

Film Diffusion Mechanism of Methyl Parathion in Biopolymers: Kinetics and Thermodynamic Equilibrium

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ABSTRACT: Sulfuric acid treated biopolymers (STB) were prepared from a lignocellulosic-based agricultural byproduct. The STB has been used as an effective adsorbent in a batch experiment for the removal of methyl parathion (MP) from aqueous solution. The as-prepared STB has been characterized by using surface area analyzer, scanning electron microscope (SEM), elemental analyzer, and proximate analysis methods. A batch adsorption study was carried out to investigate the adsorption equilibrium, kinetics, and thermodynamics as a function of agitation time, initial concentration of MP, initial pH, temperature, and carbon dose. Adsorption data were used to perform the kinetic models. The adsorption data was found to obey the Langmuir adsorption isotherm. Thermodynamic parameters of the adsorption process ΔG , ΔS , and ΔH were calculated, and their negative values indicate the feasible exothermic and spontaneous nature of the process. The diffusion of the MP molecule onto the biopolymer was confirmed by using the Weber–Morris equation. Reichenberg's equation shows the film diffusion of MP.

INTRODUCTION

Organophosphorous pesticides (OPPs) have been used extensively for agricultural purposes for more than 40 years. OPP series, widely used all over the world, are assumed to be one of the most dangerous chemicals for neurosis and carcinogenesis.^{1–3} OPPs such as methyl parathion (MP), malathion, dimethoate, phosphamidon, and monocrotophos are still extensively used worldwide, despite their high toxicity. The inappropriate disposal of waste from industries and farms is the main reason for the contamination of soil and water. MP (*O,O*-dimethyl-*O*-4-nitrophenyl phosphorothioate), a highly toxic OPP, is frequently used in cotton, wheat, rice, and sugar crops.⁴ Though the usage of MP is restricted only for agricultural crops, it has been extended illegally in other areas due to its low cost and effectiveness in controlling pests. MP is rapidly absorbed into the bloodstream through all normal routes of exposure of the human body. MP exerts its insecticidal toxicity by inhibiting acetyl cholinesterase in the peripheral nervous systems. The continuous exposure to MP can cause sweating, dizziness, vomiting, diarrhea, convulsions, cardiac arrest, respiratory arrest, and even the death of some pets.⁵ It is soluble ($60 \text{ mg} \cdot \text{L}^{-1}$ in water) and highly mobile, does not adsorb well to soil particles, and may contaminate groundwater. The U.S. Environmental Protection Agency (EPA) has detected 4-nitrophenol, a MP breakdown product, at low levels in drinking wells.⁶ The World Health Organization (WHO) classifies MP as class IA “extremely hazardous” pesticides.⁷ Consequently, it is essential to remove MP before its penetration into ground waters. There is no single method for removal of all pesticides. Several methods have been used, such as membrane filtration, photodegradation,⁸ solid-phase microextraction,⁹ ion exchange,¹⁰ chlorination and ozonation,¹¹ flocculation,¹² electrostripping,¹ and adsorption.

Adsorption is one of the most frequently applied methods because of its low maintenance costs, high efficiency, and ease of operation on large-scale applications. Adsorption on activated carbon is the most widespread technology used to deal with the purification of water contaminated by pesticides and other hazardous material.^{12–18} Activated carbon has a special place among the adsorbents. Currently, activated carbons are prepared from a variety of starting materials, that is, precursors: chickpea husk,¹³ olive stones,¹⁴ cotton stalk,¹⁵ baggasse, rice bran, fly ash, rice husk,¹⁷ date stone,^{18,19} biowaste,¹⁹ coconut tree male flower,^{20,21} clays,²² industrial solid wastes,²³ and nanometal oxides.²⁴ However, their use as a possible filter for the removal of pollutants from wastewaters revealed some technological and economical limitations. This led to a search for new nontoxic, low-cost biomass or unconventional materials for the efficient removal of pesticides from wastewaters.

India is the largest producer of jute fiber, lignocellulosic-based fibers, next to Bangladesh, in the world. Jute is one of the cheapest natural fibers and is second to cotton in the amount produced and the variety of uses. Jute fibers are composed primarily of the plant materials cellulose and lignin. Jute fibers ease availability with large quantity, making it a potential candidature as an adsorbent. Therefore, the prime objective of the present work is to evaluate the feasibility of using jute fiber biopolymer (JFB) for the effective removal of MP from simulated waters by batch adsorption over a range of experimental conditions. The effects of agitation time and initial MP concentration, temperature, pH of the pesticide solution, and adsorbent dose have been studied under batch adsorption experiments.

