Chemical kinetics modelling of the adsorption of oxytetracycline onto activated carbon in a closed loop fixed bed reactor

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ARTICLE INFO	ABSTRACT/RESUME
	Abstract: The sorption mechanism is usually described by models that contain kinetic parameters which varied with the operating conditions. They are therefore difficult to use and not practical to scale-up. Another approach is therefore proposed in this work based on the determination of the equation rates related to the sorbate-sorbent interactions instead of the system operating conditions. *Three adsorption kinetic models are presented in this paper, which have been applied to test if the integral or differential modeling approach is appropriate to describe the kinetics at the solid/solution interface.* *Activated carbon/antibiotic was the considered adsorbent-adsorbate system..The ability of activated carbon ECA08 (AC) to adsorb oxytetracycline (OTC) was investigated in batch mode in a fixed bed reactor. The fitting of experimental data showed that the differential method led to an excellent accuracy for different initial concentrations of the adsorbate; this method appeared more relevant than the integral method. The results also showed that AC was very effective in removing OTC from an aqueous solution, with up to 98% removal.*

I. Introduction

The sorption of pollutants from aqueous solutions plays an important role in wastewater treatment since it allows to avoid the need for huge sludge-handling processes. In addition, the kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface. It is therefore important to be able to predict the rate at which the pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. To develop sorption kinetics, knowledge of the rate law describing the sorption system is required [1].

The prediction of batch sorption kinetics is necessary for the design of industrial sorption columns. However, sorption kinetics shows a large dependence on the physical and chemical characteristics of the sorbent material which also influences the sorption mechanism. Other relevant factors include sorbate-sorbent chemical properties and system conditions. The sorption mechanism has usually been described by models that contain kinetic parameters that varied with the operating conditions. They are therefore difficult to use and not practical to scale-up. However, predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design; therefore an approach on the determination of the equation rates related to the sorbate-sorbent interactions instead of the system operating conditions is developed in this study.

Although the functions representing the reaction rates can take on a variety of mathematical forms, only some simples cases of integrated and differentiates rate expressions have been considered in this work. The discussion is restricted to characterize the models giving the most accurate fit of experimental data and then the determination of their intrinsic phenomenological rate coefficients.

All of these procedures are based on the calculation of kinetic parameters from the integral and differential forms of a reaction rate expression. While integral forms are most likely the most practical and useful for determining rate constants, a number of differential forms exist to accomplish this task. Moreover, omission of the integral form frequently leads to errors in the analysis and the use of kinetic data. The most relevant aspect of the approach via integral equation lies precisely in the request for less regularity a priori for the solution.

The nonlinearity of equations is often associated with phenomena such as irreversibility. Although there are exceptions, nonlinear models tend to be more difficult to study than linear ones. A common approach to nonlinear equations is the linearization, but this can be problematic if the objective is to study aspects such as irreversibility, which are strongly tied to nonlinearity [2].

To properly understand an adsorption process, two basic aspects should be addressed: equilibrium and kinetic. With regards to adsorption process, thermodynamic data only provide information about the final state of a system, while kinetics deal with changes in the chemical properties with time and is especially concerned with rates of these changes.

Various kinetics models have been suggested for adsorption; the simplest of which is Langmuirian adsorption. Despite its simplicity, surprisingly this model appears relevant to describe numerous cases. Adsorption kinetic studies include theoretical studies [3], adsorption of ions [3,4], adsorption of organic compounds [1–6], and gas adsorption. Pseudo-first-order and pseudo-second-order models have also been widely used in integral form to analyze kinetics data.

For a given model, both differential and integral equations forms are compared for their accuracy regarding the fit of experimental data in the present work. In addition, the corresponding parameters are discussed and evaluated.

II. Theory
II.1. Adsorption equilibrium
The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon an accurate description of the equilibrium separation between the two phases [7]. Several isotherm models were used to describe the equilibrium at constant temperature.

