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Adsorption of methyl parathion pesticide from water using watermelon peels as a low cost adsorbent

G. Zuhra Memon*, M.I. Bhanger, Mubeena Akhtar, Farah N. Talpur, Jamil R. Memon

National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro-76080, Pakistan

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Abstract

In the present studies chemically and thermally treated watermelon peels (TWMP) have been utilized for the removal of methyl parathion (MP) pesticide from water. The effect of process variables such as pH of solution, shaking speed, shaking time, adsorbent dose, concentration of solution and temperature have been optimized. Maximum adsorption (99 ± 1%) was achieved for $(0.38–3.80) \times 10^{-4}$ mol dm^{-3} of MP solution, using 0.1 g of adsorbent in 20 ml of solution for 60 min agitation time at pH 6. BET and SEM analysis have been carried out for the characterization of TWMP. Adsorption data has been analyzed by Freundlich, Langmuir and Dubinin–Radushkevich (D–R) adsorption isotherms. Lagergren, Morris–Weber and Reichenberg equations have been used for kinetic studies of adsorption process. Thermodynamic parameters ΔH, ΔS and ΔG have been calculated. Positive value of ΔH and negative value of ΔG show endothermic and spontaneous nature of adsorption respectively. The developed adsorption method has been employed to surface water samples with percent removal 99% ± 1.

Keywords: Watermelon (*Citrullus lanatus*) peels; Methyl parathion; Adsorption; Isotherms; Kinetics; Thermodynamics

1. Introduction

The contamination of soils, ground water and surface water by pesticides is currently a significant concern throughout the world because many of these compounds are detrimental to both human health and the environment. Increasing use of pesticides in agriculture, and domestic activities for controlling pests is polluting water resources day by day [1]. The pesticides form a strong class of water pollutants, as they are mostly non-biodegradable. Moreover, pesticides are carcinogenic in nature. Therefore toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating the environment. Among newly developed pesticides, organophosphorous pesticides are most commonly used. This class of chemicals is divided into several forms; however the two most common forms are phosphates and phosphorothionates. Methyl parathion (*O*,*O*-dimethyl *O*-4-nitrophenyl phosphorothioate) is a class I insecticide. Once methyl parathion introduced into the environment from spraying on crops, droplets of methyl parathion in the air fall on soil, plants or water. While most of the methyl parathion will stay in the areas where it is applied, some can move to areas away from where it was applied by rain, fog and wind [2].

Adsorption is one of the most efficient methods for removal of pollutants from water. Activated carbon is very efficient adsorbent for removing varieties of pesticides from water and wastewaters due to its high surface area and porosity. The use of the activated carbon in removing many pesticides from aqueous phase has been demonstrated in the literature [3]. However due to the high cost of activated carbon, its use in the field is restricted on economical consideration [4,5]. Nowadays low cost adsorbents have been investigated as an alternative to activated carbon, for example, fly ash [5], carbon cloth [6], porous polymeric adsorbents [7], wheat residue black carbon [8], bleaching earth [9], lignin [10], riverbed sand [11], wood char coal [12], waste tire rubber granules [13] etc.

In the present work, a low cost agricultural waste material watermelon peels (WMP) has been used for the adsorption of methyl parathion from aqueous solutions. The uptake conditions of methyl parathion from aqueous solution have been worked out in terms of operational parameters such as, pH of solution, initial solute concentration, dose of adsorbent and agitation time. Adsorption isotherms of methyl parathion onto WMP have also

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* Corresponding author. Tel.: +92 222 771379; fax: +92 222 771560.
E-mail address: zuhramemon_chem@yahoo.com (G.Z. Memon).

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been investigated to determine maximum adsorption capacity, and nature of adsorption.

2. Materials and methods

2.1. Reagents

All the reagents used were of analytical grade. The buffer solutions of pH 1–10 were prepared by mixing appropriate volumes of 0.1 M solutions of KCl and HCl (pH 1–3), sodium acetate and acetic acid (pH 4–6) and boric acid and sodium hydroxide (pH 7–10) solutions [14].

