

53 (2015) 2555–2564 March



Bio-adsorption of triadimenol pesticide from aqueous solutions using activated sludge of dairy plants

R. Al-Shawabkah^a, Z. Al-Qodah^{b,c,*}, A. Al-Bsoul^d

^aDepartment of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Kingdom of Saudi Arabia ^bDepartment of Chemical Engineering, Taibah University, P.O. Box 344, Madinah, KSA

^cDepartment of Chemical Engineering, Al-Balqa Applied University, P.O. Box 340558, Amman, Marka 11134, Jordan

Tel. +966560948161; *Fax:* +96648475837; *email:* zqudah@taibah.edu.sa

^dDepartment of Chemical Engineering, Al-Huson University College, Al-Balqa Applied University, P.O. Box 50, Al-Huson, Irbid, Jordan

Received 3 June 2013; Accepted 4 November 2013

ABSTRACT

In the present study, activated sludge has been utilized for the removal of triadimenol pesticide from water. The maximum adsorption capacity was 42.9 mg triadimenol per gram activated sludge obtained at 298 K. The equilibrium data were fitted to Langmuir Freundlich models and it was found that Freundlich model best fit these data with regression coefficient R^2 =0.947. The kinetic data showed that the rate of triadimenol adsorption is increased with increasing the initial concentration and mixing speed, while decreased with increasing temperature. The two-resistance mass transfer model based on the film resistance 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_f was affected by varying the initial triadimenol concentration, the agitation speed and temperature, whereas the diffusion coefficient D_e was affected by the initial triadimenol concentration and temperature.

Keywords: Adsorption; Triadimenol; Activated sludge; Adsorption isotherms; Adsorption kinetics

1. Introduction

Pesticides are among the major organic compounds that are discharged into the water resources in Middle Eastern countries, which has raised a primary public concern in the recent years [1,2]. These compounds are classified by the Agency of Toxic Substances & Disease Registry (ATSDR), USA as a group in the top priority list of chemicals that need urgent control [3]. Generally, synthetic pesticides negatively affect wild life and the health of humans. Recent report published by the Food Standard Agency (FSA), UK showed that majority of fruits and baby foods contain detectable pesticide residues, where the maximum residue level of 0.01 mg/kg for individual pesticides in infant

^{*}Corresponding author.

^{1944-3994/1944-3986 © 2013} Balaban Desalination Publications. All rights reserved.

formula and manufactured baby foods is set by the European Union [4].

Pesticides in water are an extremely complex problem as a result of a wide range of existing pesticides' chemical structures and properties [5-7]. Triadimenol is one of the most commonly used pesticides. It is well known internationally as a toxic material and could pollute water as a result of agricultural, domestic and industrial activities. Triadimenol is stable with respect to hydrolysis and thus hydrolysis is not considered to be an important pathway for the degradation of this pesticide. Hence, the removal of this pesticide from water is of great importance. Many studies dealing with the occurrence and the removal of pesticides from water have been addressed [8,9]. Relatively few works have addressed the elimination of triadimenol from water [10]. Several technological treatment methods such as catalytic photodegradation [11], Fenton-coagulation [12], flocculation [13], extraction [14] and disinfection [15] could be used for the removal of pesticides from water. However, many of these methods are costly, produce by-products, and fail to reduce the concentration of these pollutants to an acceptable level. Adsorption, on the other hand, is a cost-effective and efficient process and can be used to reduce the concentration of several solutes downstream to sub-part per million. Several adsorbent materials are employed such as activated carbon [16], carbo-aluminosilicate material [17], snail pedal mucus [18], clay minerals and soil [19,20], polymeric adsorbents [21], Diatomite [22], guartz, calcite kaolin and α -alumina [23]. Where among these adsorbents activated carbon is usually the favoured adsorbent because it can remove pesticides, organics and metal ions, which may be found in wastewater even at low concentrations [24]. Lopes et al. [25] studied the adsorptions of triadimenol on soil samples with varying contents of organic matter, and concluded that the capacity of adsorption increased as the organic carbon content in the tested samples increased. However, the high cost of activated carbon production has put forward efforts to search for low-cost raw materials such as agricultural wastes and by-products, sewage sludge, discarded tyres and asphalt [26,27]. In a recent study carried out on the adsorptions of fungicides by soils incubated with biosolids, Copaja et al. [28] concluded that incubating soils with biosolids increased the adsorptions of the fungicides. Nevertheless, little information is available in the literature for using activated biomass as an adsorbent for pesticides [29,30]. Lindane pesticide elimination from its aqueous solution using Rhizopus oryzae biomass was reported by Young and Banks [31] and a possible mechanism of biomass interaction was proposed. In the present work, low-cost activated sludge has been used for the adsorption of triadimenol from wastewater discharged from veterinary and agricultural products manufacturing company limited (VAPCO), Jordan. The effects of pH, temperature, agitation time, solute and adsorbent concentrations have also been investigated to determine the rate of triadimenol adsorption.