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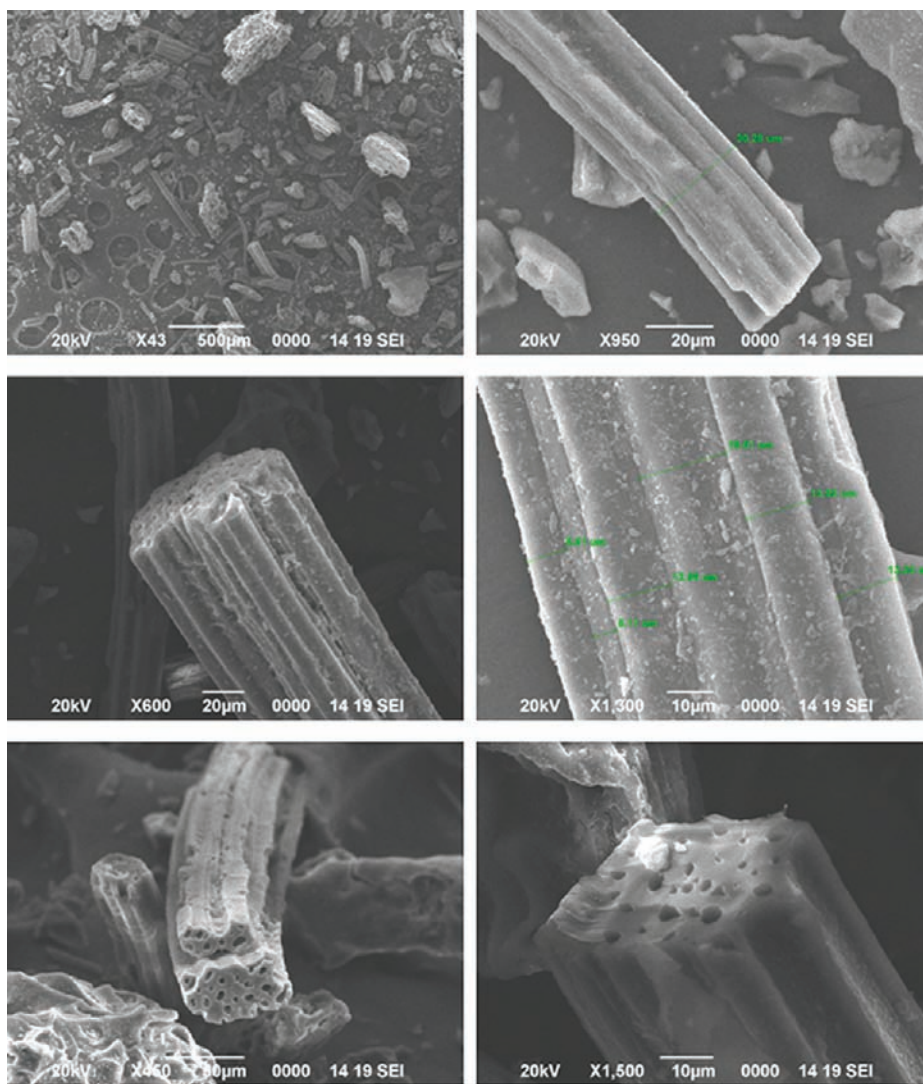


Figure 1. Scanning electron microscopic images of JFBC.

Various kinetics, isotherms, thermodynamics, and mass transfer investigations are used to study the adsorption process. UV adsorption spectroscopy was used to analyze the concentration of MP before and after adsorption onto JFB.

MATERIALS AND METHODS

Preparation of Activated Biopolymer. Jute fiber biopolymers (JFBs) were collected and washed to remove the adhering dirt and then dried, crushed, and subjected to a dehydration process using sulfuric acid. JFB was treated with sulfuric acid (SA) in the weight ratio 4:3 (JFB/SA) and kept in hot air oven, maintained at 160 °C for a period of 12 h. The resulting carbons were washed with distilled water until a constant pH of the slurry. The carbon was then dried for 4 h at 100 °C. The dried materials were ground and sieved to different geometrical sizes and labeled as JFBC.

Adsorbate MP. Commercially available technical grade MP was used as such without further purification, as a model pesticide. All of the chemicals used are of analytical reagent grade and were obtained from Qualigens (Mumbai, India). The used glassware was from Scott Duran (Germany). A stock solution of 1000 mg·L⁻¹ solution was prepared by dissolving the pesticide

in doubly distilled water. Initially the MP was dissolved in a small amount of methanol, before preparation of a buffered solution. In the absence of carbon control experiments are also carried out for the adsorption of pesticide by the container walls. It was found that there was no detectable degradation or adsorption of pesticide by the container walls.

Characterization of Jute Fiber Biopolymer Carbon (JFBC).

