_t vs. t (Figures 6-15) and the values are presented in the Table 2. According to Daneshvar *et al.*³⁶ the linear fit is better when SSE values are low. The results for the adsorption of malathion, monocrotophos and methylparathion with the low SSE value and $r^2 > 0.9$ of pseudo first order kinetic model is better for predicting the kinetic process in the experimental conditions than the pseudo second order kinetic model^{31,37}. For phosphamidon and dimethoate studied as seen from Table 2, the lower values of SSE of pseudo second order model than that of pseudo first order model support the suitability of pseudo second order kinetic model to explain the adsorption onto JFC. Several researchers^{36,38} also reported the reasonable agreement of pseudo second order kinetic model.

Pseudo-first-order kinetic model.

Figure 6. Malathion,

Figure 7. Monocrotophos,

Figure 8. Methylparathion,

Figure 9. Phosphamidon,

Figure 10. Dimethoate

Conditions: Initial pH = 6.5; JFC dose = 0.5g/L; Temperature = 28°C.

Pseudo-second-order kinetic model

Figure 11. Malathion,

Figure 12. Monocrotophos,

Figure 13. Methylparathion,

Figure 14. Phosphamidon,

Figure 15. Dimethoate

Conditions: Initial pH =6.5; JFC dose = 0.5g/L;

Temperature = 28°C.

Table 2. Comparison of correlation coefficients and SSE values obtained from different kinetic models

Name of the Pesticide	Initial Concentration, mg /L	Pseudo first order kinetic model		Pseudo second order kinetic model		Elovich kinetic model	
		r^2	SSE	r^2	SSE	r^2	SSE
Malathion	10	0.974	0.509	0.940	4.125	0.937	1.897
	20	0.955	0.708	0.906	9.662	0.930	1.856
	30	0.988	0.029	0.950	7.038	0.940	0.560
	40	0.936	0.630	0.930	15.49	0.940	1.253
Monocrotophos	10	0.973	6.901	0.938	8.520	0.954	1.795
	20	0.987	4.328	0.975	6.141	0.967	0.121
	30	0.911	9.488	0.867	16.225	0.926	0.911
	40	0.977	2.360	0.998	5.573	0.988	0.604
Methylparathion	10	0.979	2.206	0.990	2.589	0.993	0.409
	20	0.984	3.358	0.980	4.646	0.980	0.285
	30	0.959	3.312	0.977	9.792	0.961	0.431
	40	0.969	3.334	0.993	9.093	0.981	0.640
Phosphamidon	10	0.981	5.083	0.9995	0.330	0.973	0.148
	20	0.902	5.145	0.9994	0.376	0.992	0.053
	30	0.959	7.487	0.998	0.849	0.975	0.069
	40	0.973	13.001	0.990	0.628	0.982	0.063
Dimethoate	10	0.952	3.971	0.994	6.638	0.993	1.274
	20	0.950	5.467	0.998	2.804	0.998	0.265
	30	0.940	17.119	0.999	5.284	0.994	0.127
	40	0.918	6.211	0.996	4.717	0.996	0.348

The SSE values calculated from the plot of q_t vs. $\ln(t+t_0)$ (Figures 16-20) for the Elovich model are lies within 0.930 - 0.940, 0.1212-1.795, 0.2854-0.6399, 0.0632-0.148 and 0.127-1.274 for the adsorption of malathion, monocrotophos, methylparathion, phosphamidon and dimethoate onto JFC. The correlation coefficient r^2 , which are closer to one in the case of Elovich model. The agreement of the Elovich equation with experimental data may be explained as follows: The successful applications of the Elovich equation to heterogeneous catalyst surfaces helps to explain its success in predicting the sorption of all the pesticides studied on JFC^{39,40}. The general explanations for this form of kinetic equation involves a variation of the energetic of chemisorption with the active sites are heterogeneous in JFC. This supports that the heterogeneous sorption mechanism likely to be responsible for the pesticides uptake. Elovich model basically supports chemisorption.

Elovich kinetic model.

Figure 16. Malathion,

Figure 17. Monocrotophos,

Figure 18. Methylparathion,

Figure 19. Phosphamidon,

Figure 20. Dimethoate

Conditions: Initial pH =6.5; JFC dose = 0.5g/L;

Temperature = 28°C.

Conclusion

- The adsorption of the pesticide was carried with “Waste” Jute Fiber Carbon as an adsorbent.
- The prepared activated carbon was analyzed by elemental and proximate method.
- From the effect of JFC dose study, adsorption increases with increase of JFC dose up to the equilibrium. malathion, monocrotophos and methylparathion adsorption onto JFC follows the first order kinetic model. The adsorption of phosphamidon and dimethoate onto JFC, which obey the pseudo second order kinetic model.
- The adsorption was supported by Elovich model.

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