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Adsorption Kinetics of an Insecticide Diazinon onto Natural Clay

Mohammad S. El-Geundi^a and Assanousi A. Abufares^a

^aChemical Engineering Department, Faculty of Engineering, Omar Al-Mukhtar University, Libya. Email: elgandy1949@yahoo.com; assanousi@hotmail.com

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Abstract

The external mass transfer model has been used to predict the rate-controlling step for the adsorption of an insecticide diazinon onto natural clay. The external mass transfer coefficients (K_s) have been determined and correlated with respect to three variables namely, agitation speed, initial concentration, and mass of clay. It has been found that K_s varies with the variables studied and may be correlated with $(rpm)^{0.93}$, $(C_0)^{-0.96}$, and $(m)^{-0.41}$. The external mass transfer coefficient as the dimensionless mass transfer term $Sh/Sc^{1/3}$ has been correlated with the design variables. It has also been found that $Sh/Sc^{1/3}$ varies linearly with the variables studied and may be correlated with system variables via the equation: $Sh / Sc^{1/3} = A(variable)^B$.

الملخص العربي

تهدف هذه الدراسة الي إيجاد الخطوة المتحكممة في عملية الامتزاز . وعملية الامتزاز تتم على ثلاث خطوات. بداية انتقال المادة الممتزة من المحلول المائي الى السطح الخارجى لحبيبات المادة المازة. ثم انتقال المادة الممتزة إلى المراكز النشطة على سطح حبيبات المادة المازة. واخيرا إنتقال المادة الممتزة خلال المسامات بواسطة الانتشار . في البداية تم افتراض أن الخطوة المتحكممة في عملية الامتزاز هي الخطوة الأولى. وقد تم اجراء التجارب الخاصة بحركية عملية الامتزاز باستخدام حبيبات الطفلة في مفاعل متقطع الأداء . وباستخدام النموذج الرياضى المعد لذلك تم إيجاد معامل انتقال المادة الخارجى (K_s) مع كافة العوامل المؤثرة على عملية الامتزاز وهي : سرعة التقليب وتركيز المحلول وكتلة حبيبات الطفلة. وقد تبين من النتائج التي تم الحصول عليها من النموذج الرياضى أن الخطوة المتحكممة في عملية الامتزاز هي انتقال المادة الممتزة من المحلول الأعلى تركيزا الى السطح الخارجى للحبيبات.

Keywords: Natural clay, Diazinon, Adsorption Kinetics, Mass Transfer Coefficient.

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1. Introduction

The presence of excess fluoride, arsenic and natural organic matters, inorganic contaminants, heavy metals, and variety of pollutants in drinking water are the major causes for various water borne diseases. However in order to maintain safer drinking water, efficient purifying technologies must be implemented. One such beneficial and successful method that has been in use is that of purification of water using natural adsorbents. Clays offer an attractive and inexpensive option for the removal of organic and inorganic contaminants (Murray 2000). The adsorption of several organic contaminants in water such as pesticides, phenols, and chlorophenols has been reported recently in the literatures (Lemic 2006; Zadaka et al. 2009; Shariff 2012). Srinivasan (2011) reviewed the recent development of natural clays and their modified forms as adsorbing agents for the treatment of drinking water and their sources. Natural clays are abundantly available low-cost natural resource which is nontoxic to ecosystem. The suitability of natural clay as a natural adsorbent for pesticides was recognized previously, where the equilibrium adsorption capacities were determined (El-Geundi et al. 2005). To understand the mechanism of insecticide removal, knowledge on the surface mass transfer processes is required.

