Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.24183

160 (2019) 229–239
August

Performance and mechanism of removal of atrazine pesticide from aqueous media utilizing pumpkin seeds shell powder

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Received 20 November 2018; Accepted 27 March 2019

ABSTRACT

The present study was focused on the removal of atrazine pesticide from aqueous media employing pumpkin seeds shell powder (PSSP) in batch mode of experiments. This removal study was performed considering the effect of pH, time of contact, dosage of sorbent, initial pesticide concentration and temperature. Characterizations of PSSP were performed before and after removal study using SEM, EDX, FTIR and surface area analyzer. The pH study indicates that optimum pH for the removal of atrazine from aqueous media was 3.0. The best fit kinetic model among pseudo first order, pseudo second order, Elovich, intra particle and liquid film diffusion was pseudo second order due to the highest R^2 and the proximity between the values of experimental and calculated sorption capacity of this model. The adsorptive characteristic of atrazine onto PSSP was evaluated using Freundlich, Langmuir, Temkin and Dubinin–Radushkevich isotherms and demonstrates that the data fitted excellently into Langmuir isotherm due to high R^2 value. Langmuir isotherm was also used to find out the maximum sorption capacity of PSSP for atrazine and was found to be 74.62 mg g^{-1}. Thermodynamic study of the removal of atrazine implies that atrazine removal onto PSSP was spontaneous and exothermic process. It may be deduced from these findings that pumpkin seeds shell is an inexpensive, eco-friendly and promising biosorbent for the removal of pollutants from wastewater.

Keywords: Atrazine; Pumpkin seeds shell powder; Kinetics; Equilibrium; Thermodynamics

1. Introduction

To increase the yield of crops and decrease the losses of crops after harvesting, pesticides are used all over the world in modern agriculture. However, the uses of these pesticides in excess as well as the improper usage can result in contamination of water and land [1]. Among pesticides, herbicides represent approximately 50% of the total pesticides used in agriculture and become a serious environmental concern due to potential runoff of herbicides from the soil resulting to contamination of water bodies [2].

Atrazine (2-chloro-4-ethylamino-6isopropylamine-s-triazine) ($pK_a = 1.60$) is considered among those pesticides which are widely used herbicide for protection of the pre-emergence as well as post-emergence broad leaf and grassy weeds present main crops [3]. Health hazards associated with atrazine are disruption of endocrine and reproductive systems, carcinogen for human and decrease sperm levels in men [4]. It also causes birth defects, low weight at birth time and problem during menstrual cycle [5].

To reduce the contamination of pesticides, various methods have been employed such as advanced oxidation process, membrane separation, electro dialysis, ozonation and biosorption. Among these, biosorption is one of the most extensively utilized methods which easily reduce the concentration of pesticides in wastewater [6–10]. Biosorption consists of sorption of a substance on surface of biological materials. A considerable research has been performed

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on heavy metal ions biosorption but a limited literature can be found on the biosorption of pesticides [11]. Recently, biological materials of various categories have been employed for the removal of different contaminants but agricultural byproducts are predominantly interesting due to their inexpensiveness, abundant availability and ubiquity. Furthermore, vegetal materials may be included in those materials having heterogeneous compositions consisting of many biding sites [12].

Pumpkin belongs to *Cucurbitaceae* family and extensively cultivated for its fruit. Among the world, pumpkin fruit is considered as one of the most important vegetable. The fruit of pumpkin is a rich source of minerals vitamins, fiber and antioxidants [13]. The World Health Organization recommends consuming of seeds of pumpkin because these are the unique sources of mineral zinc. The seeds, their extracts and oil of the pumpkin seeds have been appreciated for their anti-viral and anti-fungal properties. The shell of the seed protects the inner seed and is a naturally occurring fibrous coat. Although the shell is a valuable source of fiber but commonly this is considered as a waste. To make better the utilization of these shells as valuable materials, it is anticipated to use as a sorbent for the treatment of wastewater. According to our knowledge seeds of pumpkin have been utilized only for the removal of various contaminants such as dyes and heavy metal [14–17] but have not been used for the removal of atrazine. The aforesaid reason prompted us to utilize the shells of pumpkin seed for sequestration of pesticide from aqueous solution. Moreover, the abundant availability of pumpkin seed shells as crop waste is the primarily reason to choice it as a biosorbent.

In the present study, pumpkin seed shells was utilized for the removal of atrazine pesticide from aqueous media under the influence of pH, time of contact, dosage of sorbent, temperature and initial atrazine concentration. The obtained data from the sorption study were interpreted by kinetic and isotherm models. Thermodynamic analysis was performed for recognition the nature and mechanism of the removal of atrazine from aqueous media.

2. Materials and methods

2.1. Preparation of biosorbent

Pumpkins were purchased in bulk quantities from local market in Faisalabad city. These were then cut with knife and the seeds were separated from the rest part of the vegetable. These seeds were then dried in sunlight and the shells were then separated manually from the seeds. The shells were then ground in an electrical grinder and sieved. A sufficient amount (20 g) of the materials was taken in a beaker. To this beaker, distilled water was added and the addition of distilled water was continued till the materials settled down and kept overnight. The upper portion of the beaker was decanted and then again distilled water was added until the material settled down. Such process was performed till the water becomes transparent and finally the materials were filtered. The materials were kept in an oven and the temperature of the oven was fixed at 100°C. These materials were transferred after drying in a bottle to store for further study.