II.1.1. Langmuir isotherm
The Langmuir model [8] is valid for monolayer adsorption onto a surface with a finite number of identical sites. The well-known expression of the Langmuir model is given by Eq. (1):

$$q_e = \frac{b\,Q_0\,C_e}{(1+bC_e)} \tag{1}$$

Where q_e (mg/g) and C_e (mg/l) are the amount of adsorbed OTC per unit weight of AC and unadsorbed OTC concentration in solution at equilibrium, respectively.. The equation is conveniently used in the nonlinear form.

II.1.2. Freundlich isotherm
The Freundlich expression (Eq. (2)) is an exponential equation and therefore assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases [8]. Theoretically using this expression, an infinite amount of adsorption can occur:

$$q_e = K_f C_e^{1/n} \tag{2}$$

In this equation, K_f and $1/n$ are the Freundlich constants characteristic of the system, indicating adsorption capacity and intensity, respectively. The constants are obtained by nonlinear fitting of the isotherm.

II.2. Kinetic models
The adsorption process can be described as molecules leaving a solution and being held on the solid surface by chemical and physical bonding [9, 10].

In order to investigate the mechanism of adsorption, the following kinetic models are used, in differential and integral forms, to fit experimental data.

II.2.1. Differential method

According to TAT.Ab [11], when surface reaction is the rate-controlling step, the rate of adsorption can be expressed as:

$$\frac{dq}{dt} = K * a\left[C(Q_0 - q) - \frac{q}{Q_0}\right] \tag{3}$$

Using the mass balance $q = \frac{(C_0 - C)}{M}$, Eq (3) yields to the modified surface reaction equation (Eq.4):

$$-\frac{dC}{dt} = K * a\left[C(Q_0 M - C_0 + C) - \frac{1}{b}(C_0 - C)\right] \tag{4}$$

Where K*a is the surface reaction rate constant (l.mg⁻¹.min⁻¹); Q_0 and b are the Langmuir adsorptive capacity (mg/g) and equilibrium constant (l/mg); respectively; and M is the mass of sorbent per unit volume (g/l).

II.2.2. Pseudo-first-order and modified pseudo-first order models

❖ **Differential method for data analysis**

The sorption kinetics may be described by a pseudo-fist order. The differential equation is the following [12, 13]:

$$\frac{dq}{dt} = K_1(q_e - q)$$ (5)

If the adsorption isotherm can be expressed by the Langmuir model; and the mass balance is used, Eq (6) gives the *modified pseudo-first-order equation*:

$$-\frac{dC}{dt} = K_1\left(C - \theta - \sqrt{\frac{C_o}{b} + (\theta)^2}\right)$$ (6)

Where

$$\theta = \frac{bC_o - 1 - MQ_0}{2b}$$ (7)

q_e and q are the amounts of OTC adsorbed onto the sorbent (mg g^{-1}) at equilibrium and at time *t*, respectively; K_1 is the rate constant of first-order (min^{-1}).

❖ **Integral method for data analysis, non linear and linear models [14]**

After integration between boundary conditions (t=0 to t and q_t =0 to q_e), Eq. (5) becomes:

$$q = q_e\left[1 - e^{-K_1 t}\right]$$ (8)

Equation (8) can be rearranged to obtain a linear form:

$$Ln\frac{(q_e - q)}{q_e} = -K_1 t$$ (9)

The rate constant, K_1, can be determined for various initial concentrations from the straight line plots of *ln* (q_e-q_t) against *t* for linear regression and by means of the Levenberg-Marquardt method (Origin 6.0 software) for nonlinear regression.

II.2.3.   Pseudo-second-order   and   modified pseudo-second-order models

❖ **Differential method for data analysis**

The main assumption of the pseudo-second-order kinetic model is that the sorption capacity is proportional to the number of active sites occupied on the sorbent, then the kinetic rate law can be written as follows [15]:

$$\frac{dq}{dt} = K_2(q_e - q)^2$$ (10)

If the adsorption isotherm can be expressed by the Langmuir model; and the mass balance is used, Eq (11) gives the *modified pseudo-second-order equation:*

$$-\frac{dC}{dt} = \frac{K_2}{M}\left(C_t - \theta - \sqrt{\frac{C_o}{b} + (\theta)^2}\right)^2$$ (11)

Where K_2 is the rate constant of second-order adsorption (g.mg^{-1} min^{-1}).