The mechanism of diazinon adsorption onto an adsorbent consists of several steps, for the purpose of this study, the overall adsorption process is assumed to occur by the following three steps (Furusawa and Smith 1973a): (i) mass transfer of the diazinon from the bulk solution to the particle surface (external mass transfer); (ii) adsorption at an interior site; and (iii) intraparticle diffusion of diazinon via either a pore diffusion, or a homogeneous solid-phase diffusion. During the establishment of the rate-limiting step, step (ii) is assumed to be rapid and hence not considered in any kinetic analysis in the present study. Consequently, the two possible rate-limiting steps considered are external mass transfer and intraparticle diffusion. The development of models based on two such mass transport steps occurring simultaneously is quite complex, requiring a coupling equation and its subsequent solution. Initially, therefore, simplifying assumptions have been made and attempts undertaken to describe the adsorption processes in terms of either an external-mass transfer coefficient or an internal-mass transfer parameter (Furusawa and Smith 1973a).

The aim of the present study is to predict the rate-controlling step for the adsorption of an insecticide diazinon onto natural clay. The external mass transfer model has been used to predict the rate-controlling step for the adsorption process. The external mass transfer coefficients are correlated as a function of a dimensionless mass transfer correlation in terms of the process variables. The variables investigated include agitation speed, initial concentration and mass of natural clay.

2. Experimental

The adsorbate used in this study was the insecticide diazinon. The chemical structure of diazinon is shown in Fig. 1.

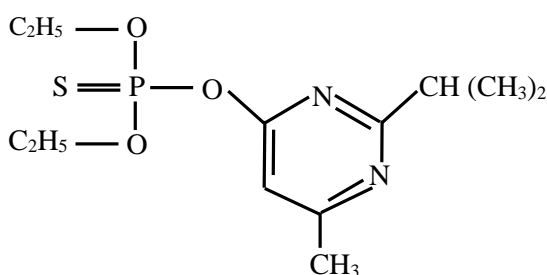


Fig. 1. Chemical structure of diazinon

The adsorbate diazinon used in this study was supplied by Egyptian company for chemical and pharmaceuticals (ADWA), Tenth of Ramadan city, Egypt. The natural clay used in the present study was crushed and sieved through different standard sieves into various particle size ranges. The clay particle size fractions obtained were vigorously stirred in 6 vol.% H_2O_2 solution (5 ml.g^{-1} sample), and then in (2 N) CH_3COOH solution (5 ml.g^{-1} sample) at 90°C to eliminate organic and carbonaceous materials, respectively (El-Geundi et al. 1995). The sample was then filtered, washed thoroughly with distilled water and finally dried at 105°C . The dried material was ground to pass through screens and stored in sealed containers until use. The chemical composition of natural clay used was found to be as; silica (54.15%) and alumina (20.33%) are the major constituents of the natural clay while other metal oxides are presenting traces or small amounts. The silica: alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) for natural clay used was quite low (2.66) and this is an important parameter which governs the uptake of adsorbates. The mineralogical analysis of the natural clay under test revealed that it consists approximately of 51% Kaolinite, 46% montmorillonite, and 3% illite.

The porosity characteristics as well as the chemical composition of adsorbent, play an important role in adsorption processes. The natural clay can thus be regarded as a macro porous material. The specific surface area of the natural clay was determined using the BET method (Brunauer et al. 1932) and the value obtained was $112 \times 10^4 \text{ cm}^2/\text{g}$.

The batch adsorber vessel with a standard tank configuration was utilized to obtain the dimensions of the vessel and its components. The batch adsorber was a 2 dm^3

glass beaker and holding a volume of 1.7 dm³ diazinon solution in each run. Constant and uniform agitation was achieved using a variable speed motor and a six bladed (flat) stainless-steel impeller. Eight anodized aluminum baffles were evenly spaced around the circumference of the adsorber and held securely in place by insertion into a thick rubber ring placed on the top of the adsorber. Further design details for the batch adsorber used in the kinetic studies have been reported previously (McKay et al. 1981).