2.2. Point of zero charge

To determine the point of zero charge of the sorbent solid addition method was applied which is given in the literature. In this method 45 mL of 0.10 M KNO_3 solution was transferred in separate beakers and the initial pH of solutions was adjusted to the values of 2, 3, 4, 5, 6, 7, 8, 9 and 10 using 0.1 M NaOH and 0.1 M HCl. To each beaker, one gram of PSSP was added stirred for 48 h with a speed of 180 rpm at room temperature. After completion of stirring the final pH of the solutions was measured and point of zero charge was determined from the difference of initial pH to that of final.

2.3. Biosorption experiments of atrazine

The removal study of atrazine from aqueous media onto PSSP was carried out in batch system by taking 10 mL of initial atrazine of a fixed concentration (33.33–183.33 µg mL^{-1}), preset dosage of sorbent (0.1–1.0 g) and solution pH (3.0–12.0) in a conical flask and stirred in an orbital shaker (150 rpm) for desirable time of contact (10–100 min) at a temperature range of 303–363 K. after equilibration the flask contents were then filtered and the amount of unadsorbed atrazine was determined at 264 nm with the help of UV/Visible spectrophotometer.

To calculate the removal (%) and sorption capacity of atrazine, the following formulae were used:

$$Sorption(\%) = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (1)$$

$$q_e = \left(\frac{C_o - C_e}{m}\right) \times V \quad (2)$$

where C_o and C_e represent initial and equilibrium concentration (µg mL^{-1}), q_e is the sorbed amount of pesticide (mg g^{-1}), *V* (mL) and *m* (g) denote the volume of solution and mass of sorbent respectively.

3. Results and discussion

3.1. Characterizations of PSSP

Different techniques were used to characterize the biosorbent PSSP before and after removal of atrazine. These include the following techniques:

3.1.1. Point of zero charge (PZC)

The point upon which sorbent surface has zero charge is known as point of zero charge. Solid addition method was applied to determine the point of zero charge of PSSP [18]. It has been suggested that the most appropriate pH for the cation removal is one which is greater than PZC while for the anion sorption the most suitable pH is less than PZC [19]. Fig. 1 indicates that the value of PZC for SPPS is 6.0 suggesting that the surface charges of SPPS is positive below PZC and negatively charged above the PZC. It signified that there is a strong contact between the atrazine molecules and positively charged PSSP surface at low pH. Therefore, the removal of atrazine was found maximum at low pH but the surface of PSSP becomes negative above the PZC due

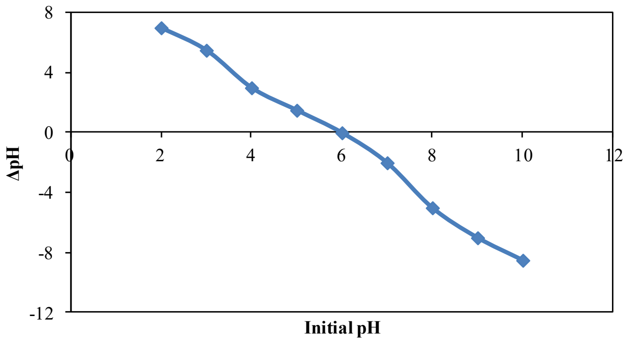

Fig. 1. Plot of point of zero charge of the PSSP.

to which repulsion occurred between the molecules of atrazine and negatively charged surface of PSSP. Consequently, the removal of atrazine using PSSP was decreased at pH higher than PZC.

3.1.2. Surface area analysis

The removal efficiency of a sorbent is greatly influenced by the surface area and pore volume of the sorbent [20]. Nitrogen adsorption isotherm was used to obtain the surface area analysis data of PSSP before and after removal of atrazine and summarized in Table 1. The results illustrate that the surface area PSSP was decreased after removal of atrazine which indicates the sorption of atrazine molecules.

3.1.3. SEM analysis

The textural properties of PSSP were studied with the help of Scanning Electron Microscopy (SEM) to check any variation in surface of PSSP before and after removal studies. It can be illustrated from Fig. 2 that a variety of cavities and pores of irregular and rough shape are present on the surface of PSSP before removal of atrazine. These cavities and pores of PSSP provide a large surface area for interaction of atrazine molecules. However, after removals process the cavities and pores were somewhat decreased and fulfilled which indicates the removal of atrazine molecules as shown in Fig. 3.

3.1.4. EDX analysis

EDX analysis was conducted in order to know any changes in elemental level of PSSP before and after removal of atrazine. Fig. 4 illustrates the EDX of PSSP which consists of C, O, Na and Mg before removal of atrazine. However, after removal of atrazine some new peaks due Ca and N were appeared which indicates that the removal of atrazine occurs through ion exchange mechanism as depicted in Fig. 5. Moreover, the presence of nitrogen after removal confirms the removal of atrazine because atrazine molecule contained nitrogen atom [21].

3.1.5. FTIR analysis

Fourier transform infra-red spectroscopic analysis was performed before and after removal of atrazine to recog-

Table 1
Surface analysis data of PSSP

Parameter	Before removal of atrazine	After removal of atrazine
Surface area ($m^2\ g^{-1}$)	6.1	1.1
Pore radius (Å)	15.07	15.08
Pore volume ($mL\ g^{-1}$)	0.005	0.001

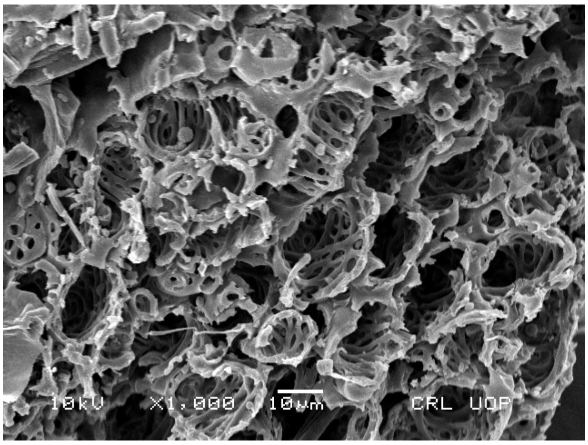

Fig. 2. SEM of PSSP before removal of atrazine.