2. Experimental

2.1. Materials

Samples of whey sludge were collected from local dairy plants, separated from water, dried in an oven at 105 °C for 24 h, ground and saved in a closed vessel for further usage. The fungicide used contains 25 wt.% triadimenol (commercial name is Vydan, IUPAC name: (1*RS*, 2RS; 1RS, 2SR)-1-(4-chlorophenoxy)-3, 3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butan-2-ol). This fungicide was kindly donated by VAPCO. The physical properties and the chemical structure of this fungicide are shown in Table 1.

Deionized water was prepared using Milli Q system (Millipore, France). All Chemicals were of

Table 1

Selected physico-chemical properties of the pesticides investigated

Property	Triadimenol
pH in aqueous solutions	Basic
Color	Off-white powder
Odor	Odorless
Solubility in water at 20°C (mg/l)	48
Density (g/cm ³)	1.24
Physical state at 25°C	Solid
Melting point	110−130°C
Vapor pressure	<1 mPa at 20℃
Soil degradation DT50 (days)	250
Chemical structure	cí
	OH CH ₃ I I CH-C-CH ₃ O-CH CH ₃ NNN NNN
Chemical formula Molecular mass (g/mol)	C ₁₄ H ₁₈ ClN ₃ O ₂ 294.7

analytical reagent grade and the pyrex glassware was washed with soap, rinsed with nitric acid and then washed with deionized water.

2.2. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) analysis of the sludge sample was performed using IPRrestige-21, FTIR-84005, SHIMADZU Corporation (Kyoto, Japan). A sample of 0.1 g was mixed with 1 g of KBr (Merk, Darmstadt, Germany) using a mortar. A part of this mix was introduced in a cell connected to the piston of a hydraulic pump giving a compression pressure of 15 kPa/cm². The mix was converted to a solid disc which was placed in an oven at 105 °C for four h to prevent interference with any existing water vapor or carbon-dioxide molecules. Then it was transferred to the FTIR analyser and a corresponding spectrum was obtained showing the wave lengths of the different functional groups in the sample.

2.3. Adsorption of triadimenol

Equilibrium isotherms for triadimenol were conducted in a set of 250 ml Erlenmeyer flasks. Hundred milli litre of the triadimenol solutions of different concentrations were contacted with 0.25 g of sludge and allowed to equilibrate in an isothermal shaker at different temperatures; 15, 25 and 40 °C for 24 h. After equilibration, the solution was separated from the solid by filtration. The final concentration was then measured using α S2 Helios UV-vis spectrophotometer at 219 nm. The effect of solution acidity was performed in a similar manner with the exception that the mass of the sludge was 0.1 g and the solution pH was buffered at pH 2.5, 5 and 9. For all these procedures, blank samples were prepared at the same conditions.

Kinetics of adsorption was studied by placing 0.2 g of the sludge sample in 1.71 of Vydan solution with an initial concentration of 200 mg/l (pH 6) at 25°C. The concentration of triadimenol was monitored over time by sampling 0.5 ml every 2 min in the first 10 min of the experiment and every 10 min thereafter. The drawn-off samples were directly centrifuged and analysed using α S2 Helios UV-vis spectrophotometer at 219 nm. The effects of adsorbent mass, solution temperature, initial adsorbate concentration and mixing speed on the kinetic parameters were studied.

3. Theoretical

The adsorption process of solutes onto the surface of a solid adsorbent is usually controlled by several resistances. These resistances are classified as bulk transport, boundary layer transport, intraparticle transport and adsorption [32]. The rates of bulk transport and adsorption are considered fast steps compared to the film and intraparticle ones. In order to develop a kinetic model that simulates the experimental data the following assumptions were considered: (1) the sludge particles are spherical with radius *R* and do not change with time, (2) the sludge particles are suspended in the solution during experiments as a result of mixing and (3) the sludge particles are initially free of pesticide while the initial concentration of the solution C_{ρ} (mg/l).