The percentage of carbon, hydrogen, oxygen, nitrogen, and sulfur present in the JFBC was found to be 52.66, 3.23, 43.05, 0.14, and 0.93, respectively, by using elemental analyzer (CHNO-RAPID, Heraeus Co., Germany). The contents (moisture 12.22 %, ash 2.69 %, volatile matter 61.28 %, fixed carbon 23.81 %) were determined by the proximate analysis method according to ASTM 3172-3175 standards. The chemical analysis of JFBC was carried out, and the calculated amount of functional groups such as phenolic, lactonic, and carboxylic were found to be (0.05, 0.01, and 0.03) mequiv·mg⁻¹, respectively. The amounts of sodium and potassium were found to be (63.02 and 0.11) mequiv·mg⁻¹, respectively. A pH_{zpc} value (6.56) was also measured. The scanning electron microscopic (SEM) pictures were taken using an FEI Quanta FEG 200 HRSEM instrument. The SEM images shows that the JFBC particles exist as fibers and are porous in

Table 1. Kinetic Parameters of MP Adsorption

| concentration of MP mg·L ⁻¹ | pseudofirst order | | | pseudosecond order | | |
|---|-------------------------------------|----------------|-------|-------------------------------------|----------------|-------|
| | $k_1 \cdot 10^{-2}/\text{min}^{-1}$ | R ² | SSE | $k_2 \cdot 10^{-2}/\text{min}^{-1}$ | R ² | SSE |
| 10 | 1.389 | 0.979 | 2.206 | 1.804 | 0.990 | 2.589 |
| 20 | 2.264 | 0.984 | 3.358 | 7.062 | 0.980 | 4.646 |
| 30 | 2.270 | 0.959 | 3.312 | 3.114 | 0.977 | 9.792 |
| 40 | 2.475 | 0.969 | 3.334 | 9.132 | 0.993 | 9.093 |

nature (Figure 1). The nitrogen adsorption–desorption isotherm was determined on the Quanta chrome at 77.35 K. The sample was outgassed at 27 K for 4 h. The specific surface area of the sample was calculated from the linear part of the nitrogen adsorption isotherm as 100.37 m²·g⁻¹. The total pore volume calculated at $p/p_0 = 0.1753$ mL was found to be 2.164 · 10⁻³ g⁻¹, and the average pore diameter was found to be 0.8347 nm.

FTIR Analysis. Several signatures are observed in the FTIR (Shimadzu, model FTIR-8201) spectrum of JFBC in the range (1400 to 4000) cm⁻¹. Since the precursor for the preparation of Jute fiber carbon is a natural material, it is very difficult to find out the exact surface functional groups present in the carbon surface. However, this suggests that various types of organic functional groups may be available on the surface of the carbon. The spectrum of JFBC (figure not given) shows that peaks obtained in the region of (3200 to 3650) cm⁻¹ indicate the surface contains bonded and nonbonded –OH groups of alcohol and phenol. The peak near to 3650 cm⁻¹ and 3600 cm⁻¹ shows the presence of nonbonded C–H stretching bands of alcohols and phenols. The signatures in the region (3100 to 2800) cm⁻¹ may be due to the presence of aliphatic C–H stretching. The observed peaks in the frequency range (2700 to 2500) cm⁻¹ are due to the overtones and combinations of OH in plane C–O stretching vibrations. The peaks in (2600 to 2550) cm⁻¹ indicate the presence of S–H stretching vibrations. The peaks seen between (1600 and 1450) cm⁻¹ indicate the C=C stretching. The weak peak corresponds to the SO₃H group appearing in 1377 cm⁻¹. Various peaks are obtained in the region [(600 to 900) cm⁻¹] due to C–C and C–H out-of-plane bending vibrations and C–S stretching vibrations.

Batch Adsorption Studies. In a typical batch studies, 50 mL of different initial MP concentrations [(10, 20, 30, and 40) mg·L⁻¹] were taken in a 100 mL conical flask containing 0.025 g of JFBC. The flasks were agitated at room temperature (28 °C) at 120 rpm for predetermined time intervals using a thermostatted rotary orbital shaker with an initial pH of 6.57. At time $t = 0$ and equilibrium, the MP concentration was measured using a Shimadzu UV–vis spectrophotometer (model: UV 1601). The maximum absorbance of MP was read at 275 nm and used to calculate the amount of MP adsorbed, q (mg·g⁻¹). The effect of JFBC dose was studied by varying the JFBC dose from (0.2 to 4.5) g·L⁻¹ for different MP concentrations [(10, 20, 30, and 40) mg·L⁻¹]. Langmuir isotherm studies were carried out by agitating a fixed amount of JFBC, 0.3 g·L⁻¹, of MP solutions of different initial MP concentrations, (60, 80, 100, 150, 200, 250, and 300) mg·L⁻¹, for 6 h. For the pH study, 50 mL of 20 mg·L⁻¹ and 40 mg·L⁻¹ of MP solution mixed with 0.025 g of JFBC were agitated at different initial pH values (2 to 10) of MP solution for 3 h at 28 °C. Hydrochloric acid and sodium hydroxide solutions were used to adjust the pH. Temperature studies were also carried out with 50 mL of 40 mg·L⁻¹ MP

solution with the effect of agitation time for four different temperatures [(28, 33, 38, and 43) °C] to evaluate the effect of temperature on the adsorption process. Generally, the JFBC dose of 0.5 g·L⁻¹ pH at 6.57 and room temperature, 28 °C, are maintained in all experiments unless otherwise stated.

