Mathematical Simulation of Sorption of Atrazine on Waste Rubber Granules

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Abstract

This paper presents an effort to study the sorption of atrazine on to waste rubber granules, choosing 120 minutes as the equilibrium time. It is seen that the rapid stage zone of kinetics profiles followed second order kinetics. Moreover, second order kinetic equation fitted very well with the experimental data with mean error less than 0.02 and maximum error 0.14. It is evident from the batch study mass transfer model that both external mass transfer resistance and pore diffusion are rate-limiting factors in this case. The LDF (Linear Driving Force) model predicted the breakthrough point well for 40 cm bed.

Keywords: Sorption; Kinetic equation; Atrazine; Rubber granule; LDF model; SPNSM model

Introduction

Atrazine is widely used for control of grassy and broad-leaf weeds. It is not new that many researchers have reported the presence of herbicides; pesticides in water in U.K., Sweden, Bulgaria as well as India (Sandberg & Erlandsson 1990, Jones & Sylvester 1992, Sandberg et al. 1996, Rita 1998). In this study, rubber granules have been used as adsorbent for removal of herbicide atrazine from water environment. The experimental data were fitted with batch model SPNSM (*Static, Physical, Non-equilibrium Sorption Model*) and column model for LDF *(Linear Driving Force)* for analyzing the adsorption uptake mechanism.

Methodology

Determination of Atrazine

Standard methods (APHA-AWWA-WPCF 1989) were adapted for the analysis of various water quality parameters. Gas Chromatograph (GC-14A, Shimadzu, Japan) with Electron Capture Detector (^{63}Ni) with 5% OV-17 was used for atrazine measurement. Temperature for column, injector, and detector was maintained at 215°C, 250°C, and 300°C, respectively. Nitrogen (99.9% purity) was used as carrier gas at a flow rate of 50-60 ml/min. Representative sample (100 ml) of aqueous solution spiked with atrazine was extracted by liquid-liquid partition in a 125 ml separating funnel using acetone. The extraction efficiency was found to be 87-95%.

Kinetic Study

Batch study has been done with the initial concentration of 4 mg/l of atrazine with adsorbent dose of 23 gm/l and size of 0.15–0.30 mm. The breakthrough curve was developed with initial concentration of 2 mg/l and bed depth of 40 cm.

Results and Discussion

Kinetic Study

Sorption kinetics is important to understand the rate of uptake of the sorbates onto the surface and to determine the equilibrium time. The removal kinetics of atrazine by the rubber granules for different concentration is shown in Fig. 1.

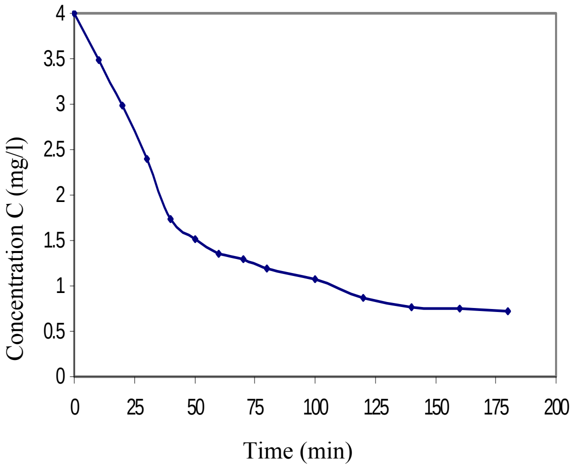

Fig. 1 Change of concentration of atrazine with time

It may be seen that more than 60% of the herbicides was sorbed with 60 min. of reaction. The attainment of the equilibrium time for sorption of herbicides or organic pesticides in CMBR was shown to be in the range of few minutes to several hours (Aly & Faust 1965).

