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Two-resistance mass transfer model for the adsorption of the pesticide deltamethrin using acid treated oil shale ash

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Abstract Adsorption characteristics of the pesticides Deltamethrin were studied in aqueous solutions using acid treated Oil Shale Ash (ATOSA) in a series of batch adsorption experiments. The maximum loading capacity of the adsorbent and the rate of adsorption were found to increase with increasing the pesticide initial concentration, mixing speed and were found to decrease with temperature and particle size. Langmuir as well as Freundlich isotherm models fit the adsorption data with $R^2 > 0.97$ in all cases. The maximum adsorption capacity for Deltamethrin was 11.4 mg/g. The two-resistance mass transfer model based on the film resistance and homogeneous solid phase diffusion was used to fit the experimental data.

A computer program has been developed to estimate the theoretical concentration-time dependent curves and to compare them with the experimental curves by means of the best-fit approach. The model predicts that the external mass transfer coefficient K was affected by varying the initial pesticide concentration, the agitation speed and temperature whereas the diffusion coefficient D was affected by the initial pesticide concentration, and temperature.

Keywords Adsorption · Pesticides · Oil shale ash adsorption isotherms · Adsorption capacity · Langmuir isotherm · Freundlich isotherm · Adsorption modeling

Abbreviations

Latin letters

a	Isotherm constant for Langmuir equation, cm^3/g solid
b	Isotherm constant for Langmuir equation, cm^3/g pesticide
C_b	Pesticide concentration in the bulk of the liquid phase, g/cm^3
C_e	Equilibrium pesticide concentration, g/cm^3
C_s	Equilibrium pesticide concentration at the particle surface, g/cm^3
D	Diffusion coefficient, cm^2/s
D_p	Particle diameter, μm
k	Isotherm constant for Fredlich equation
K	Mass transfer coefficient, cm/s
M	Mass of the adsorbent, g
n	Isotherm Exponent for Freundlich equation
Q_e	Equilibrium pesticide concentration in the particle, mg pesticide/g ATOSA
Q_i	Local pesticide concentration in the particle, mg pesticide/g ATOSA
Q_s	Equilibrium pesticide concentration at the particle surface, mg pesticide/g ATOSA
$\bar{Q}$	Average pesticide concentration in the particle, mg pesticide/g ATOSA
r	Radial coordinate, cm

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R Radius of the particle, cm
S_P Particle surface area, cm^2
t Time, s
u Transformed solid phase concentration
V Total volume of the liquid phase in the adsorber, cm^3
V_P Particle volume, cm^3
x dimensionless radial coordinate

Greek letters

ε_p Particle porosity (-)
ρ_p Particle density, g/cm^3
τ Dimensionless time

1 Introduction

Pesticides are among the major organic pollutants encountered in wastewater effluents of pesticide industry and domestic activities (Gupta et al. 2002). These compounds are considered dangerous and harmful to living systems because of their toxicity and carcinogenicity even at low concentrations (IARC 1987). Consequently, many treatment processes have been applied for the removal of pesticides from industrial wastewater. These processes include: photo oxidation, chemical coagulation, sedimentation, filtration, disinfection and adsorption in addition to the biological treatment process used for wastewater. Unfortunately, the removal of pesticides from wastewater is an extremely complex problem due to the wide range of pesticides chemical structures and properties (Hamadi et al. 2004).

Adsorption processes using suitable adsorbent such as activated carbon have shown high removal efficiency and many economical, ecological and technological advantages (Gupta and Ali 2001; Chubar et al. 2003). However, the high cost of activated carbon production had led to interest in utilizing low cost raw materials as adsorbents for pollutants including pesticides. These include: Fly ash (Gupta and Ali 2001), snail pedal mucus (Brereton et al. 1999), clay minerals and soil (Fushiwaki and Urano 2001), polymeric adsorbents (Kyriakopoulos et al. 2005), cork (Domingues et al. 2005), quartz, calcite kaolinite and α-alumina (Clausen et al. 2001), rice bran (Adachi et al. 2001), activated carbon fibers (Martin-Gullon and Font 2001), Mg Al-layered double hydroxides (Inacio et al. 2001), kerolites (Gonzalez-Pradas et al. 2003), lignin (Ludvik and Zuman 2000) etc.

Recently, it was shown that Oil shale ash is a promising and efficient adsorbent for organic pollutants such as reactive dyes (Al-Qodah 2000; Al-Qodah and Lafi 2003). This inorganic residue is obtained as a by-product ash from the direct combustion process of oil shale used as a source of energy. The total residual ash material that might be generated from oil shale reserves run, by estimate, to about 3.2×10^{11} tons (Holopainen 1991). Therefore, an inexpensive residual management technology is needed for the disposal of ATOSA or beneficial uses of this material (Al-Qodah 2000).