For safety, all of the experiments were carried out in a fume hood; polyethylene gloves and goggles were used. Pesticides are packed and labeled properly in the local language with safety instructions.

Adsorption Kinetics. Various kinetics models are useful to explain the adsorption behavior of JFC. In this experiment, the kinetics of MP uptake by JFBC has been measured.

Pseudofirst-Order Equation. The pseudofirst-order equation is generally expressed as follows,²⁵

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

where k_1 is the pseudofirst-order rate constant. After integration by applying conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, then eq 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.

Pseudosecond-Order Equation. If the rate of adsorption is a second-order mechanism, the pseudosecond-order kinetic rate in eq 3 is expressed as,²⁶

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

where k_2 is the pseudosecond-order rate constant. On integrating eq 3,

$$t/q_t = (1/k_2q_e^2) + (1/q_e)t \quad (4)$$

Selection of the Kinetic Model. The discussion of kinetic studies and comparison of calculated and experimental equilibrium adsorption capacity, the regression coefficient, r^2 , and sum of squares of the error (SSE) of pseudofirst-order and pseudosecond-order kinetic models are dealt to select the best fit model for the adsorption of MP onto JFC. The kinetic parameters calculated from the linear plots of these two models are given in Table 1. The q_e calculated obtained for the pseudofirst-order kinetic model agree with the q_e experimental than those from pseudosecond-order kinetic model. The results with the value of $r^2 > 0.9$ and low SSE show that the pseudofirst-order kinetic model is better for predicting the kinetic process in the experimental conditions than the pseudosecond-order kinetic model.¹⁸ The sum of the squares of the errors, SSE, are calculated using the equation,²⁷

$$\text{SSE} = \sqrt{\sum (q_e(\text{exp}) - q_e(\text{cal}))^2 / N} \quad (5)$$

where N is the number of data points.

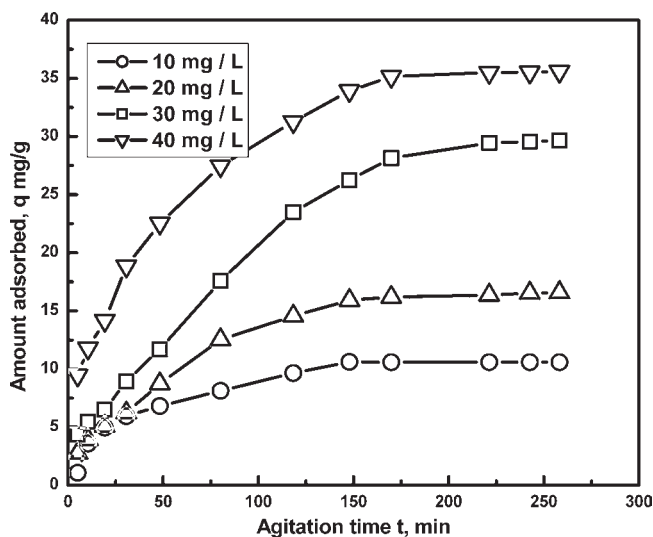


Figure 2. Effect of contact time and initial MP concentration. Conditions: MP concentration: \circ 10 $\text{mg}\cdot\text{L}^{-1}$; \triangle = 20 $\text{mg}\cdot\text{L}^{-1}$; \square = 30 $\text{mg}\cdot\text{L}^{-1}$; ∇ = 40 $\text{mg}\cdot\text{L}^{-1}$; initial pH = 6.5; temperature = 28 $^{\circ}\text{C}$; JFBC dose = 0.5 $\text{g}\cdot\text{L}^{-1}$.