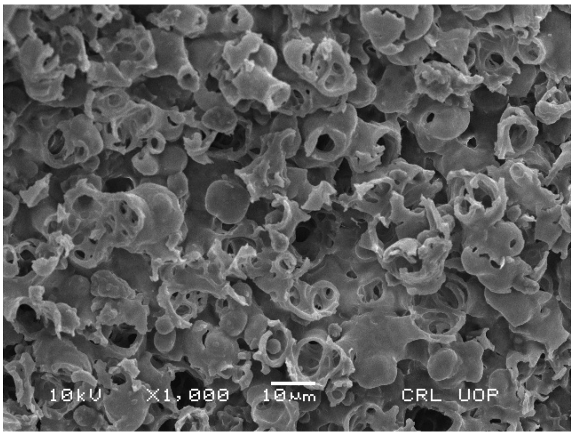

Fig. 3. SEM of PSSP afterremoval of atrazine.

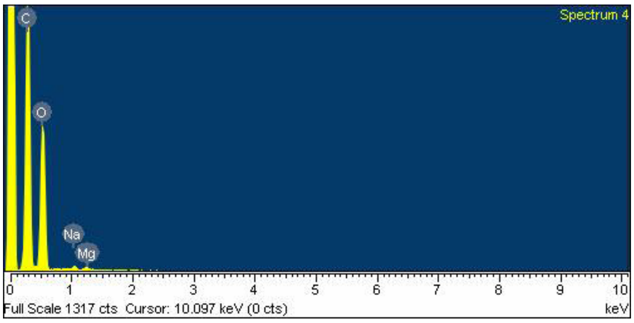

Fig. 4. EDX of the PSSP before removal of atrazine.

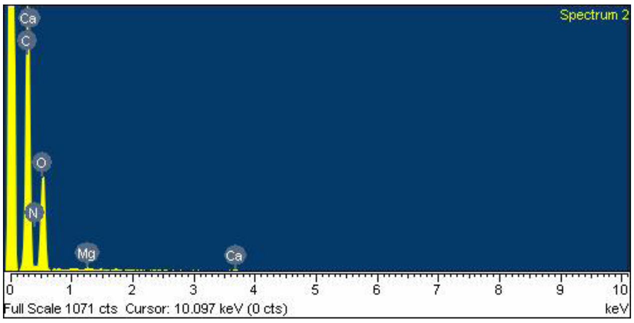

Fig. 5. EDX of the PSSP after removal of atrazine.

nize the functional groups of PSSP. Fig. 6 depicts that peak at 3388.96 cm^{-1} indicates the presence of hydroxyl group, peaks at 2918.9 and 2853.1 cm^{-1} designate –CH stretching of –CH$_2$ and –CH$_3$ groups, peak at 1596 cm^{-1} designates N-H bending and C-N stretching and peak at 1031 cm^{-1} represents P–O stretching [22–24]. The figure showed that bending shape of the surface of PSSP is greater before removal process than after removal process. Such type of results suggest that the surface of PSSP was occupied by atrazine molecules resultantly the transmittance has been decreased after removal of atrazine [25].

3.2. Effect of pH

The most important variable in the sorption study is the pH of solution which may affect the chemistry of surface of sorbent and the ionization of sorbate during the sorption process [26]. For this reason, the influence of solution pH on removal of atrazine was investigated by varying the pH of solution in the range of 3.0–12.0 with a fixed amount of sorbent dose (0.1 g) and initial atrazine concentration (33.33 µg mL^{-1}). The result is shown in Fig. 7 which indicates the removal of atrazine was decreased with increasing in pH and maximum removal of atrazine (97.67%) was obtained at pH 3.0. At low pH, the protonation of the sorbent taken place, as a result a strong electrostatic interaction develops between the protonated surface of sorbent and atrazine molecules. Therefore, at low pH, maximum removal of atrazine was observed which suggests that low pH is suitable to remove atrazine [27]. However, a decrease in electrostatic interaction between molecules of atrazine and sorbent was occurred with increase in pH, may be owing to the deprotonation of the sorbent surface and a repulsive force was developed between atrazine molecules and the negatively charged surface [28]. Consequently, at higher pH, less removal of atrazine was observed.

3.3. Effect of dosage of sorbent

Dosage of sorbent is among those factors which considerably affect the biosorption process [29]. Therefore, the influence of dosage of sorbent on the removal of atrazine was studied by changing the dosage of sorbent from 0.1 to 1g for a constant initial concentration of atrazine (33.33 µg mL^{-1}) and at optimum pH of solution (i.e. 3.0). Fig. 8 showed that the removal of atrazine was increased with increase in dosage of sorbent. This result reflects that the removal efficiency of PSSP enhances with progress in dosage of sorbent because the number of available sorptive sites increases with increase in dosage of sorbent [30]. As a result, the removal of atrazine was increased with dosage of sorbent and then a very slow increased was observed may be owing to the agglomeration of particles of sorbent [31].