In previous studies, it was found that oil shale ash has good adsorption capacity for reactive dyes (Al-Qodah 2000; Al-Qodah and Lafi 2003). This was attributed to chemical structure which consists of a wide variety of acidic, basic and amphoteric oxides. In addition, this material is usually produced at high temperatures and this implies that ATOSA is a highly porous. In a more recent study oil shale ash was used as an adsorbent for the pesticides Deltamethrin and Lambda-Cyhalothrin (Al-Qodah et al. 2007). In that study the kinetic and thermodynamic parameters for the two pesticides were investigated. On the other hand, the intent of this contribution was to apply the two-resistance mass transfer model to the batch adsorption process using acid treated oil shale ash (ATOSA) and Deltamethrin found in waste water of the Veterinary and Agricultural Products Mfg. CO. Ltd (VABCO) in order to reduce their concentration prior to the biological treatment step. The effect of some operational parameters such as initial concentration, adsorbent mass, mixing speed, temperature on the model parameters will be investigated.

2 Theory

The first models applied to predict the performance of batch adsorbers used either a liquid film resistance or pore diffusion resistance. The hydrodynamic parameters limit the applicability of these models to be either liquid film diffusion control or solid side pore diffusion control. In addition, these models are limited as they only can be applied over a short time period during the adsorption process. For this reason Mathews and Weber (1976) used a model based on a combination of the two resistances. After that, many researchers have used the two resistance's model (Mckay 1984, 1985; El-Guendi 1991; Dweib 1993; Haimour and Sayed 1997; Al-Qodah 2000) and found that this model was adequate to describe the system performance.

In the two-resistance model, the single component adsorption rate includes the following mechanistic processes:

- Solute diffusion inside the liquid boundary layer from the liquid phase to the surface of the particle.
- Solute adsorption on the surface of the particle.
- Solute diffusion in the pores of the particle.

For spherical particles, the variation of the solute concentration q with distance r and time t is given by the following diffusion equation:

$$\frac{\partial q_i}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial q_i}{\partial r}\right). \tag{1}$$

For concentration independent diffusion coefficient, (1) becomes:

$$\frac{\partial q_i}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q_i}{\partial r}\right). \tag{2}$$

The corresponding initial conditions are described by the following two equations:

$$q_i(r,0)=0, \tag{3}$$

$$c_b(0)=c_{bo}. \tag{4}$$

The boundary conditions are described by the following equations:

$$\frac{\partial q_i(0,t)}{\partial r}=0, \tag{5}$$

$$q_i(R,t)=q_s(R,t)=q_s(t). \tag{6}$$

The boundary condition described by equation (6) expresses the fact that the pesticide concentration at the surface of the particle is time dependent.

Two of the most common sorption models were used to fit the experimental data. The Langmuir model which assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent. This model can be written as:

$$Q_e=\frac{aC_e}{1+bC_e}. \tag{7}$$

Where a is a constant related to the maximum metal uptake under the given conditions, and b is a constant related to the affinity between the adsorbent and the adsorbate. The linear form of Langmuir model is:

$$\frac{1}{Q_e}=\frac{1}{aC_e}+\frac{b}{a}. \tag{8}$$

The second model is Freundlich model which can be written as:

$$Q_e=kC_e^{(\frac{1}{n})} \tag{9}$$

where, k and n are Freundlich constants, which are correlated to the maximum adsorption capacity and adsorption intensity, respectively, (Hussein et al. 2004). The linear form of this model takes the form:

$$\mathrm{Log}(Q_e)=\mathrm{Log}(k)+\left(\frac{1}{n}\right)\mathrm{Log}(C_e). \tag{10}$$

The transport of the adsorbate from the bulk into the pores is described by the mass transfer equation:

$$\frac{dQ}{dt}=\frac{3KS_P}{V_P\rho_p(1-\varepsilon_p)}(C_b-C_s). \tag{11}$$

Using $S_P=4\pi R^2$, $V_P=(4/3)\pi R^3$, (11) could be reduced to:

$$\frac{d\bar{Q}}{dt}=\frac{3K}{R_P\rho_p(1-\varepsilon_p)}(C_b-C_s) \tag{12}$$

where $\bar{Q}$ is the concentration of the adsorbate in the particle and is given by the following equation:

$$\bar{q}(t)=\frac{3}{R_P^3}\int q_i(r,t)r^2dr. \tag{13}$$

The mass balance equation of the solute can be written as:

$$V\frac{dC_b}{dt}=-M\frac{d\bar{Q}}{dt}. \tag{14}$$

By introducing the dimensionless variables $\tau=Dt/R^2$, $x=r/R$, and defining $u=xQ_i$, the model equations in dimensionless form will be;

$$\frac{\partial u}{\partial\tau}=\frac{\partial^2u}{\partial x^2}, \tag{15}$$

$$u(0,\tau)=0=u(x,0), \tag{16}$$

$$u(1,\tau)=Q_s(\tau), \tag{17}$$

$$Q_s=\frac{aC_s}{1+bC_s}, \tag{18}$$

$$\frac{d\bar{Q}}{d\tau}=\frac{3KR}{D\rho_p(1-\varepsilon_p)}(C_b-C_s), \tag{19}$$

$$\bar{Q}(\tau)=3\int_0^1 u(\tau,x)xdx, \tag{20}$$

$$V\frac{dC_b}{dt}=-M\frac{d\bar{Q}}{dt}. \tag{21}$$

The resulted system of the dimensionless equations was solved numerically as they cannot be solved analytically. The implicit finite difference scheme of Crank and Nicholsen was used by Mckay (1984) and El-Guendi (1991). In the present investigation the explicit finite difference scheme of Haimour and Sayed (1997) was employed. The general form of the solution is available elsewhere (Dweib 1993; Haimour and Sayed 1997).