3. Theoretical Analysis

In the present study, the external mass transfer model has been used to predict the rate-controlling step for the adsorption process. The model presented for determining the external mass-transfer coefficient, K_s , is based on the investigation reported by Furusawa and Smith (1973 a & b; 1974). It assumes that the external mass transport of the diazinon from the bulk solution across the boundary layer film to the external particle surface is rate-controlling step in the early stages of the adsorption process.

The uptake of dye on the solid and the solid-liquid equilibrium relationship is described by the Freundlich isotherm. The uptake of diazinon onto natural clay is given by Eq. 1:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

The Freundlich isotherm is shown in Eq. 2 and can be linearized as in Eq. 3 for determining the exponent, n , and the constant, K_F :

$$q_e = K_F \cdot C_e^{1/n} \quad (2)$$

$$\log q_e = \log K_F + (1/n) \log C_e \quad (3)$$

The values of K_F and n for diazinon-clay systems have been determined and reported previously.

In a well-agitated batch adsorber mixing in the liquid phase is rapid, hence the concentration of adsorbate in the liquid phase (C_l) and the concentration of adsorbent particles in the liquid (m_s) are assumed to be uniform throughout the vessel. Since at time $t = 0$, all the mass transfer resistance is restricted to the external layer of the particle. Consequently, m_s may be determined from the measured mass of clay and the volume of particle-free diazinon according to Eq. 4:

$$m_s = m/V \quad (4)$$

The change in diazinon solution concentration (C_t) with time is related to the fluid-particle mass transfer coefficient by the Eq. 5:

$$dC_t/dt = -K_s S_s (C_t - C_s) \quad (5)$$

Where, $C_t = C_0$ at $t = 0$

If the effective diffusion coefficients are neglected, then since C_s approaches zero and C_t approaches C_0 as $t \rightarrow 0$, Eq. 5 becomes:

$$\left[\frac{d(C_t/C_0)}{dt} \right]_{t=0} = -K_s S_s \quad (6)$$

The external surface area of the particles, S_s , can be obtained from m_s by assuming that the particles are spherical and of diameter, d_p , hence:

$$S_s = \frac{6m_s}{d_p \cdot \rho_t (1 - \varepsilon_p)} \quad (7)$$

Equation 6 can be used for obtaining K_s . Hence, the slope at $t = 0$ of a plot of (C_t/C_0) versus time is equal to $(-K_s S_s)$, and K_s can be extracted from such a slope.

The K_s value may be expressed by an equation of the general form:

$$K_s = x (\text{variable})^y \quad (8)$$

or in the logarithmic form:

$$\log K_s = \log x + y \log (\text{variable}) \quad (9)$$

The external mass transfer coefficient, K_s , can also be correlated as a function of the Sherwood number (Sh) and the Schmidt number (Sc), in a dimensionless mass transfer form, $Sh/Sc^{1/3}$ (Bird et al. 1960), where:

$$Sh = \frac{K_s d_p}{D} \quad (10)$$

and

$$Sc = \frac{\xi}{D} \quad (11)$$

The molecular diffusivity (D), used in the mass transfer expression may be obtained from the expression of Wilke and Chang (1955) as shown in Eq. 12:

$$D = 7.4 \times 10^{-8} \frac{(\alpha M_A)^{0.5} T}{\mu V_m^{0.6}} \quad (12)$$

Since the dimensionless mass transfer expression, $Sh/Sc^{1/3}$, is an important design and kinetic parameter, it is useful if $Sh/Sc^{1/3}$ can be correlated against a particular system variable. This can be expressed by an equation of the general form:

$$Sh / Sc^{1/3} = A(\text{variable})^B \quad (13)$$

Logarithmic analysis of the data yields a straight line represented by the following equation:

$$\log (Sh / Sc^{1/3}) = \log A + B \log (\text{variable}) \quad (14)$$

The variables investigated include: agitation speed, initial concentration and the mass of natural clay.

4. Results and Discussion

Molecular diffusivities have been calculated using Eq. 12 at temperature of 20 °C for different concentrations where its values have been found approximately constant through the concentration range used in the present study, $D = 5.12 \times 10^{-6} \text{ cm}^2/\text{s}$.