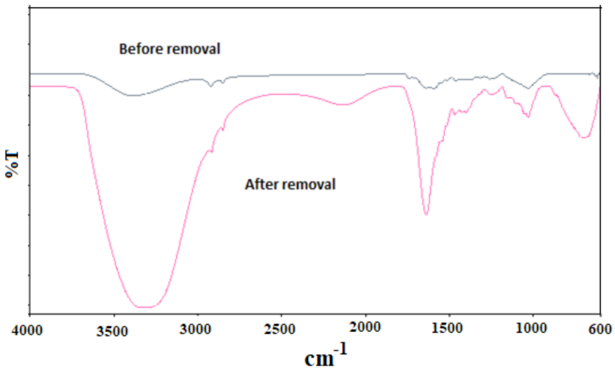

Fig. 6. FTIR spectrum of PSSP before and after removal of atrazine.

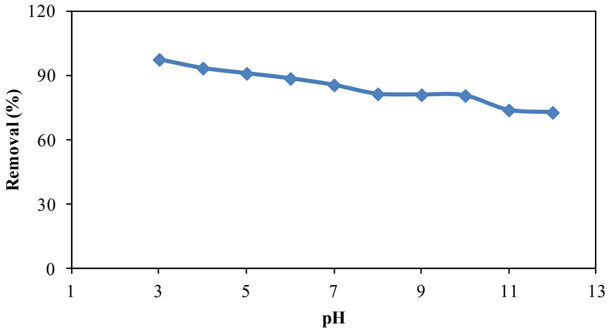

Fig. 7. Effect of pH (conditions of experiment: range of pH 3–12, dosage of sorbent 0.1 g, initial atrazine concentration 33.33 µg mL^{-1}, time of contact 30 min, volume for the sorption process 30 mL, room temperature).

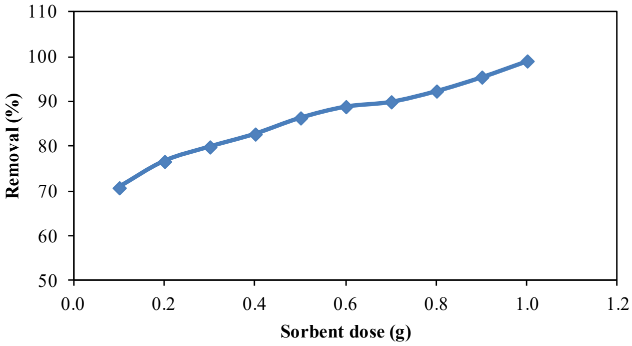

Fig. 8. Effect of sorbent dose (conditions of experiment: range of dosage of sorbent 0.1–1.0 g, pH 3.0, initial atrazine concentration 33.33 µg mL^{-1}, time of contact 30 min, volume for the sorption process 30 mL, room temperature).

3.4. Effect of time of contact

Time of contact is also included in those parameters which extensively affect the sorption process. For this reason, the removal of atrazine using PSSP was performed under the influence of time of contact by changing the time of contact in the range of 10–100 min with a fixed initial atrazine concentration (33.33 ppm) and stirring speed of 150 rpm. Solution pH was controlled at 3.0 using Britton Robinson buffer and the volume of the solution fixed (25 mL) with a fixed amount of PSSP dosage (0.1) g at room temperature. The result is illustrated in Fig. 9 which shows that the removal of atrazine using PSSP was increased with stirring time and the equilibrium was established within 50 mim. However, after 50 min, the removal efficiency of PSSP was almost become constant and no appreciable change in removal percentage was observed. In the initial stage, the removal process was rapid and slow down in the vicinity of equilibrium. Such types of results demonstrate that more vacant sites are available in the initial stage but removal process becomes very slow owing to the occupation of available sites present on the surface of PSSP [32].

3.5. Effect of initial atrazine concentration

The initial concentration of sorbate takes place a central role in the removal study. Therefore, the removal study of atrazine was conducted under the influence of initial concentration of atrazine by varying concentration of atrazine from 33.33 to 163.33 μg mL^{-1} keeping the other factors constant. The result is shown in Fig. 10 which demonstrates that the removal of atrazine onto PSSP increases with each increment in initial concentrations. A driving force is provided by the initial concentration of atrazine to overcome mass transfer resistances of atrazine between aqueous medium and solid phase due to which the removal of atrazine was increased. However, this driving force is perhaps limited owing to the occupation of all available sorptive sites at higher atrazine concentration [33]. Therefore, the process of removal was then become constant and no further prominent change in removal process was observed at high initial concentration.

3.6. Effect of temperature

Among the significant parameters which highly affect the removal process is temperature. Due to the importance of temperature, the removal of atrazine was performed under the influence of temperature by varying the temperature from 303 to 363 K and the rest the factors were kept constant. The result is shown in Fig. 11 which demonstrates that with increase in temperature, the removal of atrazine onto PSSP was decreased. Such type of liability can be owing to alteration of sites present on the surface of PSSP which are responsible for the removal of atrazine. As a consequence, the removal of atrazine was decreased with increase in temperature [34]. At high temperature, the boundary layer becomes thin and atrazine molecules easily escaped from the surface of PSSP due to which the removal process decreases with increase in temperature.

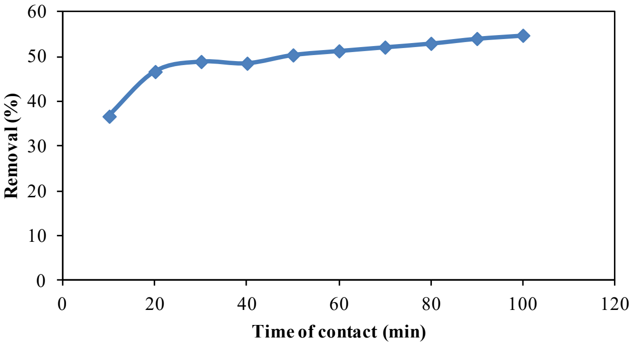

Fig. 9. Effect of time of contact (conditions of experiment: range of time of contact 10–100 min, dosage of sorbent 0.1 g, initial pH 3.0, initial atrazine concentration 33.33 μg mL^{-1}, volume for the sorption process 30 mL, room temperature).