After 120 minutes of reaction time, it was evident that the kinetics profiles were gradually becomes flat indicating the final equilibrium. In order to evaluate the order of reaction kinetics for rapid stage zone of herbicides by rubber granules, three simple and fundamental kinetics models such as zero order ($dc/dt = k_0$), first order ($dc/dt = k_1C$) and second order ($dc/dt = k_2C^2$) were used. Integral method was adopted by applying regression analysis for the experimental data. It was found that the regression coefficients were 0.89, 0.93 and 0.978 for zero order, 1st order and 2nd order, respectively The sorption of atrazine over inactive bio-mass at different concentrations and at different temperatures was rapid and shown to follow a second order kinetics. Sorption of atrazine over rubber granules at any instant of time is considered as reversible process. If the 1st order reversible kinetics is valid then the forward rate constant k_f and reverse rate constant k_r for the rapid stage zone of atrazine can be expressed as

$$\ln [1-U(t)] = -(k_f + k_r)\, t \qquad \text{..........................} (1)$$

where k is overall rate constant and $U(t) = X/X_e$ is called fractional attainment (Helfferich 1962) and X and X_e is the amount of herbicide sorption at any time and at equilibrium, respectively. A linear plot between $\ln [1-U(t)]$ and t indicates the reaction to be first order reversible. As per equation, Table 1 shows the fitting of experimental data with the 1st order kinetic equation with regression coefficient 0.962. The

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calculations with initial points created the biased error due to the initial drop (Bhattacharya & Venkobachar 1984).

The following second order equation has been found to fit well with the experimental data.

$$-dC/dt = k_1C(X_M - X) - k_2X \qquad \text{……………………} (2)$$

where k_1 and k_2 = specific rate constants, X_M = number of moles of adsorbate retained by 1 gm of adsorbent when the mono-layer is complete, $X = (C_0 - C)/2m$, C_0 = initial concentration, C = concentration at any time t, m = mass of adsorbent.

The kinetic sorption rates were found out by a computer program developed in MATLAB by using least square concept for experimental data. It was fitted very well with the experimental data with mean error less than 0.02 and maximum error 0.14 (Fig. 2).

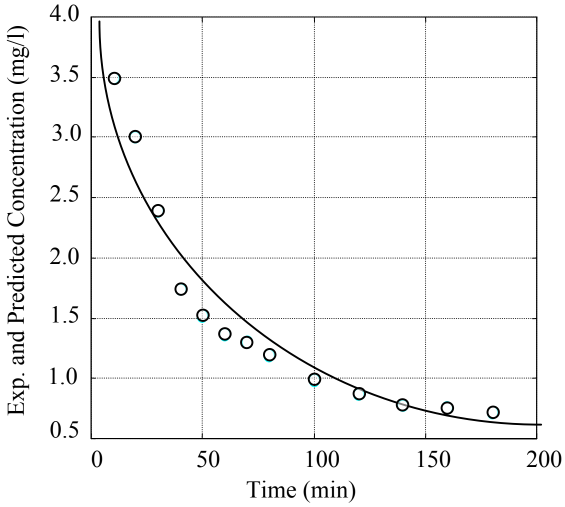

Fig. 2 Application of experimental data to second order kinetic equation

It is evident from the Table 1 that regression coefficient is better for 2nd degree equation than that of 1st degree equation (for dose 18 g/l with initial concentration 4 mg/l).

Table 1 Comparison of correlation coefficients of first degree and second-degree rate constant equation

Parameters	1st Degree Kinetics	2nd Degree Kinetics
Rate Constant (10^{-6} sec^{-1})	483	775
Regression Coefficient	0.962	0.993

[Initial concentration 4 mg/l, adsorbent dose 18 g/l, size 0.15-0.30 mm]

Simulation of Batch Study Kinetics

A simple *Static, Physical, Non-equilibrium Sorption Model* (SPNSM) based on external mass transfer effect as a significant factor, has been used to describe the kinetic of herbicides atrazine on to rubber granules. The final form of SPNSM model using sorption rate and combination of equation of freundlich isotherm can be expressed as

$$d(C/C_0)/dt = (k_{ff}V/mKN)C^{N-1}[1-(mK/V)C^N/C_0 - C/C_0] \text{ ……}(3)$$

where, C_0 = initial herbicide concentration (mg/l), C = liquid phase concentration (mg/l), m = mass of adsorbent rubber granules (g), V = volume of herbicide solution (cm^3), k_{ff} = film transfer coefficient (min).