3 Experimental

3.1 Adsorbent preparation

Samples of oil shale stones were obtained from the Authority of Natural Resources (Amman, Jordan). To prepare the ash 150 g of these stones were crushed and burned using electrical furnace at 800 °C for 2 hour. The residual ash was cooled, then milled and sieved into several fractions. Three fractions of 53–150, 150–250 and 250–355 µm diameter were obtained and analyzed. A mass of 20 g of each ATOSA fraction was first mixed with 100 ml 2M HCl and heated to 50 °C with continuous stirring for 25 minutes. This acid treatment step was necessary to activate the surface of the particles and increase the surface area by dissolving part of the soluble portion of the ash. The ash was then filtered, washed with distilled water and finally dried, in order to be analyzed for density and voidage.

Apparent density was obtained by weighting five grams of the diatomite and transferred them into 10 mL graduated cylinder. The cylinder was tamping with a rubber pad while diatomite was being added until the entire original sample was transferred to the cylinder. Tamping was continued for 5 minutes until there was no further settling produced. The volume was recorded as V_1 and the apparent density was calculated on the dry basis:

$$\text{Apparent density} = \frac{5(\text{g})}{V_1(\text{cm}^3)}. \tag{22}$$

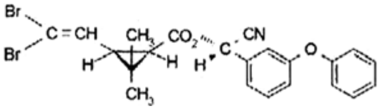
The same quantity of diatomite was transferred into 10 mL graduated cylinder containing 5 mL deionized water and left for 1 h. Then the new volume of the cylinder content was recorded as V_2. The voidage or porosity, ε of diatomite was calculated as:

$$\varepsilon = \frac{V_2 - 5}{V_1}. \tag{23}$$

3.2 Pesticides

The pesticide, namely Deltamethrin, used in this study was obtained from VAPCO. Part of its physical properties and chemical structures is shown in Table 1. The choice of this pesticide was mortified by two reasons. First, its presence in the factory effluents is a relatively high concentration. Secondly, its chemical nature of being halogenated compounds makes it difficult to be treated by other methods such as photo-oxidation. As shown in Table 1, Deltamethrin contains two Br atoms. The presence of these atoms affects the stereochemistry and could be the reason for low solubility of this pesticide in water.

Table 1 Some properties of Deltamethrin

Chemical structure	
Chemical formula	$C_{22}H_{19}Br_2NO_3$
Molecular mass (g/mol)	505.2
Density (g/cm^3)	0.55
Physical state at 25 °C	Solid
pH in solution (10 mg/l)	7.3
Solubility (g/l) at 25 °C	2×10^{-7}
Color	Colorless
Odor	Odorless

A standard solution of 1000 mg/l of pesticide was prepared by dissolving measured amount of pesticide concentrate in 200 ml of distilled water. For example, 40 ml of 2.5% stock solution were dissolved in 500 ml distilled water. After the completion of dissolution the volume of the solution was completed to 1 liter by the addition of the distilled water. The weak solutions used in the further experiments were prepared by diluting samples from the standard solution.

3.3 Adsorption isotherms

Adsorption isotherm experiments were conducted by adding 1 g of ATOSA to 100 ml of pesticide solution in a glass bottle with screw cap. The initial concentrations of pesticide were: 5, 10, and 15. The mixtures were kept at constant temperature in an orbital shaker bath (GallenKamp, UK) which is operated at 200 rpm for 72 h. The solutions were then centrifuged and the filtrate was analyzed. This procedure was repeated at three different temperatures of 30, 40 and 45 °C, and using ATOSA of 250–355 µm diameters.

3.4 Kinetic study

The kinetic study experiments were performed by batch technique using a series of Erlenmeyer flasks of 1 L volume equipped with a mixer. The working volume was 0.7 L in all the experiments. The effect of initial concentration, temperature, adsorbent mass and mixing speeds on the pesticide's equilibrium concentrations in the solution were studied. At a given time intervals, samples of the solution were withdrawn using a suitable syringe to be analyzed. Each experiment continued until equilibrium conditions were reached when no further decrease in the pesticide concentration was observed. The time needed to reach this point of equilibrium was about 3 hours.

3.5 Measurements

The conductivity was measured using Lf 537 WTW conductivity meter with WTW Tetracon 96 conductance cell. Pesticide concentrations were measured using the TOC Analyzer. The TOC measurements were performed by combustion method through measuring the CO_2 product in the effluent gases. Shimadzu® Total Carbon Analyzer (TOC-VE) was used. The system consisted of combustion glass tube filled with platinum catalyst pellets. The tube was installed in an oven whose temperature was controlled by a PID controller. Dry air was used as carrier gas as well as an oxidant. Air flow rate through the tube was regulated to 150 cm^3/min to oxidize all the organic matter found in the sample. The temperature of the oven which reflects the reaction zone temperature was maintained at 360 °C through out the analysis steps. Sample injection was made using 50 µl Hamilton® type capillary syringes. The instrument was calibrated according to the standard procedure and solution provided by the manufacturer. The syringe was cleaned thoroughly prior to each sampling-injection step. Measurements were repeated three times on average for each sample to ensure accuracy.