❖ **Integral method for data analysis, non linear and linear models[16]**

For boundary conditions (t=0 to t and q_t =0 to q_e), Eq. (10) becomes Eq. (12), the integrated rate law for a pseudo-second-order reaction.

$$q = \frac{K_2 q_e^2 t}{1 + t K_2 q_e}$$ (12)

Eq. (10) can be rearranged to obtain a linear form (Eq 13):

$$\frac{t}{q} = \left(\frac{1}{K_2 q_e^2}\right) + \frac{t}{q_e}$$ (13)

The straight line plots of *t/q* against *t* can be employed to obtain rate parameters. The K_2, q_e for linear regression and by means of the Levenberg-Marquardt method (Origin 6.0 software) for nonlinear regression. The following table (table 1) summarizes the different forms and methods for each model.

Table 1. *Various rate equations for chemical mechanism models*

Models	Equations forms
Surface reaction model	**Differential form[11]** $-\dfrac{dC}{dt} = K * a \left[C(Q_0 M - C_0 + C) - \dfrac{1}{b}(C_0 - C) \right]$ (4)
Modified pseudo-first order and pseudo-first-order models	**Differential [12,13]** $-\dfrac{dC}{dt} = K_1 \left(C_t - \theta - \sqrt{\dfrac{C0}{b} + (\theta)^2} \right)$ (6) **Integral non-linear[14]** $q = q_e \left[1 - e^{-K_1 t} \right]$ (8) **Integral linear[14]** $Ln\ \dfrac{(q_e - q)}{q_e} = -K_1\ t$ (9)
Modified pseudo-second order and pseudo-second-order models	**Differential [15]** $-\dfrac{dC}{dt} = \dfrac{K_2}{M} \left(C_t - \theta - \sqrt{\dfrac{C0}{b} + (\theta)^2} \right)^2$ (11) **Integral non-linear[16]** $q = \dfrac{K_2 q_e^2\ t}{1 + t\ K_2\ q_e}$ (12) **Integral linear[16]** $\dfrac{t}{q} = \left(\dfrac{1}{K_2\ q_e^2} \right) + \dfrac{t}{q_e}$ (13)

III. Material and methods

The sorbent used was activated carbon ECA08 marketed by the company SIGMA ALDRICH in the form of pure powder. The sorbent was rinsed with distilled water, dried in a drying oven at 80°C until constant weight. The main characteristics of the ECA08 are given in Table 2.

The adsorbate Oxytetracycline is a large molecule with several polar/ionic groups and three environmentally relevant pKa values (3.27, 7.32 and 9.11). Oxytetracycline formula and physicochemical properties are depicted in Figure 1 and Table 3.

Table 2. *Characteristics of powder activated carbon ECA08*

Particle size	Density	External porosity	% humidity
< 200 nm	~0.06 g mL^{-1}	0.38	12.91

Table 3. *Physicochemical properties of oxytetracycline*

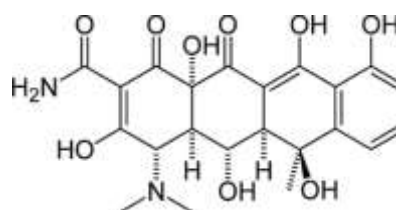|	
Empirical formula	$C_{22}H_{24}N_2O_9$
Molecular weight	460.4 g
Point melting	182°C
Specific optical activity	−196°C
pKa	3.3, 7.3 and 9.1

Figure 1. *Chemical formula of oxytetracycline*

The contact between the adsorbent and the adsorbate in a glass column was ensured *via* the circulation of the solution through the fixed bed using a peristaltic pump. Operation was in closed loop and there was no exchange of matter during adsorption with the outside. The experimental device is displayed in Figure 2. Samples are withdrawn at suitable time intervals, filtered and then analyzed by spectrophotometry.