2.2. Adsorbent

Watermelon peels, a by-product of watermelon, were collected from local market, washed thoroughly with water and then with deionized water to remove foreign impurities. It was then dried in an oven at 110 °C. The washed material was sieved in Ro-Tap type electrical sieve shaker. The sieved material was rewashed thoroughly with deionized water to remove the fine particles and dried in an electrical oven. The material was then chemically treated with 0.1 M nitric acid for 1 h, followed by soaking in methanol for 1 h to remove inorganic and organic matter from the surface of adsorbent. The chemically treated WMP were subjected to thermal treatment in a closed muffle furnace (Phoenix, Sheffield, England, 1983) to increase the surface area [15]. The chemically and thermally treated watermelon peels (TWMP) were stored in a vacuum descicator to be used as adsorbent for further analysis.

2.3. Equipments and method of characterization

A scanning electron microscope (SEM) was used to study the surface morphology. Specific surface area of adsorbent was determined by Brunauer, Emmett and Teller (BET) method using nitrogen as a standard [16] and employing surface area analyzer (Quantasorb, QS-7). The pH measurements were made on digital (Inolab level 1) pH meter, Germany. A temperature controlled water bath flask shaker (Gallenkemp No. 350–010) was used for shaking all the solutions. The concentration of the adsorbate in solution was determined by Hitachi model 6200 HPLC equipped with a Licrosorb ODS column 5 μm (Ø 250 mm × 4 mm) UV–vis detector. Deionized water (with 0.5 μS conductance, pH 6) and methanol (30:70, v/v) were used as mobile phase at a flow rate of 1 ml/min. The limit of detection (signal to noise ratio 1:3) was observed to be 0.04 ng μl^{-1} at selected wavelength of 240 nm.

2.4. Adsorption experiments

The batch adsorption experiments were used to measure the adsorption of pesticide onto adsorbent surface. The experiment was performed in an Erlenmeyer flask inside a mechanical shaker. In this process 0.1 g of adsorbent was put in a 100 ml Erlenmeyer flask containing 20 ml of methyl parathion solution at appropriate pH and the solution was shaken at desired temperature. Finally, the sample was filtered using Whatmann filter paper no. 44. A, 10 μl of sample solution was then injected to HPLC under optimized conditions. The data was used to calculate adsorbed concentration of adsorbate onto adsorbent surface by the difference in the detector response peak height (mV) before and after shaking. The distribution ratio R_d was calculated by using following equation:

$$R_\mathrm{d} = \frac{\text{Amount of analyte in adsorbent}}{\text{Amount of analyte in solution at equilibrium}} \times \frac{\text{Volume of solution (ml)}}{\text{Mass of adsorbent }(g)} \quad (1)$$

where R_d is the distribution coefficient between solid and liquid phase; V the volume of the solution (cm^3) and W is the weight of sorbent (g). Correlation among % sorption and the distribution coefficient may be located by the following equation [17]:

$$\%\,\text{Sorption} = \frac{100\ R_d}{R_d + (V/W)} \quad (2)$$

All the experiments were performed in triplicate. The linear regression computer program with one independent variable was used for slope and statistical analyses of the data.

3. Results and discussions

3.1. Characterization of adsorbent material

The surface area of untreated watermelon peels (UTWMP) was found to be 15.1 $m^2\,g^{-1}$, after treatment surface area of adsorbent was increased and found to be 23.4 $m^2\,g^{-1}$.

Scanning electron microscope was used (Fig. 1a and b) to observe the surface morphology of adsorbent material. It was revealed that chemical and thermal treatment makes adsorbent material more porous.

3.2. Effect of pH

Optimization of pH of adsorption medium plays very important role in the adsorption studies. The adsorption of pesticide was studied over the range of pH 1–10 by using 0.1 g of the adsorbent per 20 ml of 0.38×10^{-4} mol dm^{-3} of the pesticide solution with the shaking speed of 100 rpm. Fig. 2 shows that percent sorption decreases with an increase in the pH. At low pH values, the surface of the adsorbent would be surrounded by the hydronium ions, which may enhance the adsorbate interaction with binding sites of the adsorbent by greater attractive forces and hence improve its uptake on polar adsorbent.