4 Results and discussion

4.1 Properties of the ATOSA

Figure 1 shows the scanning electron microscope photograph of the acid treated oil shale ash. It is evident that the surface of the material have different sizes of the pores suggesting that this material will have relatively high surface are compared to the untreated ash. Analyses for the bulk density and voidage calculations show that the treatment of the ash with 2M HCl reduces the bulk density from 1390 to 1350 $\mathrm{kg/m^3}$ and increases the voidage from 0.42 to 0.44. This indicates that the acid treatment will improve the adsorptive capacity of the ash as will be seen from the isotherm study.

4.2 Adsorption isotherms

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase at equilibrium state. The proper isotherm model was selected by fitting it to experimental data. The selection is essential for design purposes (El-Guendi 1991).

The adsorption isotherm Deltamethrin using the acid treated oil shale ash and the untreated ash is shown in Fig. 2. It is evident from Fig. 2 that the maximum loading capacity of ATOSA reaches 11.5 mg/g whereas that of the untreated ash reaches only 5.82 mg/g. This is an indication that the ash activation by 2M HCl improves its adsorptivity towards Deltamethrin. This could be attributed to the increased pores volume resulted from the reaction between parts of the ash acidic oxides with the acid. For this reason the ATOSA will be used in the further isotherm and kinetic experiments.

The adsorption isotherms for Deltamethrin on ATOSA at different initial concentrations and three temperatures are shown in Fig. 3. It is evident that the pesticide loading capacity of the ATOSA decreases as the temperature increases. In addition, it is clear that Deltamethrin can easily be removed from the liquid phase by the ash particle. For example, when the initial concentration of the solution is 10 mg/l, the loading capacity for Deltamethrin is 7.1.

Langmuir and Freundlich models were tested to fit the isotherm data for the adsorption of Deltamethrin on ATOSA. Figures 4 and 5 show linear plots for these two models indicating that these models are adequate to describe the adsorption process for this pesticide onto ATOSA as indicated by the value of R^2 shown in Table 2. The parameters of both models for Deltamethrin at three different temperatures are given in Table 2.

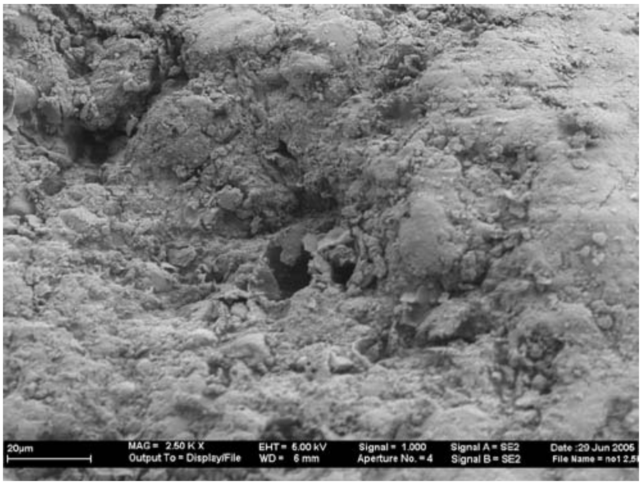


Fig. 1 SEM photograph of acid treated oil shale ash

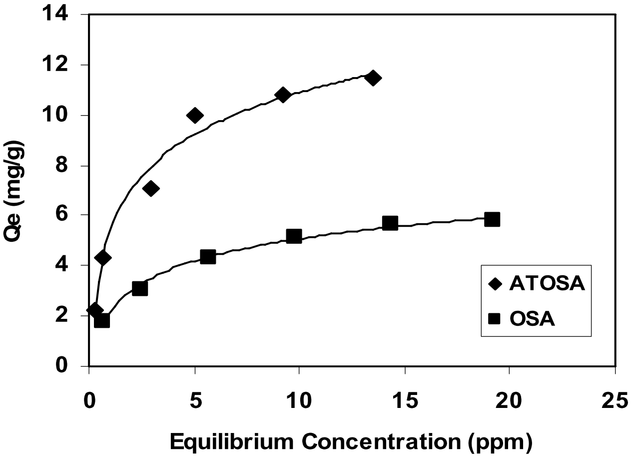


Fig. 2 Adsorption isotherms for Deltamethrin. 1 g adsorbent, $d_p = 250$–355 with 100 ml of the pesticide solution of C_o ranges from 5 to 50 ppm, at pH = 7.3, rpm = 200 and contact time 72 h using acid treated OSH and untreated OSH

Table 2 Langmuir and Freundlich constants for Deltamethrin at different temperatures

Temperature	Freundlich parameters			Langmuir parameters		
(°C)	k	n	R^2	$Q_{\max}$ (mg/g)	b (l/mol) $\times 10^{-6}$	R^2
25	4.48	2.44	0.9697	10.96	0.514	0.9907
35	3.14	2.16	0.9642	10.74	0.231	0.9971
40	2.406	2.01	0.978	8.25	0.239	0.9368

4.3 Comparison of model predictions to experimental observations

In this part of the study the effect of many parameters on the equilibrium concentration of the Deltamethrin in the adsorption mixture was investigated. These parameters include ini-