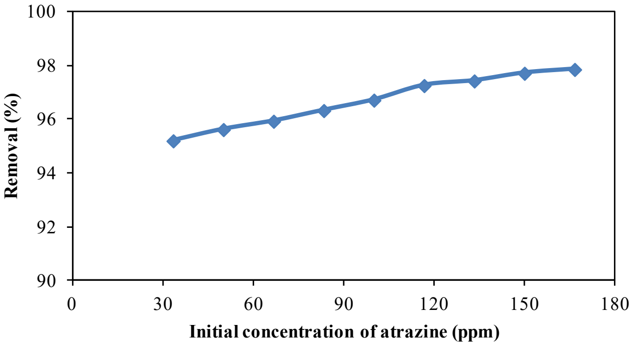

Fig. 10. Effect of initial atrazine concentration (conditions of experiment: range of initial atrazine concentration 33.33–163.33 μg mL^{-1}, pH 3.0, dosage of sorbent 0.1 g, time of contact 30 min, volume for the sorption process, room temperature).

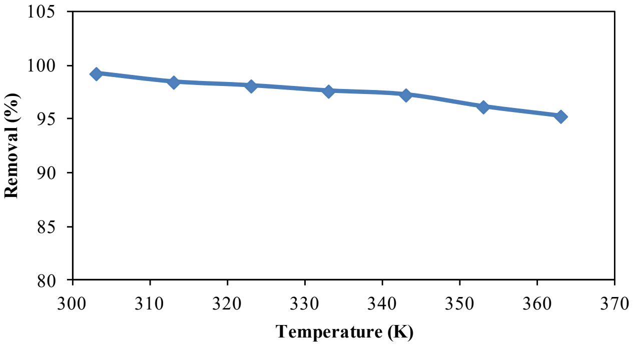

Fig. 11. Effect of temperature (conditions of experiment: range of temperature 303–363 K, initial atrazine concentration 33.33 μg mL^{-1}, pH 3.0, dosage of sorbent 0.1 g, time of contact 30 min, volume for the sorption process).

3.7. Kinetics of sorption studies

Kinetics of the process is one of the most informative studies about the uptake of atrazine molecules on the surface of PSSP which consequently controls the time of uptake of atrazine molecules at the boundary between PSSP and the solution [35]. To investigate the controlling mechanism that whether the removal process is controlled by mass transfer, diffusion or chemical reaction, the removal data of atrazine were analyzed utilizing liquid film diffusion, intraparticle diffusion, pseudo-first, Elovich, pseudo-second models.

3.7.1. Pseudo-first order model

A relationship between removal rate and the equilibrium time is described by pseudo-first order kinetic model [36]. A linearized form of this model is given as:

$$\log\left(q_e q_t\right) = \log q_e - \frac{K_1}{2.302}(t) \tag{3}$$

In the above equation K_1 (min^{-1}) expresses rate constant for this order, q_t (mg g^{-1}) and q_e (mg g^{-1}) are the sorption capacities at given time and at equilibrium respectively. The linear plot of pseudo-first order is shown in Fig. 12.

3.7.2. Pseudo-second order model

This model explains that chemical sorption is the most prominent mechanism to control the removal process and chemisorption occurs either through sharing or exchange of electrons [37]. Linearized form of this model is as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

The above equation consists of K_2 (g mg^{-1} min^{-1}) which represents the rate constant for pseudo-second order equation. The linear plot of pseudo-second order is shown in Fig. 13.

3.7.3. Intraparticle diffusion model

According to Weber and Morris the movements of sorbate molecule take place to the solid phase [38]. This model may be presented in the following equation.

$$q_t = K_{id} t^{1/2} + C \tag{5}$$

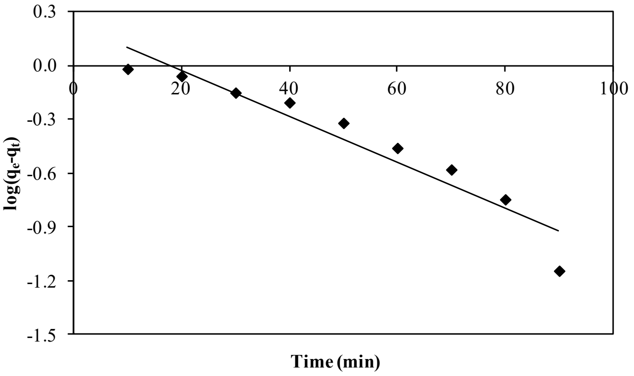

Fig. 12. Plot of pseudo first order (conditions of experiment: range of time of contact 10–100 min, dosage of sorbent 0.1 g, initial pH 3.0, initial atrazine concentration 33.33 µg mL^{-1}, volume for the sorption process 30 mL, room temperature).

In the above equation K_{id} (mg/g min$^{-0.5}$) is the rate constant and C represents the intercept. If C is equal to zero then the process will be controlled by intraparticle diffusion [39]. However, as shown from Table 2, the value of C is not zero which demonstrates that this model not only controls the process but other mechanisms are involved to control the process. The linear plot of intraparticle diffusion is shown in Fig. 14.