3.3. Adsorbent dose

The effect of adsorbent dose on removal of pesticide was studied by varying the dose of adsorbent in the range of 0.05–1 g at fixed pesticide concentration. After 0.1 g of adsorbent percent adsorption was found almost constant.

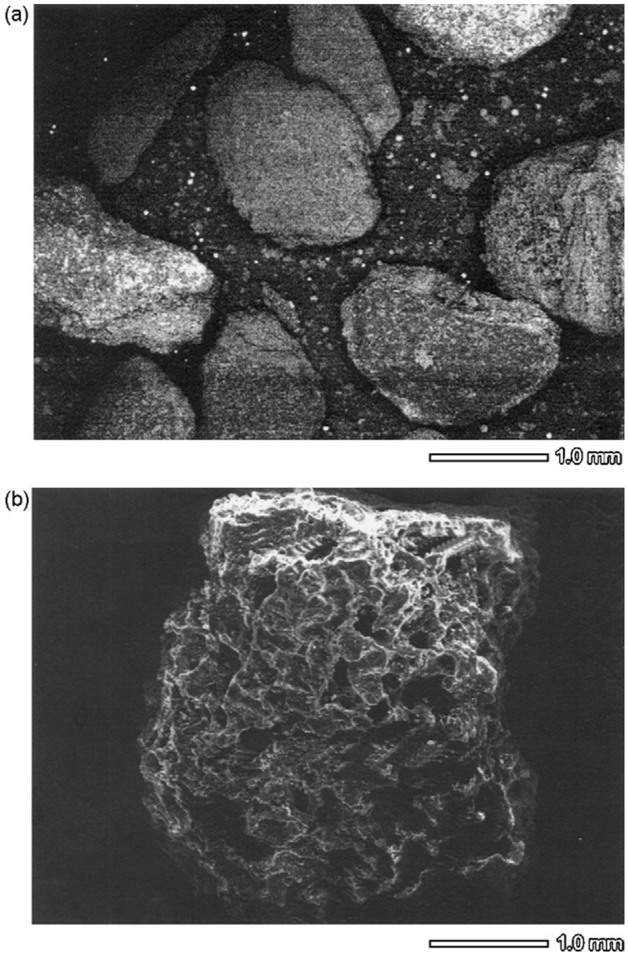

Fig. 1. Scanning electron micrographs of watermelon peels: (a) untreated watermelon peels (b) treated watermelon peels.

3.4. Effect of contact time

In order to determine equilibrium time for maximum uptake 0.1 g of adsorbent was used over a contact time of 10–100 min, at 6 pH with 100 rpm shaking speed, for 20 ml of 0.38×10^{-4} mol dm^{-3} methyl parathion solution. Results show that contact time of 60 min is enough to adsorb maximum amount of pesticide from solution.

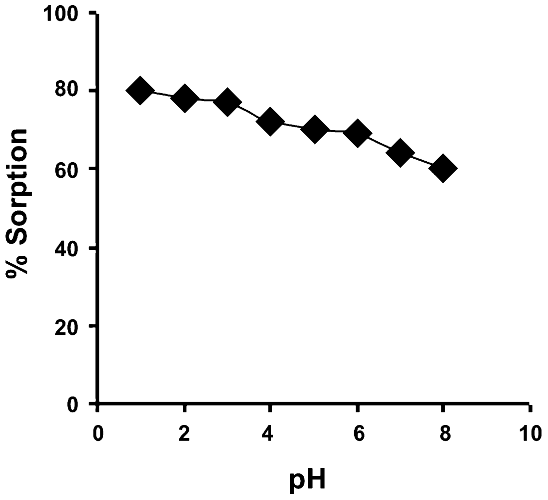

Fig. 2. Effect of pH on sorption of MP and CF onto TWMP.