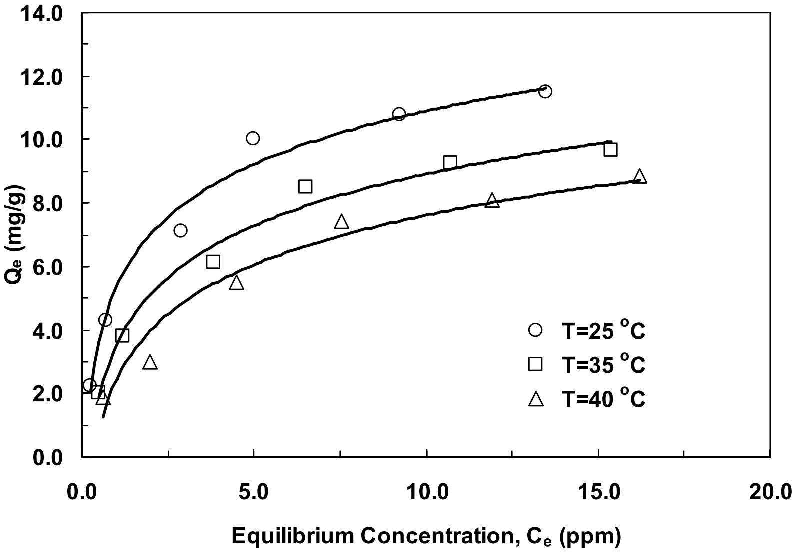


Fig. 3 Adsorption isotherms for Deltamethrin. 1 g adsorbent $d_p = 250$–355 with 100 ml of the pesticide solution of C_o ranges from 5 to 50 ppm at pH = 7.3, rpm = 200 and contact time 72 h at three different temperatures of 25, 35 and 40 °C

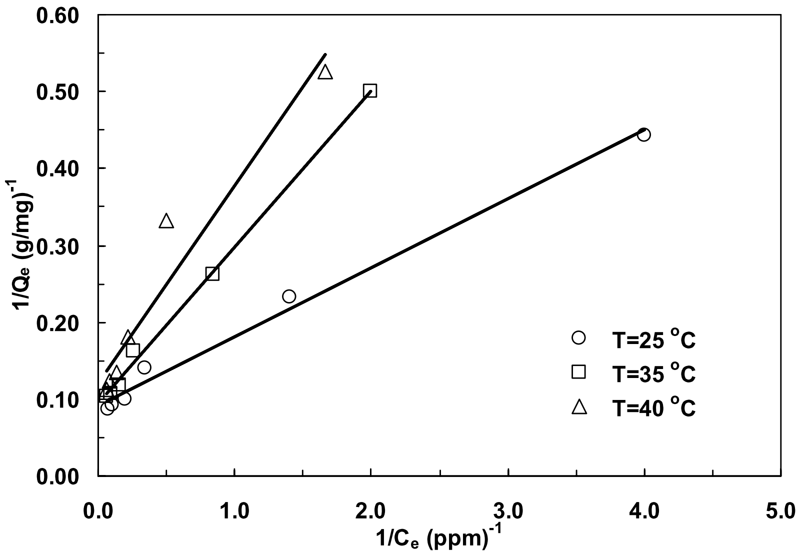


Fig. 4 Langmuir plot for the equilibrium data of Deltamethrin

tial adsorbate concentration, adsorbent mass, adsorbent particle size and mixing speed, and temperature.

4.4 Effect of initial concentration

The effect of initial concentrations of Deltamethrin on the rate of adsorption by ATOSA is shown in Fig. 6. It is evident from Fig. 6 that the quantity of pesticide adsorbed increases with time for all initial concentrations. For example, as C_o of Deltamethrin increases from 5 to 15 mg/l the loading capacity of ATOSA increases from 3.4 to 6 mg/g in the first 40 min of start up. However, the uptake rate of the pesticide drastically decreases with time until it approaches a pseudo steady state after 60 minutes. This behavior indicates negligible further removal of the pesticide and referred to the continuous decrease in the concentration driving force. This behavior is repeated in all kinetic experiments conducted to investigate the effect of other parameters such as adsorbent mass and size and stirring speed. This is a surface phenomenon behavior and it is attributed to the hydrophobic nature of the pesticide used (Mathava and Ligy 2006). Due to this effect, the adsorption sites of ATOSA are filled up with the pesticide molecules in a very short time.

The kinetic parameters, K and D, predicted by the model are listed in Table 3. It was found that the effect of changing C_o on K was relatively small. The value of K increases from 3.221×10^{-6} to 3.599×10^{-6} m/s as C_o increases from 5 to 10 mg/l. On the other hand, D increases from 0.971×10^{-10} to 1.402×10^{-10} m^2/s as the initial pesticide's concentration changes from 5 to 15 mg/l. This behavior of concentration dependent diffusivity agrees with investigations obtained by Hu et al. (1994), for the adsorption of hydrocarbons by activated carbon and those obtained by Haimour and Sayed (1997), for the adsorption of methylene blue by Jift.