The variation of triadimenol concentration inside the sludge particles, q_i (mg/g), with distance from the centre, r and time t is governed by the diffusion equation [33,34]:

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

where D_e is the surface diffusion coefficient (cm²/s). The boundary layer mass transport is controlled by the first- order ordinary equation:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = m_s \frac{\mathrm{d}q}{\mathrm{d}t} \tag{2}$$

and

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{3k_f}{1,000R\rho_P} \frac{C - C_e}{(1 - \varepsilon)} \tag{3}$$

where *q* is the average concentration of pesticide inside the particle, k_f is the external mass transfer coefficient (cm/s), ρ_P (g/cm³) and ε are the density and porosity of the particles, respectively, m_s (g/l) is the concentration of sludge in solution and C_e (mg/l) is the triadimenol concentration in equilibrium with that on the surface of the particle

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

$$q_e = \frac{bC_e q_o}{1 + bC_e} \tag{4}$$

where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e is the amount of adsorbate

adsorbed per unit mass of adsorbent (mg/g), q_o is the Langmuir constant related to adsorption capacity (mg/g) and b (l/mg) is a constant related to the affinity between the adsorbent and the adsorbate. The linear form of the Langmuir model is given by:

$$\frac{C_e}{q_e} = \frac{1}{bq_o} + \frac{1}{q_o}C_e \tag{5}$$

The values of q_o and b can be determined by plotting C_e/q_e vs. C_e .

The Freundlich model is applicable when an adsorption is followed by a condensation of the adsorbate on the surface of the adsorbent where a logarithmic fall in the enthalpy of adsorption with surface coverage occurs. This isotherm model is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves [35]. This model is written as:

$$Q_e + K_b C_e^{(1/n)} \tag{6}$$

where K_b ((l/mg)^{1/n}) and *n* are Freundlich constants. The coefficient K_b can be related to the surface energy by the proportionality relation:

$$K_b \propto RT n b e^{\Delta H/RT}$$
 (7)

The constant n gives an indication of how favourable the adsorption process is. The linear form of this model takes the form:

$$\log Q_e = \log K_b + (1/n) \log C_e \tag{8}$$

The values of K_F and n can be obtained by plotting log Q_e vs. log C_e .

The average concentration of triadimenol inside the particle is obtained by integrating the point concentrations q_i over the volume of the particle according to the equation:

$$q = \frac{\int_0^R 4\pi r^2 q_i dr}{\frac{4}{3}\pi R^3}$$
(9)

The initial and boundary conditions to Eq. (1) are:

 $C(0) = C_0 \tag{10}$

$$q(0,r) = 0 \tag{11}$$

$$q(t,R) = q_e \tag{12}$$

The above equations were solved using MATHEMATICA (Version 5) to obtain a set of bulk solution concentration values as a function of time :

$$q_{k,i} = \left[1 - \Omega\left(2 + \frac{2\Delta r}{r}\right)\right] q_{k-1,i} + \Omega\left[\left(1 + \frac{2\Delta r}{r}\right)q_{k-1,i+1} + q_{k-1,i-1}\right]$$
(13)

where $\Omega = \frac{D\Delta t}{(\Delta r)^2}$, and k, i are the indicess that are related to the differential change in time Δt , and radius Δr , respectively.

The average concentration of triadimenol over the sludge particle is,

$$q_{av,t} = \frac{3}{R^3} \sum_{0}^{R} q_{k,t} r \Delta r \tag{14}$$

and

$$q_{av,t} = q_{av,t-\Delta t} + \frac{3\Delta tk_f}{1,000R\rho_P(1-\varepsilon)}(C_t - C_e)$$
(15)

4. Results and discussion

4.1. Adsorbent characterization

An FTIR spectroscopic study for the activated sludge materials is shown in Fig. 1. The samples showed several major absorption bands at 2,500–3,500,



Fig. 1. FTIR of sludge sample.

1,250–1,750 and 560–1,100 cm⁻¹. The sludge sample showed a wide band at around 3,400 cm⁻¹ followed by a sharp peak at 2,900 cm⁻¹. This wide band is assigned to the intra-molecular H-bonded (–OH), O–H stretching mode of hydroxyl groups and the adsorbed water [36].