The external mass transfer coefficient may be determined from Eq. 6 where, it is dependent on drawing slopes at $t = 0$ on the concentration versus time decay curves. Fig.2 shows the experimental results obtained from a series of contact time studies for the adsorption of diazinon onto natural clay at concentration of 40 mg.dm^{-3} , temperature of $20 \pm 1^\circ\text{C}$, and mass of clay 2 g in which the degree of agitation was varied from 250 to 450 rpm. The curves represent solid-phase concentration (q_t) - time profiles for moderately short contact times; the experiments were conducted over 180 min. period. The results indicate that the removal of diazinon increases with increasing agitation speed. The increase in the extent of removal can be explained by the following basis:

1. the solute species, diazinon may get activated due to a gain in kinetic energy and easily cross the potential barrier,
2. the increase in agitation speed decreases the boundary layer resistance to mass transfer in the bulk solution and increases the driving force of solute ions.

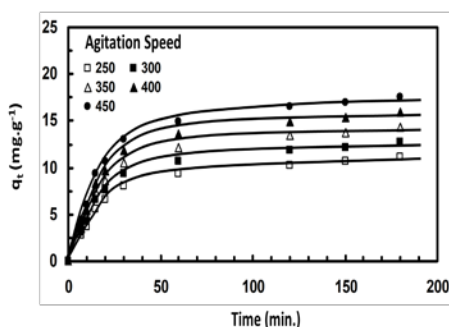


Fig. 2. Effect of agitation speed on the adsorption of diazinon onto natural clay.

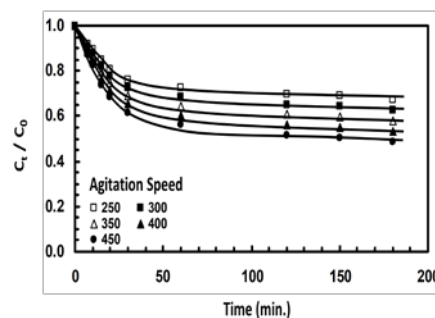


Fig. 3. Typical time-concentration ratio at different agitation speeds.

The experimental results of the effect of agitation speed are shown in Fig. 3 as a plot of (C_t/C_0) against time of the adsorption of diazinon onto natural clay. The initial gradients $(d(C_t/C_0)/dt)_{t=0}$ of the various curves have been determined which is equal to $(-K_s S_s)$. From such slopes, K_s can be extracted.

The external mass-transfer coefficients, K_s , for different agitation speeds have been determined from initial gradients and plotted as $\log K_s$ against $\log \text{rpm}$, as shown in Fig. 4. Linear variation was observed and the values of constants, x and y , associated with Eq. 8 have subsequently been determined using the least-squares method.

The data indicate that the external adsorption of diazinon onto natural clay is controlled by the degree of agitation (since the plot in Fig. 3 is linear) and that the effect of increasing agitation is to decrease the boundary layer resistance to mass transfer and hence increase the mobility of the solid/fluid system.

The equation relating K_s to agitation speed in the range (250-450 rpm) for the adsorption of diazinon onto natural clay is:

$$K_s = 6.49 \times 10^{-6} (\text{rpm})^{0.93} \quad (15)$$

Although no literature values for diazinon mass-transfer coefficient are available, its order of magnitude is comparable to the mass transfer of certain dyestuffs onto maize cob, wood and natural clay. A similar trend has been reported previously (El-Geundi 1990 & 1996) for the adsorption of certain dyestuffs onto natural clay, maize cob and wood particles.

The major controlling factor in external mass transfer is the thickness of the boundary layer. All experiments were undertaken at 450 rpm to achieve completely mixed systems. Consequently, there was a considerable shear force on the boundary layer

which made this initial resistance to mass transfer fairly low, and hence the intrinsic adsorption rate was very rapid until an external surface coverage of diazinon had occurred on the clay particles.