The oxytetracycline concentration was spectrophotometrically determined (Jenway spectrophotometer 6,105 model UV/visible with 1 cm quartz cells). The wavelength is given following a spectral sweeping of the sample.

The optimal wavelength of adsorption was found to vary according to the pH of the solution. The pH value was also measured on each sample. The results obtained with the column with fixed bed indicated the relevance of this system for kinetic study. The following equation was used to compute the specific uptake by the sorbent, q (mg/g):

$$q = \frac{(C_0 - C_t)}{M} \qquad (14)$$

Where q the amount of solute sorbate on the surface of the sorbent at any time t (mg/g), C_0 is the initial adsorbate concentration (mg/L), C_t is the residual concentration of OTC at any time t (mg/L).
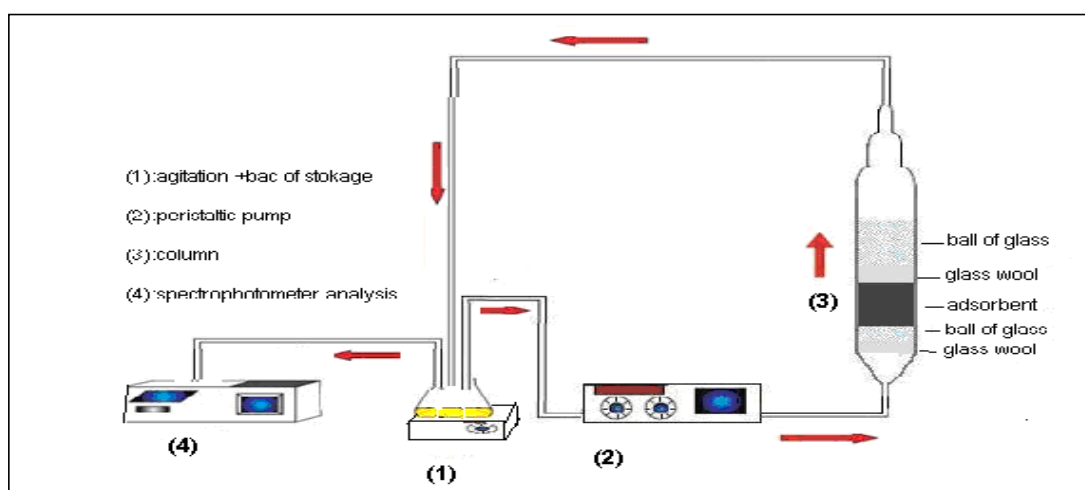

Figure 2. Experimental apparatus.

IV. Results and discussion

IV.1. Equilibrium study

The fit of OTC adsorption onto AC by means of Langmuir and Freundlich equations are shown in Figure 3, and the corresponding parameter values are provided in Table 4. It was observed that equilibrium data were slightly most accurately fitted by the Langmuir equation when compared to the Freundlich equation, predicting monolayer coverage of OTC onto the adsorbent. The adsorbent showed larger maximum adsorption capacity as compared with others adsorbents, such as coal-based activated carbon 207EA (60 mg/g) [17] and clays (76.82 mg/g) [18]. These results are in agreement with other findings involving the Langmuir isotherm to describe the behavior in aqueous solutions [17-20].

Table 4.Isotherm parameters for OTC adsorption

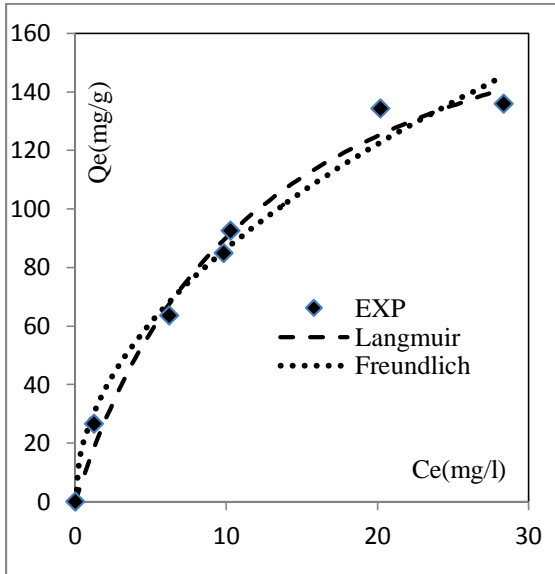| Langmuir model	$Q_0(mgg^{-1})$	$b(lmg^{-1})$	R^2
	203.51	0.15	0.981
Freundlich model	$K_f(mgg^{-1}(mgL^{-1})^{-1/n})$	n	R^2
	39.39	2.06	0.926