In the 1,250–1,750 cm⁻¹ region, peaks at 1,700 cm⁻¹ show the existence of hydroxyl group while the peak at 1,550 cm⁻¹ might be related to the presence of amino groups [37]. The peak at 1,420 cm⁻¹ is attributed to the scissoring vibration of (–CH₂) group, which may overlap with the methyl group asymmetrical bending, or to in-plane bending of H-bonded hydroxyl group [38], while the peak at 1,250 cm⁻¹ is due to the C–H hydrogen bonds. The peak at 1,050 cm⁻¹ refers to a C–O–C strong symmetrical band.

The last region has two major peaks at 875 and 560 cm⁻¹ which they assigned to the out- of- plane alkenes (–C–H) bending and in-plane and out-of-plane aromatic ring deformation vibrations, respectively.

4.2. Adsorption isotherms

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. In addition, it shows the effect of equilibrium concentration on the loading capacity at different temperatures. The analysis of the equilibrium data by fitting them to different isotherm models is an important step to find a suitable model that can be used for design purposes.

Fig. 2 shows a plot of the fungicide triadimenol loading on the adsorbent against the equilibrium concentration in the liquid phase at three different

160 **X** 15 oC □ 25 oC 140 O 40 oC 120 qe (mg/g) 100 80 60 40 20 0 0 20 40 60 80 100 120 Ce (mg/l)

Fig. 2. Adsorption isotherm of triadimenol at different solution temperatures.

temperature values (5, 25 and 40 °C). Moreover, Fig. 3 illustrates similar isotherm data but at different solution pH values. It is clear that the adsorption capacity of the activated sludge increases as the equilibrium concentration increases for all the operating temperatures. This increase is more significant at higher equilibrium concentrations. The loading capacity q_e increases from 29 to 148 mg/g when the equilibrium concentration increases for 112 mg/l at 25 °C. This suggests the formation of multilayers of the adsorbate on the activated sludge caused by the possible adsorbate–adsorbate interactions on the adsorbent surface.

Furthermore, the loading capacity of the activated sludge decreases as the temperature increases. This behaviour suggests the exothermic nature of the adsorption process of triadimenol into the activated sludge. It is evident from Fig. 2 that the changes of loading capacity q_e with temperature is more pronounced at higher equilibrium concentrations. For example, q_e decreases from 15 to 3 mg/g as the temperature increases from 5 to 40°C when the equilibrium concentration was 25 mg/l, whereas it decreases from 160 to 48 for the same temperature change and for an equilibrium concentration of 105 mg/l. This behaviour could be due to the effect of temperature on the adsorption process of triadimenol into the activated sludge which is characterized by a reversible nature. It is suggested that as the temperature increases, the viscosity of the solution decreases which enhances the intraparticle diffusion of the triadimenol molecules. However, as the temperature increases, the adsorbate-adsorbate molecules interaction is weakened and the desorption phenomenon is expected to be enhanced causing more molecules to



180

160

140

120

100

80

60

qe (mg/g)

pH 2.5

pH 5

- pH 9

Fig. 3. Adsorption isotherm of triadimenol at different pH values.

Isotherms	Temperature (K)	Constants		R^2
Langmuir		$Q_a (\mathrm{mg/g})$	<i>b</i> (l/mg)	
$\frac{C_e}{C} = \frac{1}{k\Omega} + \frac{1}{\Omega}C_e$	278	90.9	0.0055	0.852
$Q_e = UQ_o = Q_o$	298	42.9	0.007	0.855
	313	10.7	0.0078	0.849
Freundlich		$K_b \; ((1/mg)^{1/n})$	п	
$\log Q_e = \log K_b + (1/n) \log C_e$	278	138.6	0.697	0.943
	298	40.9	0.56	0.947
	313	23.9	0.66	0.947

Table 2

Isotherm model constants and correlation coefficients for the adsorption of triadimenol by activated sludge

leave the particles into the solution. Accordingly, this behaviour indicates that an efficient adsorption process of fungicide from solutions by activated sludge could be conducted at relatively low temperatures.

The adsorption isotherm data were fitted to the Langmuir and Freundlich isotherm models. The values of the models constants (the plots are not shown) in addition to the values of the correlation coefficient, R^2 are shown in Table 2. It is evident that the Freundlich isotherm gives the best fit to these data as indicated by the relatively high values of R^2 . n addition, the applicability of the Freundlich isotherm model is confirmed since the calculated values of the model constants are within the range for this model. This result demonstrates that the adsorption of triadimenol by activated sludge is characterized by the multilayer coverage of the adsorbate molecules on the adsorbent's outer surface. The values of the Freundlich model exponent (1/n) which is the slope of the plot of log q_e vs. log C_e are greater than unity, which indicates a cooperative adsorption. Consequently, the Freundlich model was inserted in the kinetic model to calculate the kinetic parameters like the external mass transfer coefficient, k_f and the internal diffusivity D_e .