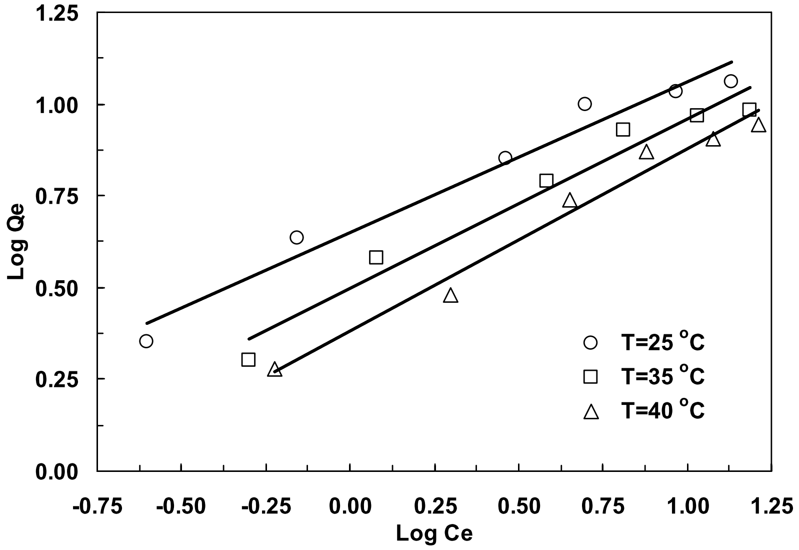


Fig. 5 Freundlich plot for the equilibrium data of Deltamethrin

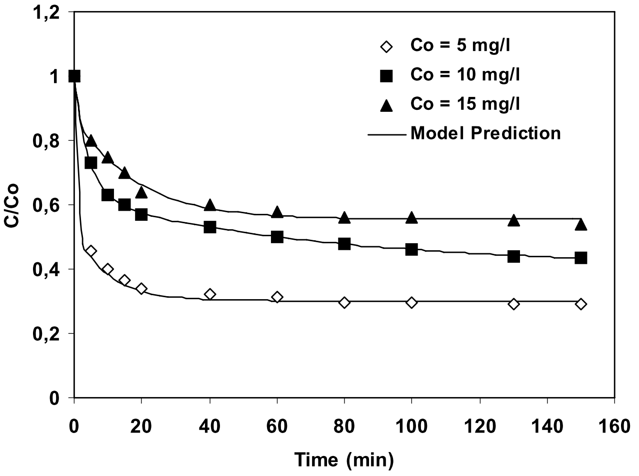


Fig. 6 Effect of initial concentration on the adsorption rate of Deltamethrin onto ATOSA. Adsorbent mass 1 g/100 ml solution, pH = 7.3, $T = 25\,°\mathrm{C}$, Mixing speed = 400 rpm, particle size = 202.25 μm, C_o ranges from 5 to 50 ppm

Table 3 Variation of K and D with operational parameters

Parameter	Value	Mass transfer coefficient K (m/s) × 10^6	Diffusivity D (m^2/s) × 10^{10}
C_o	5	3.221	0.971
(ppm)	10	3.467	1.244
	15	3.599	1.402
m/v	0.01	3.467	1.244
(g/ml)	0.02	3.467	1.244
	0.03	3.467	1.244
Particle size	150–255	3.467	1.244
(μm)	250–355	2.865	1.034
	350–500	2.231	0.912
Mixing speed	200	2.767	1.011
(rpm)	400	3.467	1.244
	600	3.967	1.634
Temperature	25	3.432	1.244
(°C)	35	3.765	1.432
	40	3.964	1.654

4.5 Effect of adsorbent mass

The effect of varying the ash mass on Deltamethrin adsorption is shown in Fig. 7. It can be seen that as the adsorbent mass changes from 1 to 3 g, in a solution of $C_o = 10$ mg/l, the overall pesticide removed from the solution increases from 3.6 to 4.5 mg after 150 min of start up. This is an expected increase in the quantity of the pesticide removed since increasing the adsorbent mass implies increasing the number of adsorption sites for pesticides uptake. This indicates that the pesticide equilibrium concentration can be reduced to very low value by increasing the solid to liquid ratio of the adsorption system. However, the adsorption capacity decreases from 3.6 to 1.6 mg/g if the adsorbent mass increases from 1 to 3 g in the same solution which means losing the adsorbent before being exhausted. The decrease in capacity with increase in dose implies that there is an optimum adsorbent dose for the adsorption system. This optimum dose will reduce the adsorbate concentration to an acceptable value while keeping loading capacity reasonably high.

The mathematical model predicts that the mass transfer coefficient, K, and the diffusivity coefficient, D don't change as the adsorbent mass changes. The values of K and D were 3.432×10^{-4} cm/s, and 1.230×10^{-6} cm^2/s. These results are at agreement with those of Mckay (1985) for the adsorption of Acid dye 25, and El-Guendi (1991).