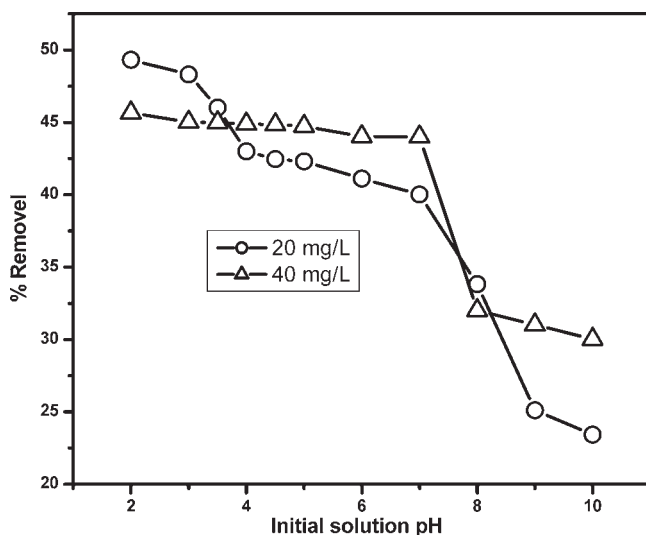


Figure 3. Effect of initial pH on MP removal. Conditions: MP concentration: \circ = 20 $\text{mg}\cdot\text{L}^{-1}$; \triangle = 40 $\text{mg}\cdot\text{L}^{-1}$; JFBC dose = 0.5 $\text{g}\cdot\text{L}^{-1}$; temperature = 28 $^{\circ}\text{C}$; initial pH = 2.00 to 10.00.

RESULTS AND DISCUSSION

Effect of Agitation Time and Initial Concentration on the Removal of MP. It is seen from Figure 2, the amount of MP adsorbed increases with increase in the initial concentration of MP from (10 to 40) $\text{mg}\cdot\text{L}^{-1}$. From the above observation, it is evident that after the equilibrium time the MP adsorption was not significant from time to time. Similar results have been reported by Hameed et al.¹⁸ This may be due to the formation of monolayer coverage of adsorbate on carbon surface. The higher equilibrium time taken for higher concentration may be due to the reason of increased competition for the active adsorption sites.

Effect of Carbon Dose. The percent removal of MP increased with the increase in carbon dose and reaches a constant value after a particular amount of JFBC for the entire concentration of

Table 2. Langmuir Adsorption Isotherm of MP

| concentration of pesticide $\text{mg}\cdot\text{L}^{-1}$ | R_L | b $\text{L}\cdot\text{mg}^{-1}$ | Q_0 $\text{mg}\cdot\text{g}^{-1}$ | R^2 |
|---|-------|--------------------------------------|--|--------|
| 60 | 0.032 | 0.508 | 225.73 | 0.9846 |
| 80 | 0.024 | | | |
| 100 | 0.019 | | | |
| 150 | 0.013 | | | |
| 200 | 0.009 | | | |
| 250 | 0.008 | | | |
| 300 | 0.007 | | | |

MP studied (figure not given). An increased concentration of JFBC results in the increase of external surface area, which provides more adsorptive sites for the adsorption reaction to occur. A further increase in JFBC may not affect sorption, which may be due to interference between binding sites of JFBC doses.

Effect of pH. The percentage adsorption of pesticide at different pH level is shown in Figure 3. The percentage adsorption decreases with an increase in the pH. At various pH values, the potential binding sites of functional groups present in the surface are playing a vital role in the adsorption process. At very low pH values, the more attractive force is raised between the adsorbent and the adsorbate molecule. This attractive force is due to surface functional groups which may be surrounded by the hydronium ion obtained from pesticide solution. At a higher pH value a portion of surface functional groups should become more deprotonated. This causes the weak interaction between the adsorbent and the adsorbate molecules. A similar result was reported in various adsorption processes.^{15,16}

Adsorption Isotherms. The Langmuir isotherm was applied for adsorption equilibrium,²⁸

$$(C_e/q_e) = (1/bQ_0) + (C_e/Q_0) \quad (6)$$

where C_e is the equilibrium concentration of the MP solution ($\text{mg}\cdot\text{L}^{-1}$) at equilibrium, q_e is the amount of MP adsorbed at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), and Q_0 and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. Plotting C_e/q_e against C_e , a straight line, has a slope ($1/Q_0$), and the intercept ($1/Q_0b$) is obtained. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor R_L ,²⁹

$$R_L = 1/(1 + bC_0) \quad (7)$$

where C_0 is the initial MP concentration ($\text{mg}\cdot\text{L}^{-1}$). The value Q_0 monolayer capacity, b Langmuir constant, R^2 correlation coefficient, and R_L dimensionless separation factor values for the concentration of pesticides from (60 to 300) $\text{mg}\cdot\text{L}^{-1}$ are given in Table 2. The formation of monolayer coverage of the adsorbent on the surface of carbon can be clearly confirmed by Langmuir isotherm data. The R_L values lies between 0 and 1 ($0 < R_L < 1$), suggesting that the adsorption of pesticides on the JFBC is favorable.¹⁸ The adsorption capacities of the other available agricultural biomaterials reported in the literature,^{30,31} such as rice bran, moringa oleifera, rice husk, bagasse fly ash, and watermelon peels, are found to be (102.7, 94.8, 92.12, 102.7, and 6.4) $\text{mg}\cdot\text{g}^{-1}$.