The initial concentration of triadimenol in pH experiments was varied from 0 to 260 mg/l and the temperature was maintained constant at 25°C. Each experiment continued until the equilibrium concentration reached a constant value, then the loading capacity, q_{max} , of the adsorbent was calculated. As shown in Fig. 4, q_{max} decreases as pH increases for the same equilibrium concentration. For example, q_{max} decreases from 195 to 18 mg/g as pH increases from 2.5 to 9 at the fixed solution concentration of 95 mg/l. This means that the adsorption of these fungicides is enhanced in acidic media. The reason for this behaviour could be attributed to the fact that triadimenol is a Lewis-base due to the presence of three nitrogen atoms in its molecule. In acidic medium, protonation occurs to the amino groups and the fungicides become positively charged. For this reason more electrostatic attraction may occur between the fungicides and the adsorbent. As mentioned above, the adsorbent or the dried whey sludge contains many types of functional groups including basic oxides. Upon increasing the acidity i.e. reducing the pH, hydrogen ion could react with those oxides and result in activation or impregnation of the adsorbent surface. As a result, adsorption of triadimenol is enhanced with decrease pH. It should be noted that dry sludge was stable in distilled water for a period of 24 h. The distilled water's initial pH of 7 has remained constant during this period.

4.3. Kinetic study

In this part of the study, the effect of many parameters on the equilibrium triadimenol concentration in the adsorption mixture was investigated. These parameters include initial triadimenol concentration, adsorbent mass, adsorbent particle size, temperature



Fig. 4. Effect of initial concentration of triadimenol on the rate of adsorption.

and mixing speed. The experimental results in each case were compared to the theoretical solution obtained by the proposed model. By altering the values of the models' parameters (D_e and k_f), it was possible to obtain the best fit for the experimental data.

4.3.1. Effect of initial concentration

The effect of initial fungicide concentration on the rate of adsorption by activated sludge is shown in Fig. 3. The experimental results are expressed as discrete points while those obtained from the model are expressed by solid lines. It is evident from Fig. 5 that, in the three experiments where the initial concentration varies from 100 to 300 mg/l, the model best fits these data. For a particular experiment, the rate of adsorption decreased with time until it gradually approached a plateau, owing to the continuous decrease in the concentration driving force. In addition, the initial rate of adsorption was greater for higher initial dye concentration as a result of decreasing the resistance to the fungicide uptake with increasing mass transfer driving force.

The values of the kinetic parameters predicted by the model, k_f and D_e are listed in Table 3. It was found that the effect of changing C_o on the mass transfer coefficient k_f was very little. k_f increases from 3.5×10^{-5} to 3.8×10^{-5} m/s as C_o increases from 100 to 300 mg/l. Moreover, the diffusion coefficient inside the particle pores, D_{e_i} is increased from 9.2×10^{-10} to 12.4×10^{-10} m²/s with increasing initial dye concentration from 100 to 300 mg/1.

4.3.2. Effect of adsorbent mass

The effect of varying the sludge mass on fungicide adsorption is shown in Fig. 5. It is shown that that the experimental results are in good agreement with



Fig. 5. Effect of sludge mass on the rate of adsorption of triadimenol, initial concentration of 200 mg/l, pH 6, particles size 250–500 μ m, mixing speed equal 500 rpm and temperature of 25 °C.

those simulated by the model. As expected, the equilibrium fungicide concentration in the solution decreases at a faster rate with increasing adsorbent mass. For example, the relative fungicide concentration is decreased within 30 min. from 0.78 to 0.48 when the adsorbent concentration is increased from 0.1 to 0.3 g/1.

The values of the mass transfer coefficient, $k_{f'}$ and the diffusivity coefficient, D_e are kept constant at 3.5×10^{-5} m/s and 9.2×10^{-10} m²/s, respectively. These results are in good agreement with those obtained by McKay [38] for the adsorption of acid dye 25.