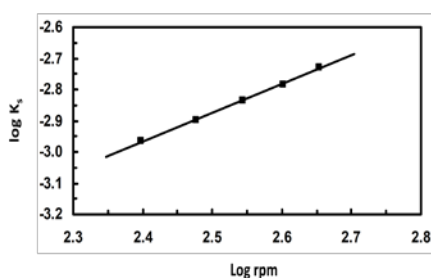


Fig. 4. Effect of agitation speed on surface mass transfer coefficient.

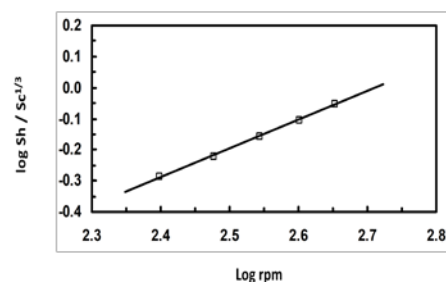


Fig. 5. Effect of agitation speed on dimensionless mass transfer correlation.

The mass transfer coefficient in dimensionless form has been obtained for different agitation speeds and plotted as $\log Sh/Sc^{1/3}$ against $\log rpm$, yielding a linear graph being obtained as shown in Fig. 5.

An empirical equation was sought to fit data and related the dimensionless mass-transfer to agitation speed as follows:

$$Sh / Sc^{1/3} = 3.09 \times 10^{-3} (rpm)^{0.93} \quad (16)$$

The influence of initial diazinon concentration has also been studied and the experimental results obtained are depicted in Fig. 6 as a plot of (q_t) against time for the adsorption of diazinon onto natural clay. The external mass transfer coefficients, K_s , have been determined as mentioned before at different initial concentrations (Fig. 7) and these results have also been plotted as $\log K_s$ versus $\log C_0$ using Eq. 6 as shown in Fig. 8 and linear variation was observed.

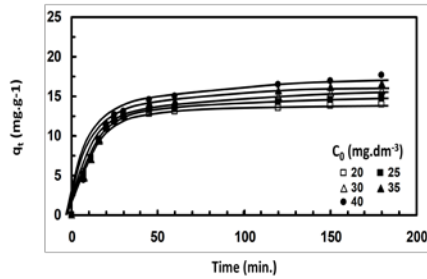


Fig. 6. Effect of initial concentration on the adsorption of diazinon onto natural clay.

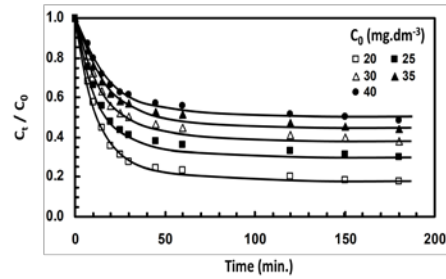


Fig. 7. Typical time-concentration ratio at different initial concentrations.

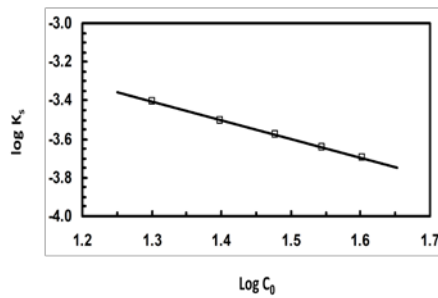


Fig. 8. Effect of initial concentration on surface mass transfer coefficient.

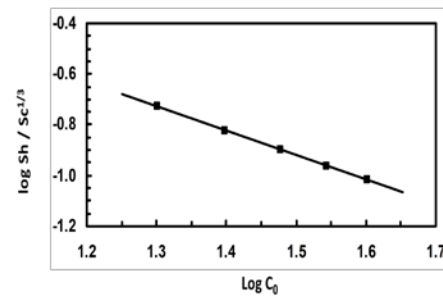


Fig. 9. Effect of initial concentration on dimensionless mass transfer correlation.