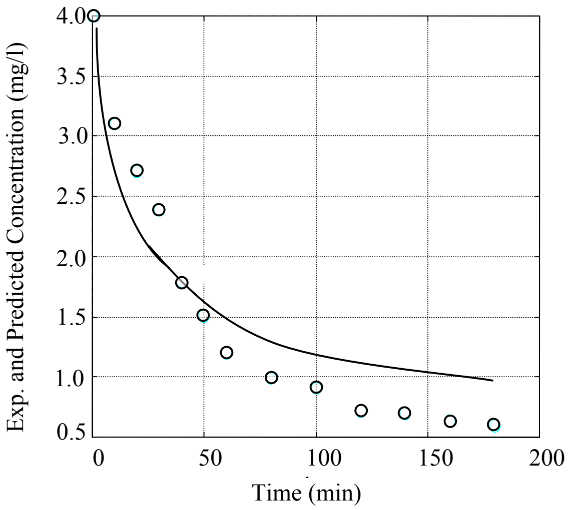

Fig. 3 Application of SPSMN model to the experimental data of sorption of atrazine on waste tyre rubber granules

This is called SPNSM model equation. This model was solved numerically by constructed a program based on Runga-Kutta method. The experimental data was fitted with this model with error 0.89. It is evident from Fig. 3 that the lower parts deviated slightly from the experimental data. For early time portion of batch study, external resistance to pore diffusion played more dominant role (Weber & Digiano 1996). It may be due to effect of pore diffusion, which was not considered in SPNSM model. In order to get idea about the mechanism of sorption of atrazine on waste tyre rubber granules, the model of Huang & Li (1973) where both the external mass transfer and intra-particle mass transfer coefficient were used, was implemented

$$C/C_0 = 1 - 1/(1+\alpha)[1 - \Sigma 6B_i(1+\alpha)e^{-\tau\beta n}/\{9/\alpha + \alpha\beta_n + 9)B_i^2 - (6+\alpha)\beta_n B_i + \alpha\beta_n^{\,4}\}] \text{ …………………………..}(4)$$

$$\tan \beta_n/\beta_n = (3B_i - \alpha\beta_n)/\{(B_i - 1)\alpha\beta_n^{\,2} + 3B_i\}$$

where $B_i = k_{ff} R/D_p$ and $\alpha = mq_0/(VC_0)$, m is the weight of adsorbent and V is the volume of solution (Suzuki 1990), $q_0 = kC_0^{\,1/n}$, $\tau_f = k_st/R(C_0/\rho q_0)$ and Σ is summation for n = 1 to infinity.

β_n is the positive root of above equation. It was solved numerically using Muller method in FORTRAN. A batch sorption experiment was conducted to generate such type of parameters. In this work, the solid-phase transfer coefficient was estimated from equation developed by Mathews & Zayas (1989). The external mass transfer coefficient (k_{ff}) was computed from kinetics rate data using the following equation (Mathews & Zayas 1989). The value of k_{ff} was found to be 2.2×10^{-5} cm/sec.

Fig. 4 shows the plot of $ln(1-F)$ vs. time t [where F is fraction of species up-taken by rubber granules at time t] shows comparison between the experimental and the theoretical curve based on both external mass transfer coefficient (fluid to particle transfer) resistance and pore diffusion. This small deviation may be due to deviation of the pores from the ideal model of straight (Satterfield & Sherwood 1963), non-linear nature of sorption isothermal coefficient and spherically of sorbent particle (Crittenden 1973). However it is evident from the curve portion of initial part of graphs that intra-particle diffusion played important role in sorption kinetics (Huang and Li 1973). If it would be linear relationship then external mass transfer coefficient would be rate-controlling step (Huang & Li 1973). So, almost linear relationship demonstrates that at 150 rpm, the external mass transfer is more important than the intra-particle diffusion.