Effect of Temperature. The effect of temperature study was carried out with an MP solution of concentration 40 $\text{mg}\cdot\text{L}^{-1}$ containing a fixed carbon dose of 0.5 $\text{g}\cdot\text{L}^{-1}$ at different

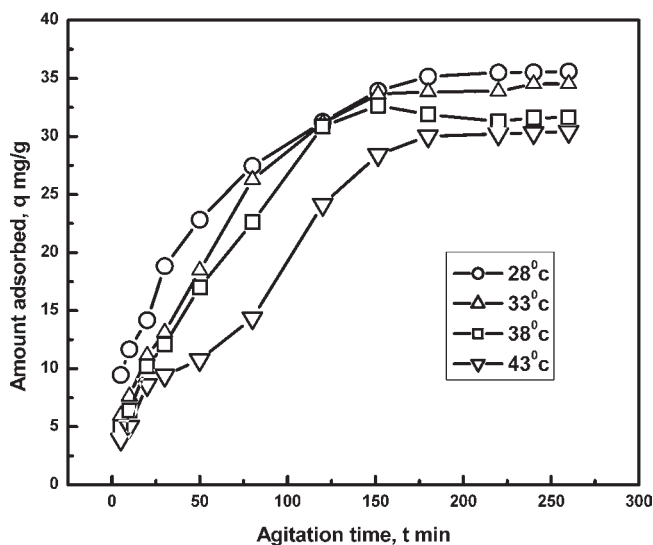


Figure 4. Effect of temperature on MP removal. Conditions: temperature, $\circ = 28\text{ }^{\circ}\text{C}$; $\Delta = 33\text{ }^{\circ}\text{C}$; $\square = 38\text{ }^{\circ}\text{C}$; $\nabla = 43\text{ }^{\circ}\text{C}$; MP concentration = $40\text{ mg}\cdot\text{L}^{-1}$; initial pH = 6.5; JFBC dose = $0.5\text{ g}\cdot\text{L}^{-1}$.

Table 3. Thermodynamic Data for the Removal of MP

| temperature $^{\circ}\text{C}$ | $-\Delta G^{\circ}$ | | ΔS° | | ΔH° |
|-----------------------------------|---------------------------------|--------|--|--|--------------------|
| | $\text{kJ}\cdot\text{mol}^{-1}$ | K_c | $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ | $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ | |
| 28 | 1.966 | 0.7987 | -42.04 | -14.62 | |
| 33 | 1.76 | 0.7590 | | | |
| 38 | 1.545 | 0.6542 | | | |
| 43 | 1.335 | 0.6142 | | | |

temperatures [(28, 33, 38, and 43) $^{\circ}\text{C}$]. The amount of MP adsorbed decreases with the increase in temperature (Figure 4), indicating the exothermic nature of the process. It was also observed that the maximum adsorption obtained at 28 $^{\circ}\text{C}$ for MP and the order of the adsorption was found to be $28 > 33 > 38 > 43\text{ }^{\circ}\text{C}$. This type of adsorption may be due to the increase in the solubility of MP with the rise of temperature of the process. Hence, there is a lesser tendency of pesticide molecules to reach the carbon surface. Similar observations were reported in the adsorption of drin pesticide¹⁹ and carbofuran.²³

Thermodynamic Parameters. Thermodynamic parameters, ΔH and ΔS , for the adsorption process are also determined using Eyring's plot,²⁰

$$\ln K_c = \Delta S/R - \Delta H/RT \quad (8)$$

where $K_c = C_{ad}/C_e$. K_c is the equilibrium constant of the MP which is a ratio of C_{ad} , the concentration of the MP in the adsorbent, and C_e , the concentration of the MP in the adsorbate. A plot was drawn with the values of $\ln K_c$ and $1/T$. ΔS and ΔH values were evaluated for the temperatures [(28, 33, 38, and 43) $^{\circ}\text{C}$] studied. ΔG was calculated using eq 9 and is presented in Table 3.