3.5. Effect of adsorbate concentration

For observing the effect of concentration of the adsorbate, the concentration range 0.38–3.8 × 10^{-4} mol dm^{-3} was taken for the methyl parathion at 30 °C by using 0.1 g of adsorbent under optimized conditions. With an increase in adsorbate concentration, a corresponding decrease in the distribution coefficient (R_d) was observed suggesting limiting number of adsorption sites available for adsorption at higher concentration of adsorbate molecules.

3.6. Adsorption isotherm

The adsorption isotherms are useful to evaluate adsorption capacities of adsorbent and thermodynamic parameters like energy of adsorption. The adsorption data have been subjected to different adsorption isotherms, namely Freundlich, Langmuir and Dubinin–Radushkevich (D–R).

The linearized form of Freundlich isotherm is tested in the following form:

$$\log C_{\mathrm{ads}} = \log C_{\mathrm{m}} + \frac{1}{n} \log C_{\mathrm{e}} \tag{3}$$

where $1/n$ is a characteristic constant related to adsorption intensity, C_{ads} the adsorbed concentration of sorbate onto adsorbent (mol g^{-1}), C_{e} represents equilibrium concentration of adsorbate in solution and C_{m} is the multilayer adsorption capacity of adsorbent (mol g^{-1}). A plot of log C_{ads} versus log C_{e} would exhibit in a straight line with a slope of 1/n and intercept of log C_{m} as shown in Fig. 3 and the results are listed in Table 1.

The results of the adsorption of the pesticide on watermelon peels were fitted into Langmuir isotherm. Langmuir isotherm has been used by various workers for the adsorption of a variety of compounds; the linear form of this isotherm is given by the

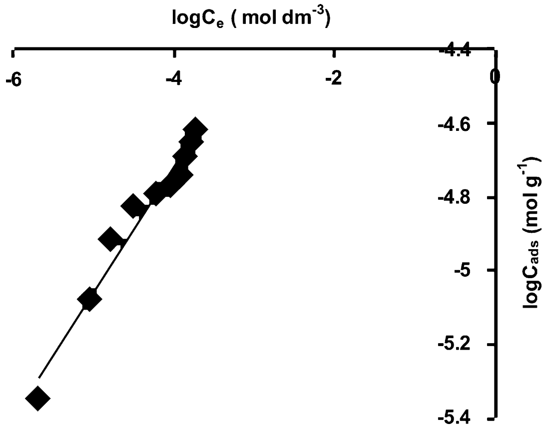

Fig. 3. Freundlich sorption isotherm plot of MP onto TWMP.

Table 1
Isotherm constants and values of R^2 for the adsorption of MP onto TWMP

Parameters	Value	R^2
Freundlich isotherm C_m (mmol g^{-1})	0.42 ± 0.0001	0.963 ± 0.045
$1/n$	0.34 ± 0.023	
Langmuir isotherm Q (μmol g^{-1})	24.3 ± 1.6	0.966 ± 0.24
b (mol dm^{-3})	$(4.32 \pm 0.39) \times 10^4$	
D–R isotherm β (kJ^2 mol^{-2})	0.7001 ± 0.05	0.97 ± 0.15
X_m (μmol g^{-1})	75.0 ± 6.5	
E (kJ mol^{-1})	12.6 ± 0.14	

equation [18]:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{4}$$

where Q is the monolayer adsorption saturation capacity (mol g^{-1}), and b represents the enthalpy of adsorption (dm^3 mol^{-1}), independent of temperature. A plot of C_e/C_{ads} versus C_e yields a straight line with its slope of $1/Q$ and intercept of $1/Qb$ as shown in Fig. 4 and the results are enlisted in Table 1. From the value of b, a dimensionless parameter, R_L [19], was estimated in the concentration range $(0.38–3.8) \times 10^{-4}$ mol dm^{-3} by using the relationship:

$$R_L = \frac{1}{(1 + bC_i)} \tag{5}$$

where b is the Langmuir constant (dm^3 mol^{-1}) and C_i is the initial concentration (mol dm^{-3}). The computed values of R_L are in the range of $(37.9–5.74) \times 10^{-2}$, indicates higher adsorption at low concentrations.