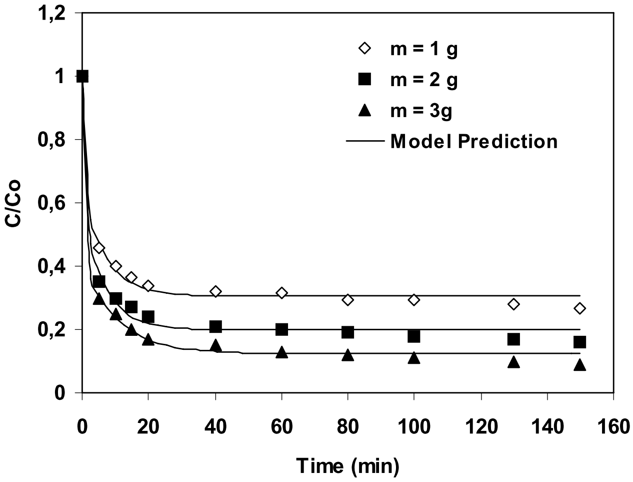


Fig. 7 Effect of adsorbent mass on the adsorption rate of Deltamethrin onto ATOSA. Initial concentration 10 mg/l, pH = 7.3, $T = 25\,^\circ\mathrm{C}$, Mixing speed = 400 rpm, particle size = 202.25 µm

4.6 Effect of particle size

Figure 8 shows Deltamethrin concentration in the solution as a function of contact time for three different adsorbent particle sizes of ATOSA. The average sizes of the fractions used are 202.5, 302.5 and 425 µm. The results shown in Fig. 8 indicate that the rate and extent of pesticide adsorption by ATOSA decreased by increasing the particle size. The pesticide removed from the solution after 40 minutes from start up decreases from 3.7 to 2.9 mg/g as the average particle size increases from 202.5 to 425 µm. However, this difference starts to diminish after 120 minutes of start up and it could be negligible after reaching the steady state conditions. This behavior can be attributed to the diffusion in the internal pores of the particles. Large particles with deep pores need longer time to be saturated with the adsorbate molecules, whilst small particles with shallow pores do not need such time. This means that the particle size has very limited effect on the maximum adsorption capacity of the pesticide used. This also can be explained from the relation between the effective specific surface area of the adsorbent particles and their sizes. The effective surface area decreases as the particles size increases and as a consequence, the saturation adsorption per unit mass of the adsorbent decreases in the rapid rate region of the adsorption process (Wu et al. 1997; Al-Qodah 2000). The particles of 302.5 were selected for further adsorption studies due to their relatively high rate of adsorption and easiness of its preparation.

Table 3 indicates that K and D remain constants and equal to 3.467×10^{-6} m/s and 1.244×10^{-10} m^2/s when the particle size increases from 202.25 to 425 µm. This behavior is in consistence with the theory, because the variations in the particle size in this study did not affect the hydrodynamics as the total adsorbent concentration is very low Cooney et al. (1983).

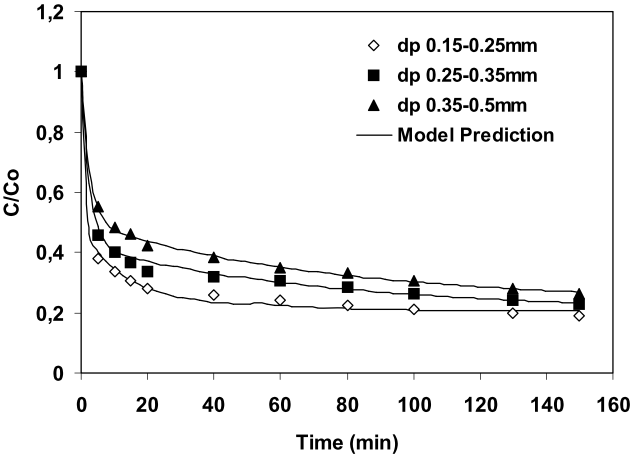


Fig. 8 Effect of adsorbent particle size on the adsorption rate of Deltamethrin onto ATOSA. Adsorbent mass 1 g/100 ml solution, pH = 7.3, $T = 25\,^\circ\mathrm{C}$, Mixing speed = 400 rpm, Initial concentration 10 mg/l

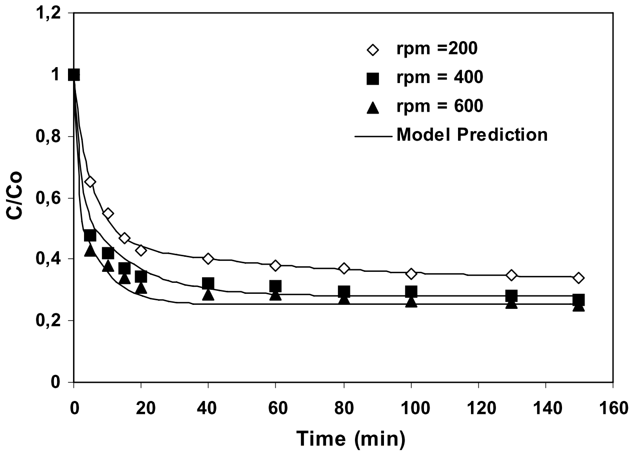


Fig. 9 Effect of mixing speed on the adsorption rate of Deltamethrin onto ATOSA. Adsorbent mass 1 g/100 ml solution, pH = 7.3, $T = 25\,^\circ\mathrm{C}$, particle size = 202.25 µm, Initial concentration 10 mg/l

4.7 Effect of agitation speed

The effect of contact time on adsorption of Deltamethrin with ATOSA at different agitator speeds is shown in Fig. 9. It is evident from Fig. 9 that the rate of adsorption increases as the agitator speed increases. This effect can be attributed to the increased turbulence and as a consequence, the decrease boundary layer thickness around the adsorbent particles as a result of increasing the degree of mixing. It can be seen that as the mixing speed increases the adsorption capacity increases until reaching a mixing speed of 400 rpm the $Q_{\max}$ reaches a high value. Beyond this mixing speed the increase in $Q_{\max}$ is very low which means inefficient energy consumption. This implies the search for an optimum mixing speed.