3.7.4. Elovich model

According to Elovich model, the process is controlled by chemisorption mechanism occurs on a surface having active site of unequal energies [40]. The following equation is a linearized form of this model:

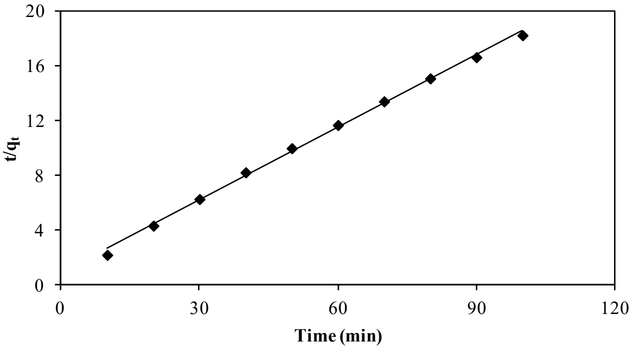

Fig. 13. Plot of pseudo second order (conditions of experiment: range of time of contact 10–100 min, dosage of sorbent 0.1 g, initial pH 3.0, initial atrazine concentration 33.33 µg mL^{-1}, volume for the sorption process 30 mL, room temperature).

Table 2
Comparison of the kinetic parameters for the removal of atrazine onto PSSP

Model	Parameter	Values
Pseudo-first-order	q_e, mg g^{-1}, (exp)	5.475
	q_e, mg g^{-1}, (cal)	1.702
	K_1, min^{-1}	0.027
	R^2	0.9119
Pseudo-second-order	K_2, g mg^{-1}min^{-1}	0.0349
	q_e, mg g^{-1}	5.652
	R^2	0.9978
Intraparticle diffusion	K_{id}, mg g^{-1}min$^{-0.5}$	2.381
	C	−6.291
	R^2	0.9897
Elovich	α, mg g^{-1} min^{-1}	0.703
	β, g mg^{-1}	0.141
	R^2	0.9302
Liquid film diffusion	K_{fd}, min^{-1}	0.029
	Intercept	1.167
	R^2	0.9119

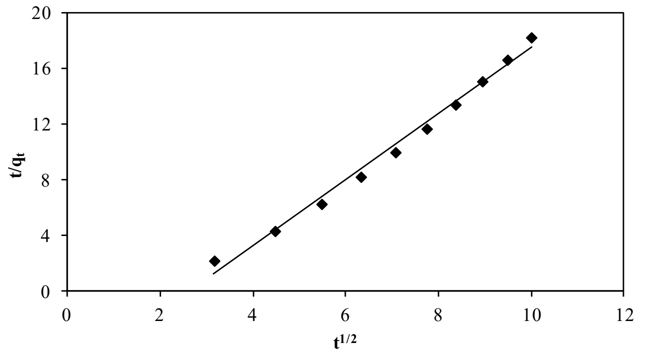

Fig. 14. Plot of intraparticle diffusion model (conditions of experiment: range of time of contact 10–100 min, dosage of sorbent 0.1 g, initial pH 3.0, initial atrazine concentration 33.33 µg mL^{-1}, volume for the sorption process 30 mL, room temperature).

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (6)$$

In the above equation the initial sorption rate is represented by α (mg g^{-1} min^{-1}) and β (g mg^{-1}) is correlated to the degree surface coverage. The linear plot of Elovich model is shown in Fig. 15.

3.7.5. Liquid film diffusion

This model is applied to the sorption data in those circumstances in which the removal process occurs through transportation of molecules of atrazine from solution to the solid surface [41]. The following equation expresses the linearized form of this model:

$$\ln(1-F) = -K_{fd}(t) \quad (7)$$

In the above equation K_{fd} is the rate constant and F represents the fractional attainment of equilibrium and equal to q_t/q_e.

If intercept of the plot –ln(1–F) vs. time is zero then the diffusion process in controlled through liquid film [42]. Nevertheless, as shown from Fig. 16, the intercept has not zero value which implies that kinetics of atrazine is not controlled by liquid film diffusion model but there are the possibilities of the involvement of some other kinetic mechanisms.

The slopes and intercepts of each kinetic model were utilized to calculate the constant parameters of each kinetic model and are tabulated in Table 2. Based on the R^2 (R^2 = 0.9999), pseudo-2nd-order model has the highest as compared to the models signifying that the removal of atrazine using PSSP is controlled by pseudo-2nd-order kinetic model. Moreover, the calculated q_e value of pseudo-2nd-order is much closer to that of experimental q_e value which indicates a confirmation of the fitness of the kinetic data in to pseudo-2nd-order kinetic model.

3.8. Sorption isotherm studies

The isotherms describe a relationship between the amount of sorbate in solution and the sorption capacity at constant temperature. The fundamental physiochemical data may be obtained from isotherms which in turn can be utilized to assess the appropriateness of sorption process. Each isotherm has certain constant parameters whose values give important information about the affinities of sorbent toward sorbate, the surface properties of sorbent and the sorption capacity of sorbent and nature of sorption [43]. In the present study, Freundlich, Langmuir, Temkin and Dubinin–Radushkevich (DR) were applied to understand all the above information about the removal of atrazine using PSSP.

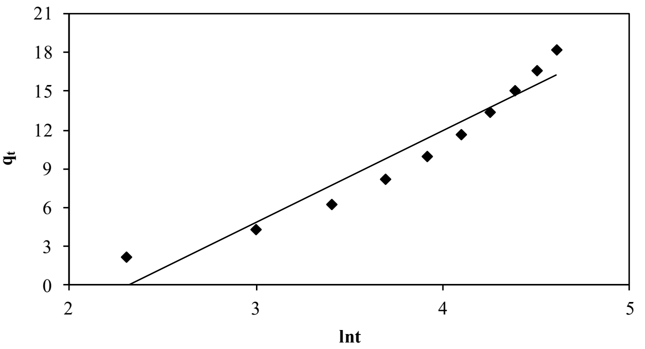

Fig. 15. Plot of Elovich model (conditions of experiment: range of time of contact 10–100 min, dosage of sorbent 0.1 g, initial pH 3.0, initial atrazine concentration 33.33 µg mL^{-1}, volume for the sorption process 30 mL, room temperature).