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

The negative values of ΔH give a measure of the amount of heat energy lost (exothermic nature) in the transfer of MP from the free solution state to a carbon surface area. The negative value of

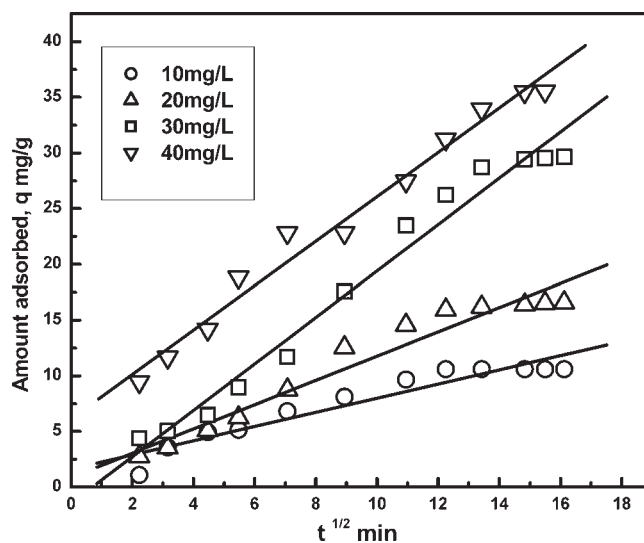


Figure 5. Intraparticle diffusion. Conditions: MP concentration, $\circ = 10\text{ mg}\cdot\text{L}^{-1}$; $\Delta = 20\text{ mg}\cdot\text{L}^{-1}$; $\square = 30\text{ mg}\cdot\text{L}^{-1}$; $\nabla = 40\text{ mg}\cdot\text{L}^{-1}$; initial pH = 6.5; temperature = $28\text{ }^{\circ}\text{C}$; JFBC dose = $0.5\text{ g}\cdot\text{L}^{-1}$.

Table 4. Intraparticle Diffusion Parameters of MP Adsorption

| concentration of MP $\text{mg}\cdot\text{L}^{-1}$ | K_{id} min^{-1} | R^2 | SSE |
|--|-------------------------------|--------|--------|
| | | | |
| 20 | 1.089 | 0.9744 | 0.003 |
| 30 | 2.084 | 0.9881 | 10.459 |
| 40 | 1.994 | 0.9902 | 2.7784 |

ΔS indicates an increase in the state of orderness during adsorption. The negative value of ΔG indicates that the adsorption of MP is spontaneous and feasible, and the obtained results are in agreement with the other studies of pesticides adsorption onto various materials.^{19,23}

Mass Transfer Effects. Kinetic and equilibrium isotherm studies help us to identify the mechanism of adsorption process. A prediction of the mechanism is required for designing the batch adsorber. According to Weber and Morris,³² an intraparticle diffusion coefficient K_{id} is given by eq 10,

$$q_t = K_{id}t^{1/2} + C \quad (10)$$

The plots of q_t versus $t^{1/2}$ as shown in Figure 5 and the two regions in the q_t vs $t^{1/2}$ plot suggest that the adsorption process proceeds by surface adsorption and intraparticle diffusion. The initial curved portion of the plot indicates a boundary layer effect, while the second linear portion is due to intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined to yield the intraparticle diffusion parameter K_{id} . On the other hand, the intercept of the plot reflects the boundary layer effect. The calculated intraparticle diffusion rate constant, K_{id} , values are listed in Table 4. The value of $R^2 > 0.9$ in this model justifies the mechanism for the diffusion of pesticides.

To determine the actual rate-controlling step involved in the MP adsorption process, the adsorption data were further analyzed using the kinetic expression given by Boyd et al.³³ This is in

Table 5. Diffusion Coefficient Values of MP for Adsorption at Various Concentrations and Temperatures

| diffusion coefficient, $D_i \cdot 10^{-10}, \text{m}^2 \cdot \text{s}^{-1}$ | | | | diffusion coefficient, $D_i \cdot 10^{-12}, \text{m}^2 \cdot \text{s}^{-1}$ | | | |
|---|------------------------------------|------------------------------------|------------------------------------|---|-------|-------|-------|
| 10 $\text{mg} \cdot \text{L}^{-1}$ | 20 $\text{mg} \cdot \text{L}^{-1}$ | 30 $\text{mg} \cdot \text{L}^{-1}$ | 40 $\text{mg} \cdot \text{L}^{-1}$ | 28 °C | 38 °C | 43 °C | 48 °C |
| 2.707 | 3.012 | 2.582 | 2.875 | 2.089 | 3.073 | 3.559 | 1.277 |