4.3.3. Effect of temperature

Fig. 6 depicts the rate of adsorption of triadimenol by the activated sludge at three different temperatures

Table 3

The kinetic parameters predicted by the model, k_f and D_e for the adsorption of triadimenol by activated sludge

Set of experiments	$C_o \mathrm{mg/L}$	$M/V \text{ kg/m}^3$	D_p (μ m)	Temp. (°C)	rpm	$k_f \times 10^5$	$D_{e} \times 10^{10}$
1	100	0.2	150-250	25	500	3.5	9.2
	200	0.2	150-250	25	500	3.67	10.6
	300	0.2	150-250	25	500	3.8	12.4
2	200	0.1	150-250	25	500	3.5	9.2
	200	0.2	150-250	25	500	3.5	9.2
	200	0.3	150-250	25	500	3.5	9.2
3	200	0.2	150-250	15	500	3.5	9.2
	200	0.2	150-250	25	500	5.3	10.4
	200	0.2	150-250	40	500	8.1	12
4	200	0.2	150-250	25	250	3.5	9.2
	200	0.2	150-250	25	500	6	10.5
	200	0.2	150-250	25	1,000	2.5	8.9



Fig. 6. Effect of solution temperature on the rate of adsorption of triadimenol, initial concentration of 200 mg/l, pH 6, particles size 250–500 μ m, mixing speed equal 500 rpm and adsorbent mass equal 0.2 g.



Fig. 7. Effect of mixing speed on the rate of adsorption of triadimenol, initial concentration of 200 mg/l, pH 6, temperature equal 25° C, particles size 250–500 µm and adsorbent mass equal 0.2 g.

of 15, 25 and 40 °C. It is shown that as the temperature increases, the amount of triadimenol removed per unit time is decreased. This could be attributed to the exothermic nature of contact between the triadimenol and the sludge surface. Increasing the temperature from 15 to 40 °C showed an increase of k_f value from 3.5×10^{-5} to 8.1×10^{-5} m/s while D_e increased from 9.2×10^{-10} to 1.2×10^{-11} m²/s.

4.3.4. Effect of agitation speed

The effect of mixing on the adsorption of triadimenol is shown in Fig. 7. It is shown that the rate of adsorption increases as the mixing speed increases from 250 to 500 rpm and decreases when the mixing speed reaches 1,000 rpm. This behaviour is attributed to the fact that as the mixing speed increases in the range below 500 rpm, the turbulence in the solution is increased and consequently the boundary layer thickness around the adsorbent particles will be decreased. On the other hand, at a relatively high mixing speed the mixing becomes poor as a result of the vortices formed in the solution. The corresponding values of k_f were 3.5×10^{-5} , 6×10^{-5} and 2.5×10^{-5} m/s, whereas the values of D_e were 9.2×10^{-10} , 10.5×10^{-10} and 8.9×10^{-10} m²/s at 250, 500 and 1,000 rpm, respectively. These results are in agreement with those of Asfour et al. for the removal of dyes with sawdust [39].

5. Conclusions

Activated sludge from dairy products was used as an adsorbent for the removal of triadimenol from aqueous solutions. The maximum removal capacity for triadimenol could be as high as 42.9 mg/g sludge at ambient temperature. At a given solution concentration, the rate of triadimenol uptake is increased with increasing the agitation speed for the mixture, decreasing the particle size of the sludge particles and the solution temperature. A two- resistance model could be employed to predict this rate of adsorption in order to obtain the mass transfer coefficient and effective diffusivity of the system. The removal of triadimenol by activated sludge is an economical, safe and environment- friendly process.

Nomenclature

—	constant related to the affinity between the
	adsorbent and the adsorbate (l/mg)
_	the adsorption energy constant
_	the equilibrium concentration of the
	adsorbate (mg/l)
_	the initial concentration of the solution is
	(mg/L)
_	the surface diffusion coefficient (cm^2/s)
—	Freundlich constant ($(1/mg)^{1/n}$)
—	the external mass transfer coefficient (cm/s)
—	indexes that related to the differential
	change in radius
—	the concentration of sludge in solution (g/L)
—	Freundlich constant related to the intensity
	of adsorption
—	the average concentration of pesticide inside
	the particle (mg/g)
—	the average concentration of pesticide over
	the sludge particle (mg/g)
—	the amount of adsorbate adsorbed per unit
	mass of adsorbent (mg/g)

q_i	—	the point concentrations of pesticide (mg/g)
q0		Langmuir constant related to adsorption
		capacity (mg/g)
R		particles radius (cm)
R^2	_	correlation coefficient
R	_	the universal gas constant
r	_	distance from the center (cm)
Т	_	temperature (K)
t	_	time (min)
Greek	letters	
ΔH	_	Enthalpy of adsorption
Ω	_	indexes that related to the differential
		change in time
З	_	porosity of the particles