The adsorption data was also tested on another isotherm, namely D–R in the following form [20]:

$$\ln C_{ads} = \ln X_m + \beta\varepsilon^2 \tag{6}$$

where C_{ads} is the amount of adsorbate sorbed onto adsorbent surface (mol g^{-1}), X_m the maximum adsorption capacity of adsorbent (mol g^{-1}), β a constant related to adsorption energy, while ε is Polanyi adsorption potential which is equal to [21,22]

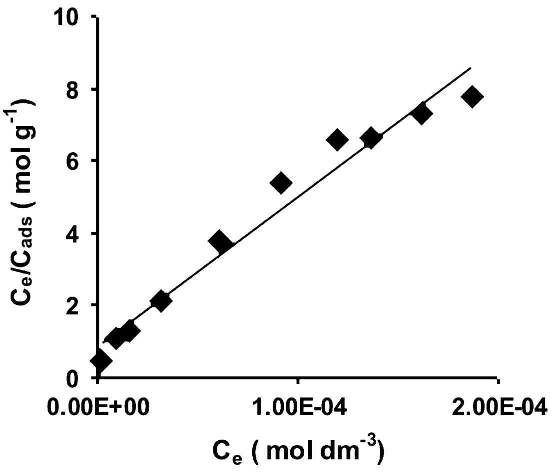

Fig. 4. Langmuir sorption isotherm plot of MP onto TWMP.

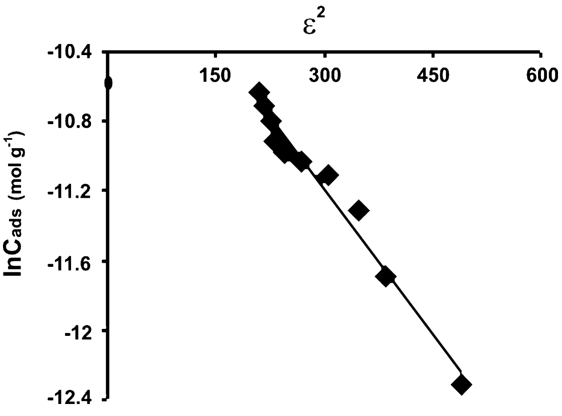

Fig. 5. D–R sorption isotherm of MP onto TWMP.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

R is a gas constant in kJ mol^{-1} K^{-1}, T the temperature in Kelvin and C_e is the equilibrium concentration of adsorbate in solution (mol dm^{-3}). The plot of $\ln C_{ads}$ versus ε^2 is a straight line with the slope of β and intercept of X_m as exhibited in Fig. 5 and the value of adsorption energy, E, can be correlated to β using the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

The results of D–R model are also given in Table 1.

3.7. Dynamic modeling

Kinetics of adsorption is/are an important characteristic from the point of view of determining the efficiency of adsorption processes [23]. A number of kinetic models have been used by various workers, where the adsorption has been considered as first-order [24,25], pseudo-first-order [26,27] and pseudo-second order process [28]. Lagergren's rate equation [29] is most widely used [30] for the adsorption of adsorbate from a solution. The first-order Lagergren's rate equation is

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \tag{9}$$

where q_e and q_t are the amounts of pesticide adsorbed at equilibrium and at time t, respectively, and k is the first-order rate constant.