The driving force for mass transfer (based on the difference between the bulk liquid concentration and the particle surface liquid concentration) is time dependent. This concentration difference, relative to C_0 , will affect the way in which the external mass transfer coefficient varies with diazinon concentration. Thus, the external mass transfer coefficients decrease as C_0 increases for diazinon being adsorbed onto natural clay.

The K_s values were correlated in terms of (C_0) by Eq. 17 in the range (20 - 40 mg. dm^{-3}).

$$K_s = 7.06 \times 10^{-3} (C_0)^{-0.96} \quad (17)$$

The data of external mass transfer coefficient in dimensionless form have been plotted as $\log (Sh/Sc^{1/3})$ versus $\log (C_0)$, a linear graph being obtained as shown in Fig. 9 indicating that K_s varies with C_0 in a definite logarithmic manner.

An empirical correlation was sought to fit the data and to correlate the external mass transfer coefficient in dimensionless form with the initial diazinon concentration and the predicted equation for this variation is:

$$\text{Sh} / \text{Sc}^{1/3} = 3.37 (C_0)^{-0.96} \quad (18)$$

In order to vary the solid-to-liquid ratio, effect of the mass of natural clay on the adsorption rate has been studied keeping the other experimental conditions constant. The results are shown in Fig. 10 as a plot of (q_t) against time for the adsorption of diazinon onto natural clay. The initial gradients of the various curves in Fig. 11 allow the determination of the K_s values for the different masses and the results have been plotted as $\log K_s$ versus $\log m$ (Fig. 12). The resulting linear graph indicated that K_s varies with the mass of natural clay in a logarithmic manner.

The external mass transfer coefficient depends on the driving force per unit area, and in this case, since C_0 is constant, increasing the mass of natural clay increases the surface area for adsorption. Hence, the rate of diazinon removal increases. Since the particle size range is constant, the surface area will be directly proportional to the mass of natural clay in the system. The K_s values as appears in (Fig. 12) indicate only a small dependence on mass, with K_s decreasing with increasing mass of natural clay. This effect is probably due to the fact that for small masses, a small amount of external surface is presented to the diazinon and therefore there is a large driving force from the diazinon per unit surface area of natural clay. The K_s values were correlated in terms of mass of natural clay (m) for the adsorption of diazinon by Eq. 19 in the range 0.5 - 2 g:

$$K_s = 2.56 \times 10^{-4} (m)^{-0.41} \quad (19)$$

As before, data of the external mass transfer coefficient have been plotted as $\log \text{Sh}/\text{Sc}^{1/3}$ against $\log m$, a linear variation is again observed as with all other previous variables as shown in Fig. 13, the predicted equation for this variation is,

$$\text{Sh} / \text{Sc}^{1/3} = 0.12 (m)^{-0.41} \quad (20)$$

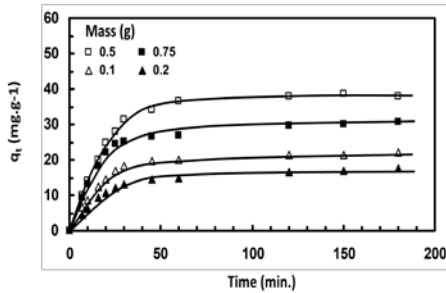


Fig. 10. Effect of mass on the adsorption of diazinon onto natural clay.

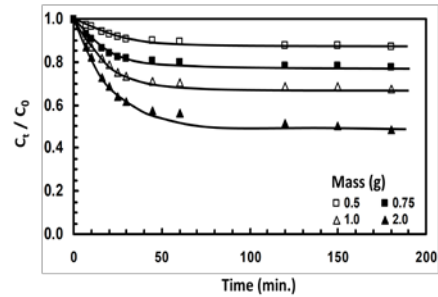


Fig. 11. Typical time-concentration ratio at different masses.