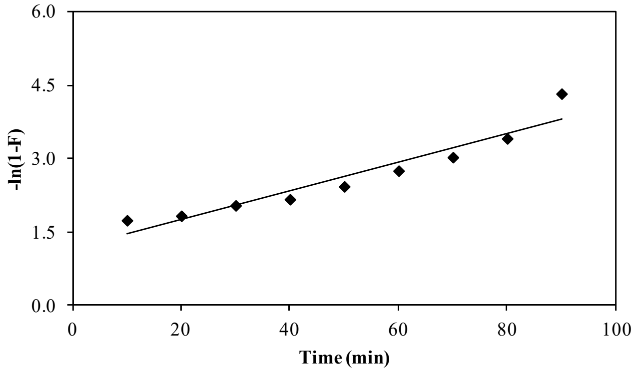

Fig. 16. Plot of liquid film diffusion model (conditions of experiment: range of time of contact 10–100 min, dosage of sorbent 0.1 g, initial pH 3.0, initial atrazine concentration 33.33 µg mL^{-1}, volume for the sorption process 30 mL, room temperature).

3.8.1. Freundlich isotherm

The sorption occurs in multilayer on a surface having site of different energies according to this isotherm [44]. This isotherm can be represented in the following linearized form:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (8)$$

In the above equation K_F is a constant and represents the relative sorption capacity (mg g^{-1}). (L mg^{-1})$^{1/n}$ while

n expressed the affinity of sorbate molecules with sorbent. Usually, physiosorption has value of n greater than one while for chemisorption n is less than one [45]. These parameters were calculated from the plot log q_e vs. log C_e and summarized in Table 3. The table demonstrates that the n has greater value than one which indicates that the removal of atrazine using PSSP physical in nature.

3.8.2. Langmuir isotherm

This isotherm describes sorption in monolayer on a homogenous surface and the sorbate molecules independent from each other [46]. The following equation represents linearized form of this isotherm:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e \tag{9}$$

where Q_0 and K_L indicate the sorption capacity (mg g^{-1}) and rate of sorption (L mg^{-1}) respectively.

One of the significant parameter of the Langmuir isotherm is dimensionless constant (R_L) and can represented in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{10}$$

In the above equation K_L (L mg^{-1}) represents the Langmuir constant while C_0 (μg mL^{-1}) is the initial concentration of atrazine. For favorable sorption the value of R_L occurs between 0 and 1, while for unfavorable its value is greater than one. Equally, for an irreversible sorption the value of R_L is equal to zero while the linear sorption it is equal to one [47]. It can be seen from Fig. 17 that R_L has values in the range of 0 to1, suggest that the removal of atrazine onto PSSP is favorable process.

3.8.3. Temkin isotherm

According to this isotherm there is a linear relationship between heat of sorption and temperature instead of logarithmic relationship. This isotherm also explains that free energy for the sorption is a function of coverage of the surface [48]. The linearized form of this isotherm is as:

Table 3
Comparison of constant parameters of various isotherms

Isotherm	Parameter	Values
Freundlich	K_F, (mg g^{-1})·(L mg^{-1})$^{1/n}$	14.112
	N	1.681
	R^2	0.9955
Langmuir	K_L, L mg^{-1}	0.205
	Q_o, mg g^{-1}	74.626
	R^2	0.9914
Temkin	K_T, L g^{-1}	0.00432
	b_T, J mol^{-1}	147.632
	R^2	0.9923
Dubinin-Radushkevich	Q_m, mg g^{-1}	40.804
	K	5 × 10^{-7}
	E, kJ mol^{-1}	1.000
	R^2	0.8940

$$q_e = RTlnK_T + \frac{RT}{b_T} \ln C_e \tag{11}$$

where b_T (J mol^{-1}) is related with the heat of sorption and K_T (L g^{-1}) denotes the Temkin constant.

3.8.4. Dubinin–Radushkevich (D-R) isotherm

To investigate that whether the sorption process is chemisorption or physiosorption this isotherm is applied to the sorption data [49]. This isotherm can be expressed in the following linearized form:

$$\ln q_e = \ln Q_m - K\varepsilon^2 \tag{12}$$

where Q_m represents the maximum sorption capacity (mg g^{-1}), K is related with mean sorption free energy (mol^2 J^{-2}) and ε is the Polanyi potential and the following equation was used to calculate the value of this parameter:

$$\varepsilon = RTln\left[1 + \frac{1}{C_e}\right] \tag{13}$$

Mean sorption free energy (E) is defined as the energy expending during the process in which one mole of sorbate molecule transferred from the solution to the surface of sorbent. The value of E can be calculated from the following equation:

$$E = \frac{1}{\sqrt{2K}} \tag{14}$$

The magnitude of E is a significant factor which can be used to investigate the mechanism of sorption. The process which occurs through physical sorption has value of E less than 8 kJ mol^{-1} while if the sorption occurs through chemical sorption then its value is greater than 16 kJ mol^{-1} [50].