 ρ_p — the particle density (g/cm³)

References

- [1] S. Boudesocque, E. Guillon, M. Aplincourt, F. Martel, S. Noël, Use of a low-cost biosorbent to remove pesticides from wastewater, J. Environ. Qual. 37 (2008) 631–638.
- [2] A.E. Ghaly, D.G. Rushton, N.S. Mahmoud, Potential air and groundwater pollution from continuous high land application of cheese whey, Am. J. Appl. Sci. 4 (2007) 619–627.
- [3] ATSDR, CERCLA Priority List of Hazardous Substances, Agency of Toxic Substances & Disease Registry, 2007. Available from: http://www.atsdr.cdc.gov/ cercla/07list.html.
- [4] FSA, EURO, Make Health Eating Your Goal, The Food Standards Agency-UK, 2008. Available form: http:// www.foodstandards.gov.uk/safereating/chemsafe/pes ticides/pesticidesmainqa/.
- [5] N. Kadian, A. Gupta, S. Satya, R.K. Mehta, A. Malik, Biodegradation of herbicide (atrazine) in contaminated soil using various bioprocessed materials, Bioresour. Technol. 99 (2008) 4642–4647.
- [6] G.Z. Memon, M.I. Bhanger, M. Akhtar, F.N. Talpur, J.R. Memon, Adsorption of methyl parathion pesticide from water using watermelon peels as a low cost adsorbent, Chem. Eng. J. 138 (2008) 616–621.
- [7] M.P. Ormad, N. Miguel, A. Claver, J.M. Matesanz, J.L. Ovelleiro, Pesticides removal in the process of drinking water production, Chemosphere 71 (2008) 97–106.
- [8] N. Stamatis, D. Hela, I. Konstantinou, Occurrence and removal of fungicides in municipal sewage treatment plant, J. Hazard. Mater. 175 (2010) 829–835.
- [9] A.I. García-Valcárcel, J.L. Tadeo, Determination of hexabromocyclododecane isomers in sewage sludge by LC-MS/MS, J. Sep. Sci. 32 (2009) 3890–3897.
- [10] S. Navarro, J. FenoÎl, N. Vela, E. Ruiz, G. Navarro, Photocatalytic degradation of eight pesticides in leaching water by use of ZnO under natural sunlight, J. Hazard. Mater. 172 (2009) 1303–1310.
- [11] S.G. Muhamad, K.M. Shareef, H.A. Smail, Thermal adsorption and catalytic photodegradation studies of carbendazim fungicide in natural soil and water, Int. J. Chem. 3 (2011) 218–226.