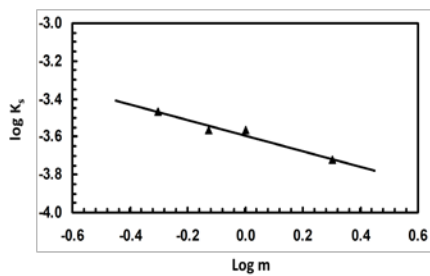


Fig. 12. Effect of clay mass on surface mass transfer coefficient.

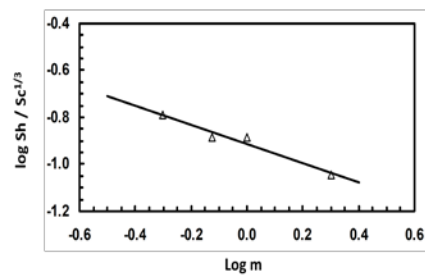


Fig. 13. Effect of clay mass on dimensionless mass transfer correlation.

5. Conclusions

The kinetic studies clearly indicated that, the external mass transfer is rate-controlling step in the early stages of the adsorption process and the deviation thereafter is due to the development of intraparticle diffusion resistance. The external mass transfer model proposed for estimating the external mass transfer coefficient (K_s) of the adsorption process is found to be applicable in the present study. The external mass transfer coefficient (K_s), has been determined and correlated with the design variables. It has been found that $K_s = 6.49 \times 10^{-6} (\text{rpm})^{0.93}$, $K_s = 7.06 \times 10^{-3} (C_0)^{-0.96}$ and $K_s = 2.56 \times 10^{-4} (m)^{-0.41}$. The dimensionless mass transfer term has been shown to vary with such variables, according to general equation: $\text{Sh}/\text{Sc}^{1/3} = A(\text{variable})^B$, and the constant A and the exponent B have been determined for each design variable.

Nomenclature

A	constant in Eq. 13
B	exponent in Eq. 13
C_0	initial liquid-phase concentration ($\text{mg}\cdot\text{dm}^{-3}$)
C_e	equilibrium liquid-phase concentration ($\text{mg}\cdot\text{dm}^{-3}$)
C_s	liquid-phase concentration at outer surface of particle ($\text{mg}\cdot\text{dm}^{-3}$)
C_t	liquid-phase concentration at time t ($\text{mg}\cdot\text{dm}^{-3}$)
D	molecular diffusivity of diazinon in water (cm^2/s)
d_p	adsorbent particle size range (μm)
K_F	parameter of Freundlich isotherm (dm^3/g)
K_s	external mass transfer coefficient ($\text{cm}\cdot\text{s}^{-1}$)
m	mass of particle-free liquid in the adsorber (g)
M_A	molecular weight of solvent ($\text{g}/\text{g mol}$)
m_s	mass of adsorbent particles per unit volume of particle-free diazinon ($\text{g}\cdot\text{dm}^{-3}$)
n	Freundlich exponent (dimensionless)
q_t	solid-phase concentration at time t ($\text{mg}\cdot\text{g}^{-1}$)
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
S_s	outer surface area of adsorbent particles per unit volume of particle-free liquid (cm^{-1})
t	contact time (min)
T	temperature (K)
V	volume of particle-free liquid in the adsorber (dm^3)
V_m	molal volume of solute ($\text{cm}^3/\text{g mol}$)
x	pre-exponential constant, defined by Eq. 8
y	exponential factor, defined by Eq. 8

Greek symbols

α	association number for diazinon in water (=2.6)
ε_p	porosity of particles (-)
ρ_t	true density ($\text{g}\cdot\text{cm}^{-3}$)
μ	dynamic viscosity ($\text{g}/\text{cm}\cdot\text{s}$)
ξ	kinematic viscosity (cm^2/s)

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