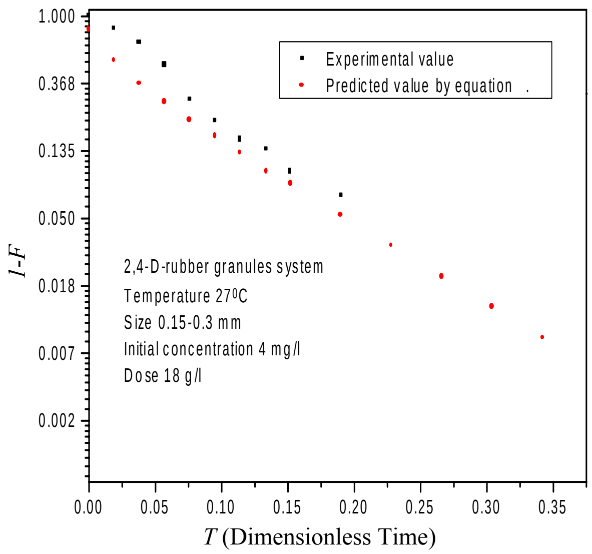

Fig. 4 Comparison of experimental results and the theoretical equation taking into account intra-particle diffusion and film diffusion for sorption of atrazine on waste tyre granules (ln(*1-F*) vs. time; *F* is fraction of species up-taken by rubber granules at time, *t*, dimensionless time $T = vt/L$ where v is the flow rate, t is time and L is height)

Inclusion of any term related with time and instantaneous concentration for pore diffusion into this model may give more precise result (Al-Asheh & Duvnjak 1999). Considering $\varepsilon(t)=\chi t C^N$ for pore diffusion in the SPNSM model, where χ is a constant and C is a concentration at any time (t), predicted the experimental behavior well shown in the Fig. 5 for atrazine with error 0.3737. Al-Asheh & Duvnjak (1999) also predicted similar type of term for pore diffusion in the case of heavy metal sorption on to biomass.

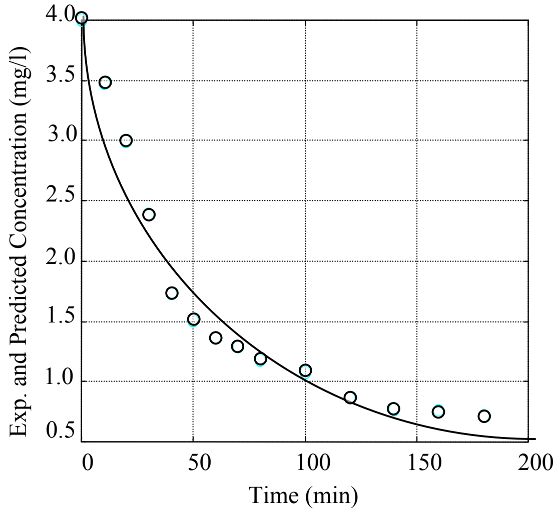

Fig. 5 Application of experimental data to model considering both external mass transfer diffusion and internal mass transfer diffusion for atrazine sorption onto waste tyre rubber granules

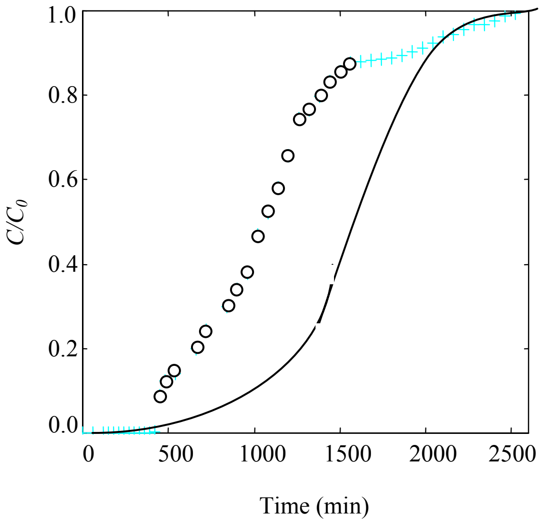

Fig. 6 Column dynamics of atrazine passing through bed of waste tyre rubber granules