In large-scale continuous adsorption processes there are two possible modes of operation. These are the use of a batch stirred adsorber or a continuous fixed bed adsorber. The above results indicate that the rate of adsorption in a stirred adsorber increases with increasing the degree of mixing. In continuous fixed bed operations, the boundary layer thickness can be reduced by increasing the pesticide solution flow rate by circulating part of the effluents or by using a fluidized bed adsorber, as these multi-phase contractors are characterized by intensive mixing and high mass transfer rates (Al-Qodah 2000). These two alternatives will be examined in our future studies.

The mass transfer coefficient K increases from 2.767×10^{-6} to 3.967×10^{-6} cm/s as the agitator speed increases from 200 to 600 rpm. These results are at agreement with those of Haimour and Sayed (1997) for the adsorption of methylene blue with Jift. In the other hand, the diffusion coefficient inside the particle pores was slightly increases from 3.357 to 3.536×10^{-10} $\mathrm{m^2/s}$ for the same range of mixing speeds.

4.8 Effect of temperature

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate depending on weather the reaction is endothermic or exothermic (Al-Qodah 2000).

Figure 10 depicts the effect of temperature on the equilibrium concentration of the Deltamethrin in adsorption solution. These results confirm the adsorption isotherm result which implies that the adsorption of Deltamethrin onto ATOSA is an exothermic process. In addition, the effect of the exothermic nature of reaction exceeds the effect of increasing the diffusion rate as the temperature increase. The rate of adsorption is relatively higher at lower temperatures. The equilibrium concentrations after 150 min of start up is still higher than those obtained from the adsorption isotherm part in which experiments continues 72 hours. For example the equilibrium concentration of Deltamethrin obtained from the adsorption isotherm experiments at 25 °C when $C_o = 15$ mg/l is 7.76 mg/l while that obtained from the kinetic study is 8.1 mg/l indicating about 3% difference. This means that the adsorption process approaches equilibrium after 2 h from start up.

The mass transfer coefficient, K increases from 3.432×10^{-6} to 3.964×10^{-6} m/s and the diffusion coefficient D increases from 1.244×10^{-10} to 1.654×10^{-10} $\mathrm{m^2/s}$ as the temperature increases from 25 to 45 °C. These results agree with those of Mckay and Allen (1980).

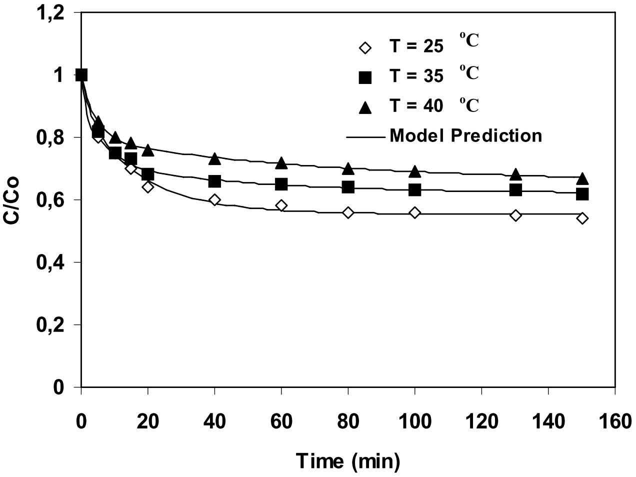


Fig. 10 Effect of temperature on the adsorption rate of Deltamethrin onto ATOSA. Adsorbent mass 1 g/100 ml solution, Initial concentration 10 mg/l, Mixing speed = 400 rpm, particle size = 202.25 µm, pH = 7.3

5 Conclusions

Based upon the experimental results in this study the following conclusions can be drawn:

(1) Oil shale ash produced from energy plants seems to have high potentials towards organic pollutants including pesticides.
(2) The adsorption isotherm data fit to both Langmuir and Freundlich isotherms.
(3) The adsorption process was found to be exothermic which means increasing the temperature will reduce the maximum loading capacity of the adsorbent.
(4) The adsorption rate was very high in the first 15 min after start up and most of the pesticide were adsorbed in this period.
(5) Reduction of the adsorbent size was found to reduce the time needed to reach equilibrium, but does not significantly affects the maximum loading capacity of the adsorbent.
(6) The kinetics of the adsorption of the pesticide Deltamethrin with the acid treated oil shale ash can easily be describe by the two-resistance's model.
(7) The rate of adsorption was found to increase by increasing the initial concentration, adsorbent mass, agitation speed and temperature.
(8) The mass transfer coefficient D was affected by the mixing sped and temperature whereas the diffusivity was affected by the initial concentration and temperature.

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