- [12] S. Chen, D.Z. Sun, J.S. Chung, Treatment of pesticide wastewater by moving-bed biofilm reactor combined with Fenton-coagulation pretreatment, J. Hazard. Mater. 144 (2007) 577–584.
- [13] P. Thebault, J.M. Cases, F. Fiessinger, Mechanism underlying the removal of organic micropollutants during flocculation by an aluminum or iron salt, Water Res. 15 (1981) 183–189.
- [14] D.A. Souza, F.M. Lancas, Solventless sample preparation for pesticides analysis in environmental water samples using solid-phase microextration-high resolution gas chromatography/mass spectrometry, J. Environ. Sci. Health., Part B 38 (2003) 417–428.
- [15] Y.Z. Mason, E. Choshen, C. Rav-Acha, Carbamate insecticides: Removal from water by chlorination and ozonation, Water Res. 24 (1990) 11–21.
- [16] G. Kyriakopoulos, D. Doulia, Adsorption of pesticides on carbonaceous and polymeric materials from aqueous solutions, Sep. Pur. Rev. 35 (2006) 97–191.
- [17] R.A. Shawabkeh, Adsorption of chromium ions from aqueous solution by using activated carbo-aluminosilicate material from oil shale, J. Colloid Interface Sci. 299 (2006) 530–536.
- [18] C. Brereton, W.A. House, P.D. Armitage, R.S. Wotton, Sorption of pesticides to novel materials: Snail pedal mucus and blackfly silk, Environ. Pollut. 105 (1999) 55–65.
- [19] A.L. Gimsing, J.C. Sørensen, B.W. Strobel, H.C.B. Hansen, Adsorption of glucosinolates to metal oxides, clay minerals and humic acid, Appl. Clay Sci. 35 (2007) 212–217.
- [20] A. Monkiedje, M. Spiteller, Sorptive behavior of the phenylamide fungicides, mefenoxam and metalaxyl, and their acid metabolite in typical Cameroonian and German soils, Chemosphere 49 (2002) 659–668.
- [21] C.F. Chang, C.Y. Chang, K.E. Hsu, S.C. Lee, W. Höll, Adsorptive removal of the pesticide methomyl using hypercrosslinked polymers, J. Hazard. Mater. 155 (2008) 295–304.
- [22] Z. Al-Alqodah, Adsorption of methylene blue with diatomite, J. Eng. Technol. 17 (1998) 128–137.
- [23] H.C. Oudou, H.C.B. Hansen, Sorption of lambdacyhalothrin, cypermethrin, deltamethrin and fenvalerate to quartz, corundum, kaolinite and montmorillonite, Chemosphere 49 (2002) 1285–1294.
- [24] N.P. Cheremisinoff, P.N. Cheremisinoff, Carbon Adsorption for Pollution Control, Engleweed Cliffs, NJ, PTR Prentice Hall, 1993.
- [25] N.P. Lopes, M.E.L.R.D. Queiroz, A.A. Neves, Influence of organic matter on the adsorption of triadimenol fungicide by soil, Quím. Nova 25 (2002) 544–547.
- [26] M.I. Kandah, R. Shawabkeh, M.A. Al-Zboon, Synthesis and characterization of activated carbon from asphalt, Appl. Surf. Sci. 253 (2006) 821–826.
- [27] F. Rozada, M. Otero, A. Morán, A.I. Garcia, Activated carbons from sewage sludge and discarded tyres: Production and optimization, J. Hazard. Mater. 124 (2005) 181–191.
- [28] S.V. Copaja, H.R. Bravo, P. Muňoz, Adsorption of fungicides in chilean soils incubated with biosolids, J. Chil. Chem. Soc. 57 (2012) 1091–1094.
- [29] M. Kahle, I.J. Buerge, A. Hauser, M.D. Muller, T. Poiger, Azole fungicides: Occurrence and fate in wastewater and surface waters, Environ. Sci. Technol. 42 (2008) 7193–7200.

- [30] Y. Ju, T. Chen, J.C. Liu, Study on the biosorption of lindane, Colloids Surf., B 9 (1997) 187–196.
- [31] E. Young, C.J. Banks, The removal of lindane from aqueous solution using fun-gal biosorbent: The influence of pH, temperature, biomass concentration andculture age, Environ. Technol. 19 (1998) 619–625.
- [32] A.P. Mathews, W.J. Weber, Effects of external mass transfer and intraparticle diffusion on adsorption rates in slurry reactors, AIChE Symp. Ser. 73 (1977) 91–98.
- [33] Z. Al-Qodah, Adsorption of dyes using shale oil ash, Water Res. 34 (2000) 4295–4303.
- [34] Z. Al-Qodah, W. Lafi, Adsorption of reactive dyes using shale oil ash in fixed beds, J. Water Supp. Res. Technol.—AQUA 52 (2003) 189–198.
- [35] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (2010) 2–10.

- [36] S.K. Khare, T. Maruyama, T.M. Kuo, M. Nakajima, Modification of Chromobacterium viscosum lipase by stearic acid, J. Plant Biochem. Biotechnol. 12 (2003) 73–76.
- [37] S.J. Hug, D. Bahnemann, Infrared spectra of oxalate, malonate and succinate adsorbed on the aqueous surface of rutile, anatase and lepidocrocite measured with *in situ* ATR-FTIR, J. Elect. Spect. Rel. Phenom. 150 (2006) 208–219.
- [38] G. McKay, Adsorption of dyestuffs from aquoeous solutions using activated carbon: An external mass transfer and homogeneous surface diffusion, AIChE J. 31 (1985) 335–339.
- [39] H.M. Asfour, M.M. Nassar, O.A. Fadali, M.S. El-Geundi, Colour removal from textile effluents using hardwood sawdust as an absorbent, J. Chem. Technol. Biotechnol. 35 (1985) 28–35.