Column Dynamic Study using LDF Model

In this study, *Linear Driving Force* (LDF) model for mass transfer was used for column dynamics for getting rough idea about breakthrough points. Assuming constant pattern condition, i.e. $C/C_0 = \bar{q}/q_0$, the solution of above equation is as given below by Suzuki (1990) and Miura & Hashimoto (1975),

$$C/C_0 = [(\alpha r + 1) X_s + \alpha(1-r) X_s^{\,2}]/[(1+\alpha)\{r + (1-r) X_s\}]$$

where $\alpha = k_{ff}a_v/(k_s a_v \gamma)$, r = separation factor of Langmuir isotherm, X_s = surface concentration ratio given by following equation

$$\theta_T - X_T = 1/(1+\alpha)[1/(1-r) \ln X_s - r/(1-r) \ln \{(1-X_s)\} - \ln\{r + (1-r) X_s\} - r/(1-r) \ln r + 1] + \alpha/(1+\alpha)\{r/(1-r) \ln X_s - r/(1-r) \ln (1-X_s) - 1\},$$

where, $\theta_T = \{k_{ff}a_v/\rho_b\gamma(1+\alpha)\}(t-\varepsilon_b Z/u)$, $X_T = \{k_{ff}a_v/(1+\alpha)\}Z/u$, Z = depth of column, ε_b = porosity of bed, u = velocity, $\gamma = q_0/C_0$

The above-mentioned LDF model has been implemented using MATLAB. Breakthrough curves of the herbicides were simulated by LDF analytical model shown Fig. 6 show the experimental data and the predicted breakthrough curve for atrazine. This model contains solid-phase mass transfer coefficient as kinetic parameter. In packed beds, the main parameters of transport of adsorbents are axial dispersion coefficients and the fluid to particle mass transfer coefficient (k_{ff}). In this work, the solid-phase transfer coefficient was estimated from imperial equation developed by Wakao & Funazkri (Suzuki 1990). The value of k_{ff} was found 2.2×10^{-5} cm/sec. Parameters for simulation of column dynamics are $k_s a_v$= 0.02808 gm/cm^3-sec, $k_f a_v$= 0.21875 min^{-1}, $\alpha = k_f a_v/k_s a_v \gamma$ = 0.05189; γ = density of rubber granules.

Table 2 Calculation of parameters for simulation of column dynamics (d = 3.0 cm, u = 1.13 cm/min)

Parameter	Atrazine
L	40cm
X_T	7.66
θ_T	0.0049011(t-11.48)

On the basis of data of Table 2, breakthrough curves were predicted through LDF model shown in Fig. 6 for atrazine. It was found that LDF model shows same shape of pattern, but shows deviation from the experimental breakthrough curves. Assumption of parabolic distribution of the concentration profile within the particle, the calculation of intra-particle mass transfer coefficient by conventional method in LDF model may be the reasons for the difference (Buzenowski & Yang 1991, Nako & Suzuki 1983). Moreover LDF simplification is applicable for strong sorption process (Do & Rice 1986, 1990). In the case of rubber granules bed, adsorption of the herbicide molecules was not first. As a result the concentration gradient played a major role in the system. But this is not accounted for in the LDF approximation (Carta & Lewus 2000). The aim of using of LDF model, in this study is to set a rough idea about the shape of the breakthrough curve and breakthrough point. Application of axial dispersion coefficient, more complicated concentration profile (rather than parabolic) would provide more accurate result (Lee et al. 1997).

Conclusions

Experimental data fitted very well with second order kinetic equation with mean error less than 0.02 and standard deviation 0.14 in the case of 4 mg/l initial concentration and 18 g/l adsorbent dose. It is evident from the above study that both external mass transfer diffusion and intra-particle diffusion played important role in sorption of atrazine on waste tyre rubber granules. The experimental data fitted well with SPSMN model well up to 40-60 min, after that intra-particle diffusion played important role in sorption process which was not considered in SPSMN model. As a result experimental data deviated to some extent from the model. Considering the pore diffusion with SPNSM model, the model predicted the experimental behavior very well.

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