Fig. 6 shows the kinetic study of adsorption of methyl parathion onto WMP at optimum conditions while investigating effect of agitation time on % sorption; log (q_e–q_t) was plotted versus agitation time resulting in a straight line with coefficient of determination, R^2, 0.987 ± 0.16, and the value of k, the first-order rate constant, computed from the slope of the linear plot as 0.0573 ± 0.0058 min^{-1}. The kinetics of adsorption was also examined using Morris–Weber equation [31] in the following form:

$$q_t = R_d\sqrt{t} \tag{10}$$

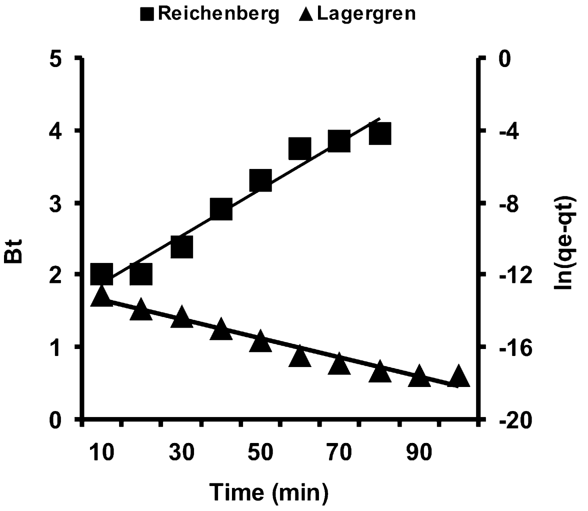

Fig. 6. Lagergren and Reichenberg plots of MP onto TWMP.

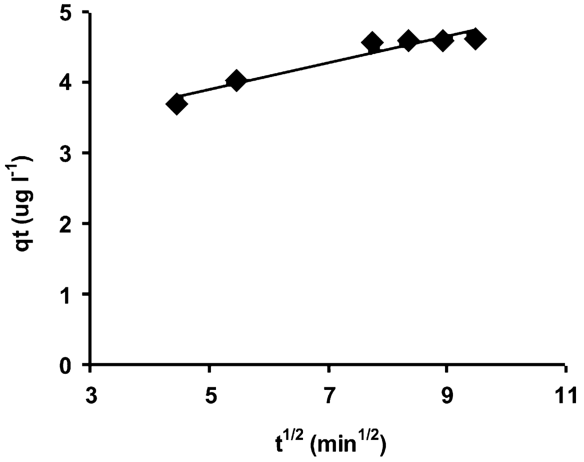

Fig. 7. Morris–Weber plots of MP onto TWMP.

where q_t is the sorbed concentration at time't', and R_d is the rate constant of intraparticle transport. The q_t was plotted against $t_{1/2}$ in Fig. 7.

The adsorption data follow linearity as per Eq. (10) up to 60 min with coefficient of determination, R^2, (0.93), and the value of R_d computed from the slope of the plot comes out 185 nmol g^{-1} min$^{-1/2}$. The effectiveness of the diffusion of the adsorbate species within the adsorbent particles of radius "r" and control of film diffusion in adsorption may be deduced from the linear fit of the data to the Reichenberg equation [32]

$$Q = 1 - \frac{6e^{-B_t}}{\pi^2} \qquad (11)$$

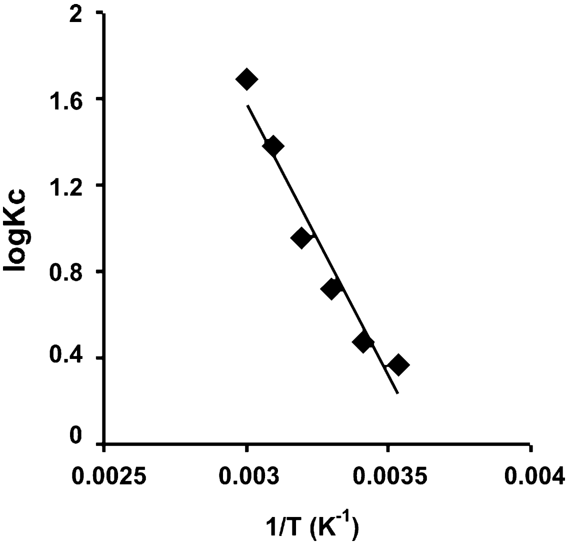

Fig. 8. Effect of temperature on sorption of MP onto TWMP.

where $Q = q_t/q_m$, $B_t = \pi^2 D_i/r^2$ and q_t and q_m are adsorbed concentration at time t and the maximum adsorption capacity of the sorbent and D_i is the effective diffusion coefficient of the adsorbate species inside the adsorbent particle. The value of B_t which is a mathematical function of Q, can be evaluated for each value of Q, using following equation:

$$B_t = -0.4977 - \ln(1 - Q) \qquad (12)$$

The plot of B_t versus time (Fig. 6) follows linearity from 0 to 80 min, which indicates the formation of film coating of the adsorbate on the adsorbent surface.