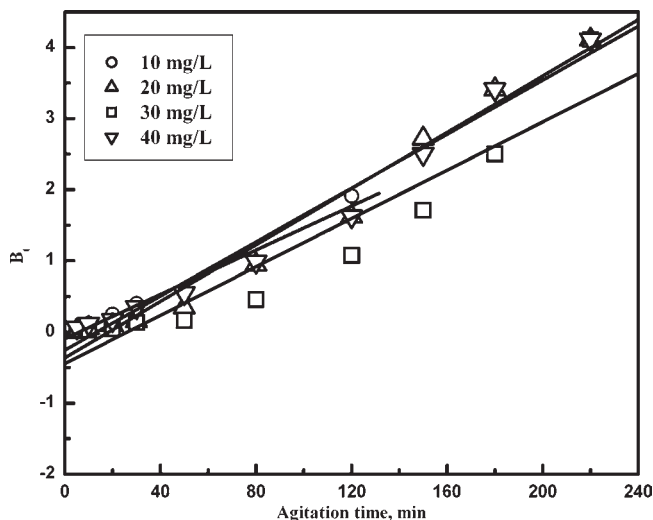


Figure 6. Effect of concentration of MP on the diffusion coefficient. Conditions: MP concentration, $\circ = 10 \text{ mg} \cdot \text{L}^{-1}$; $\triangle = 20 \text{ mg} \cdot \text{L}^{-1}$; $\square = 30 \text{ mg} \cdot \text{L}^{-1}$; $\nabla = 40 \text{ mg} \cdot \text{L}^{-1}$; initial pH = 6.5; temperature = 28 °C; JFBC dose = $0.5 \text{ g} \cdot \text{L}^{-1}$.

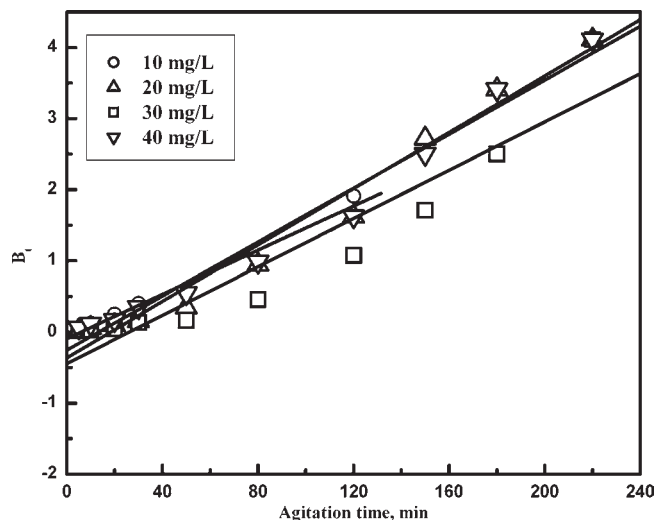


Figure 7. Effect of temperature on the diffusion coefficient of MP. Conditions: temperature, $\circ = 28 \text{ °C}$; $\triangle = 33 \text{ °C}$; $\square = 38 \text{ °C}$; $\nabla = 43 \text{ °C}$; MP concentration = $40 \text{ mg} \cdot \text{L}^{-1}$; initial pH = 6.5; JFBC dose = $0.5 \text{ g} \cdot \text{L}^{-1}$.

accordance with the observations of Reichenberg,³²

$$F = 1 - 6/\pi^2 \sum_t (1/n^2) \exp - n^2 Bt \quad (11)$$

$$F = \frac{Q_t}{Q_\infty} \quad (12)$$

$$Bt = \frac{\pi^2 D_i}{(r_o)^2} = \text{Time constant} \quad (13)$$

where F is the fraction of solute adsorbed at different times t and B_t is a mathematical function of F , D_i is the effective diffusion coefficient of adsorbate in adsorbent phase, r_o is the radius of adsorbent particle assumed to be spherical, and Q_t and Q_∞ represent the amount adsorbed ($\text{mol} \cdot \text{g}^{-1}$) at any time t and at infinite time.

For every calculated value of F , corresponding values of B_t are obtained from the Reichenberg table,³⁴ the values of D_i are given in the Table 5. Boyd considered two kinds of diffusion processes, “particle diffusion” and “film diffusion”. The linearity test of B_t versus time plots was employed to distinguish between the film-diffusion and the particle-diffusion-controlled adsorption with the change in concentration and temperature. If the plot of B_t versus time is a straight line passing through the origin, then the adsorption rate is governed by the particle diffusion mechanism; otherwise, it is governed by film diffusion.^{35,36} In Figures 6 and 7, the plots do not pass through the origin, indicating film diffusion nature of MP with the variation in concentration as well as temperature. Since the adsorption of MP onto JFBC is an

exothermic process, the value of D_i decreases with the rise of temperature.

CONCLUSION

Dehydrated carbons prepared from JFBs were capable of removing MP from aqueous solution. The effect of low pH was favorable for MP adsorption. It was found that the adsorption follows pseudofirst-order kinetic model. From the carbon dose study, the adsorption increases with increases of carbon dose up to the equilibrium. It is noteworthy that, from the results obtained from the effect of temperature studies, the rate of adsorption decreases with the increase in temperature. The equilibrium adsorption data were best described by the Langmuir isotherm model. The negative value of ΔG , ΔS , and ΔH indicated that the adsorption of MP by JFBC is spontaneous and exothermic in nature. Mass transfer studies show the film diffusion mechanism during the adsorption process.

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