Linearized form of each isotherm was used to calculate the values of these parameters and tabulated in Table 3. It may be shown from the table that R^2 value of the Freundlich

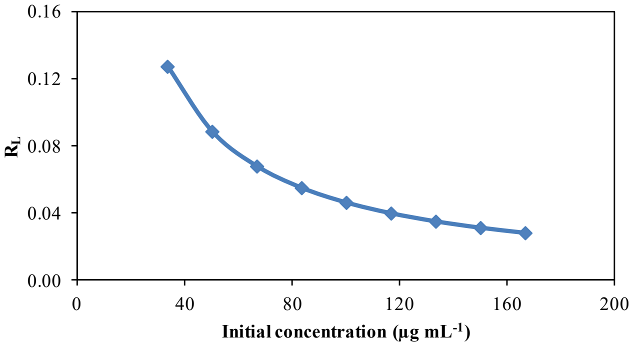

Fig. 17. Effect of initial atrazine concentration on dimensionless separation factor (conditions of experiment: range of initial atrazine concentration 33.33–163.33 μg mL^{-1}, pH 3.0, dosage of sorbent 0.1 g, time of contact 30 min, volume for the sorption process, room temperature).

Table 4
Comparison of sorption capacities of different biosorbents for various pollutants

Sorbent	Sorbate	Sorption capacity (mg g^{-1})	Reference
Pumpkin seed shells	2,4,6-trichlorophenol	41.50	51
Fluted pumpkin seed shell activated carbon	Pb(II)	14.286	52
Pumpkin seed hull activated carbon	2,4-dichlorophenoxyacetic acid	260.79	53
Moringa oleifera lam	Atrazine	0.653	54
Banana peels	Metribuzin	167	55
Pea (Pisum sativum) peels	Pb(II)	140.84	56
Pumpkin seeds shell powder	Atrazine	74.626	Present study

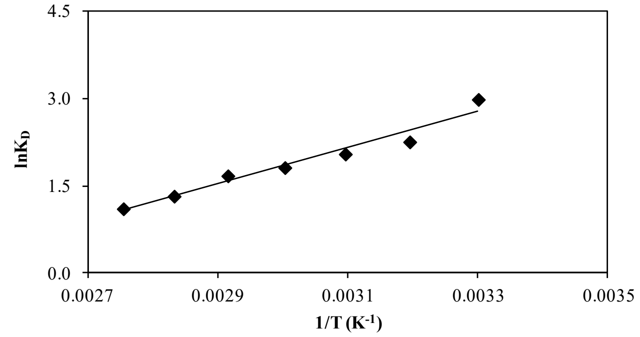

Fig. 18. Plot of ln K_D versus 1/T (conditions of experiment: range of temperature 303–363 K, initial atrazine concentration 33.33 µg mL^{-1}, pH 3.0, dosage of sorbent 0.1 g, time of contact 30 min, volume for the sorption process.

isotherm is higher ($R^2 = 0.9955$) from the rest of isotherms signifying that the removal data of atrazine onto PSSP well interpreted by Freundlich isotherm. Monolayer sorption capacity of PSSP for atrazine of the Langmuir isotherm was found to be 74.626 mg g^{-1}. The sorption capacities ofsome low cost biosorbents were compared to pumpkin seeds shell used for atrazine is given in the literature and given in Table 4. It can be demonstrated from this table that sorption capacity of PSSP for atrazine is comparable to that the biosorbents investigated for various pollutants. The value (1.000 kJ mol^{-1}) of mean free sorption energy (E) suggests that the removal of atrazine onto PSSP is physical in nature.

3.9. Thermodynamic studies

Thermodynamics of the sorption of atrazine onto PSSP were investigated using the values of enthalpy, free energy and entropy. Thermodynamic parameters were evaluated utilizing the following equations:

$$K_D = \frac{q_e}{C_e} \tag{15}$$

$$\Delta G^\circ = -RTlnK_D \tag{16}$$

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{17}$$

In the above equations K_D represents the distribution coefficient, R is the universal gas constant and T is the temperature. The linear plot of this equation is shown in Fig. 18. The slope and intercept of the plot were used to find out the values of ΔH° and ΔS° and summarized in Table 5. The values of ΔG° are negative which indicates that the removal process of atrazine onto PSSP is spontaneous while the negative value of ΔH° reflecting that the removal of atrazine is exothermic process [57]. The negative value of ΔS° reveals that atrazine molecules are stable on the surface of PSSP. A decline in the entropy is the result of decreasing in degree of free of molecules of atrazine during sorption process [58].

Table 5
Thermodynamic parameters for the removal of atrazine using PSSP

Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
303	–7.523		
313	–5.871		
323	–5.497		
333	–5.022	–25.938	–0.062
343	–4.769		
353	–3.880		
363	–3.338		

4. Conclusions

The present study tells that pumpkin seeds shell powder (PSSP) appears an eco-friendly, effective and low cost biosorbent for the removal of atrazine from aqueous media. This removal study was performed considering the effect of pH, time of contact, dosage of sorbent, initial pesticide concentration and temperature. Characterizations of PSSP were performed before and after removal study using SEM, EDX, FTIR and surface area analyzer which confirms the removal of atrazine onto PSSP. The pH study indicates that optimum pH for the removal of atrazine from aqueous media was 3.0. The best fit kinetic model was pseudo second order due to the highest R^2 and the proximity between the values of experimental and calculated sorption capacity of this model. The adsorptive characteristic of atrazine onto PSSP was excellently fitted into Langmuir isotherm due to high R^2 value. Langmuir isotherm was also used to find out the maximum sorption capacity of PSSP for atrazine and was found to be 74.62 mg g^{-1}. Thermodynamic study of the removal of atrazine implies that atrazine removal onto PSSP was spontaneous and exothermic process. It may be concluded from these results that pumpkin seeds shell is an economical, eco-friendly and promising biosorbent for the removal of pollutants from wastewater.

Acknowledgement

The authors highly acknowledge the support of Higher Education Commission Pakistan.

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