3.8. Thermodynamics

The variation in temperature, influencing the distribution of adsorbate between solid and liquid phases was examined in the range 283–323 K, under optimized conditions mentioned earlier. The plot of ln K_c versus $1/K$ gives a straight line with coefficient of determination 'R^2' (0.95 ± 0.13) as shown in Fig. 8.

$K_c = F_e/(1 - F_e)$, where F_e is the fraction adsorbed at equilibrium, while K is the temperature in Kelvin. The thermodynamic parameters, such as enthalpy ΔH, entropy ΔS and Gibbs free energy ΔG were estimated [33,34] using following equations:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (13)$$

$$\Delta G = -RT \ln K_c \qquad (14)$$

From the slope and intercept of plot, the values of ΔH and ΔS have been computed, while ΔG is calculated using Eq. (14). The

Table 2
Thermodynamic parameters for the adsorption of MP onto TWMP

ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})	ΔG (kJ mol^{-1})					
		283 K	293 K	303 K	313 K	323 K	333 K
48.82 ± 5.53	0.176 ± 0.006	−1.99	−2.67	−4.18	−5.72	−8.53	−10.77

Table 3
Percent adsorption and percent recoveries of MP from spiked water samples onto TWMP

Sample	Removal (%)	Recovery (%)
A	99 ± 1	97 ± 0.6
B	98 ± 0.8	96 ± 0.5

results are presented in Table 2. It may be deduced from the positive value of ΔH the adsorption process is endothermic in nature, and the negative values ΔG suggests the spontaneous nature of adsorption. The decrease in the value of ΔG with the increase of temperature shows that the reaction is more spontaneous at high temperature. The decrease in the value of ΔG with an increase in temperature indicates that the reaction became fast with the rise in temperature.

4. Application of the proposed method

The proposed methodology was applied to contaminated surface water samples. Surface water samples (samples A and B) were collected from two different agricultural areas of district Matiari. The contaminated water samples were spiked with 10 μg/ml of the methyl parathion pesticide. Amount of methyl parathion pesticide in sample A (0.85 ± 0.03) and in sample B (0.74 ± 0.02) μg/ml was determined.

For the removal of methyl parathion from contaminated water samples onto TWMP, at optimized experimental conditions, 100 ml portions of the spiked water samples were agitated for 60 min by using 0.4 g of adsorbent. 10 μl was injected to HPLC for the analysis by using adsorption procedure as stated in the experimental part. TWMP effectively removed methyl parathion pesticide from contaminated water samples. The sorbed amount of methyl parathion was recovered with 5 ml of methanol by sonication on an ultrasonic bath for 10 min. The percent adsorptions along with percent recoveries are presented in Table 3.

5. Conclusion

The experimental results showed that chemically and thermally treated watermelon peels are effective adsorbent for the removal of methyl parathion pesticide from water. Removal of methyl parathion pesticide is higher at acidic pH range. Freundlich adsorption isotherm proposes adsorption capacity of sorbent is better for lower concentration solutions rather than higher concentration solution, where as Langmuir isotherm depict favorable adsorption process. Adsorption energy obtained from D–R isotherm shows the physiosorption nature of the sorption process. Kinetic of adsorption follows a first-order rate equation.

Thermodynamic parameters ΔS, ΔG and ΔH indicate that adsorption process is thermodynamically favorable, spontaneous and endothermic in nature. Methyl parathion pesticide was successively removed from real surface water samples. Methanol was found to be better solvent for desorption of methyl parathion pesticide from surface of treated watermelon peels.

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