Figure 3. *Langmuir and Freundlich fit of the adsorption isotherm*

IV.2. Kinetic modeling

It appears from Figure 4 that OTC adsorption increased with increasing initial concentration, but the time required to reach equilibrium varied with the initial concentration. The process was very fast initially and then slowly until equilibrium is reached.
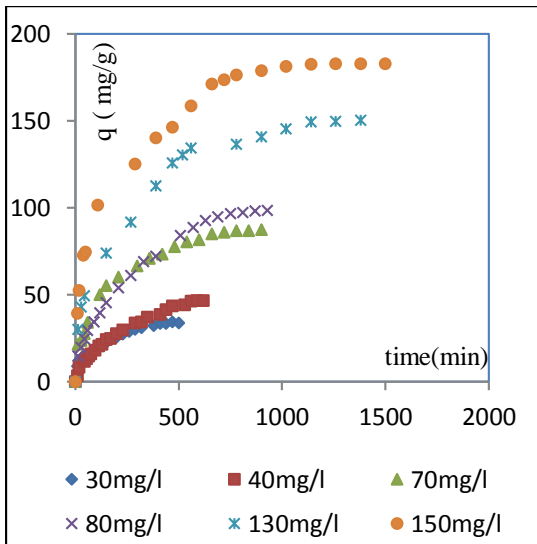

Figure 4. *Adsorption kinetics at different initial concentrations of OTC by AC (V=2L,m_{AC}=1.5g).*

Equation rates of each considered model, namely pseudo-second order, pseudo-first order and surface reaction were applied to experimental data at various initial concentrations for OTC adsorption onto AC, and the K_*a, K_1 and K_2, values are given in Table 5.
As can be seen the surface reaction, the pseudo-first order (differential method) and pseudo-second

order (linear form) kinetic models led to accurate fit of experimental data with high R^2 values for all tested initial OTC concentrations. In all cases, the correlation coefficients are good enough to choose which model describes experimental data. However, the kinetic parameters K_1 and K_2 varied with the initial OTC concentration and hence appeared not useful to scale-up. Contrarily, the K_*a values obtained from eq.2 did not vary with the operating conditions and can be useful for engineering design.
To find the method and/or the model which describe perfectly experimental data and the rate of reaction, the predicted and experimental values were compared by using graphical (Figures 4, 5 and 6) and statistical (table 6) analysis.
All experimental data are presented in parity diagram (Figure. 5, 6 and 7); this graphical analysis shows that the whole of the points obtained was aligned around the first bisectrix. For the three tested models, most points were very close to the straight line showing parity for these data. The difference to the model is the vertical distance of any observation point from the bisecting line. To quantify the dispersion around the first bisectrix, the vertical distance was determined by calculating the empirical variance, using the following relation:

$$\sigma^2 = \frac{\sum_{i=1}^{n}[(y_i)-(\overline{y})]^2}{n-1} \qquad (15)$$

With

$$(\overline{y}) = \frac{\sum_{i=1}^{n}(y_i)}{n} \qquad (16)$$

Where y_i represents the values of the variables studied, in our case it is the rate of adsorption.
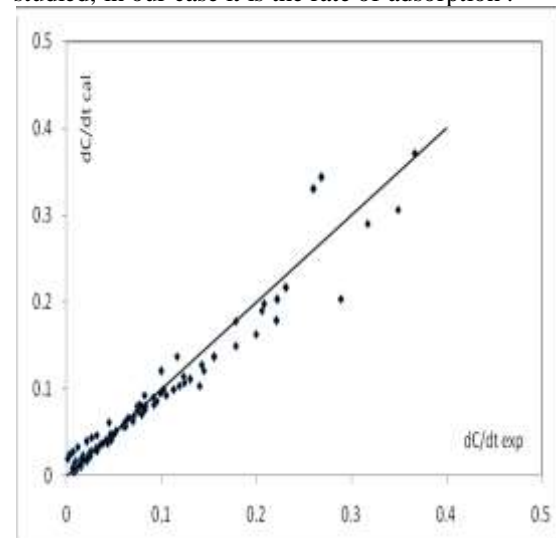

Figure 5. *Correlation diagram between, experimental and calculated kinetic data the modified Surface reaction model (eq2)).*

Table 6. *Effect of the initial concentration (C₀) of oxytetracycline on the rate constants and the correlation coefficient for pseudo-second-order (K₂), pseudo-first-order (K₁) and surface reaction model (K∗a)*

	Pseudo-first order					
	Differential form		**Integral and Non-linear form**		**Integral and linear form**	
C₀(mg/L)	**R^2**	**K_1(min⁻¹)**	**R^2**	**K_1(min⁻¹)**	**R^2**	**K_1(min⁻¹)**
30	0.9932	0.0044	0.9400	0.0079	0,9891	0.0068
40	0.9785	0.0041	0.9807	0.0044	0.9871	0.0043
70	0.9854	0.0041	0.9588	0.0071	0.9877	0.0042
80	0.9784	0.0035	0.9749	0.0039	0.9719	0.0042
130	0.9905	0.0037	0.9351	0.0044	0.9762	0.0031
150	0.9517	0.0045	0.8845	0.0097	0.9753	0.0038
	Pseudo-second ordre					
	Differential form		**Integral Non-linear form**		**Integral linear form**	
C₀(mg/L)	**R^2**	**K_2(gmg⁻¹ min⁻¹)**	**R^2**	**K_2(gmg⁻¹ min⁻¹)**	**R^2**	**K_2(gmg⁻¹ min⁻¹)**
30	0.8327	0.00015	0.9804	0.00005	0,9829	0.00029
40	0.8190	0.0002	0.9965	0.00003	0.9781	0.00008
70	0.9221	0.00009	0.9808	0.00009	0.9956	0.00009
80	0.8667	0.00007	0.9866	0.00003	0.9814	0.00004
130	0.9747	0.00005	0.9625	0.00005	0.9940	0.00005
150	0.9478	0.00005	0.9449	0.00005	0.9922	0.00004

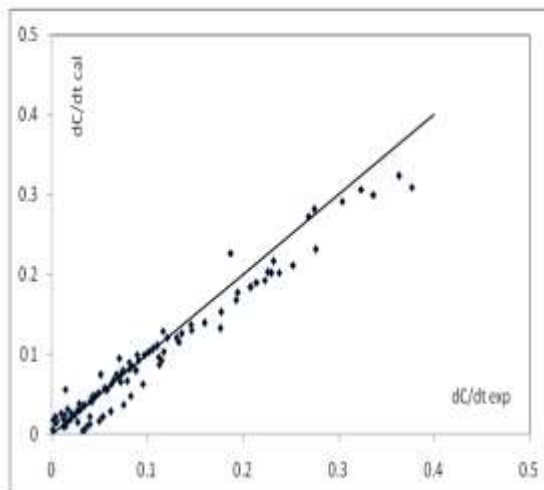| Surface reaction model		
Differential form		
C₀(mg/l)	**R^2**	**$K∗a$(l.mg⁻¹.min⁻¹)**
30	0.9970	0.00003
40	0.9833	0.00003
70	0.9829	0.00003
80	0.9566	0.00003
130	0.9739	0.00003
150	0.8243	0.00003

Figure 6. *Correlation diagram between, experimental and calculated kinetic data (the modified pseudo-first-order model equation (eq.4)).*
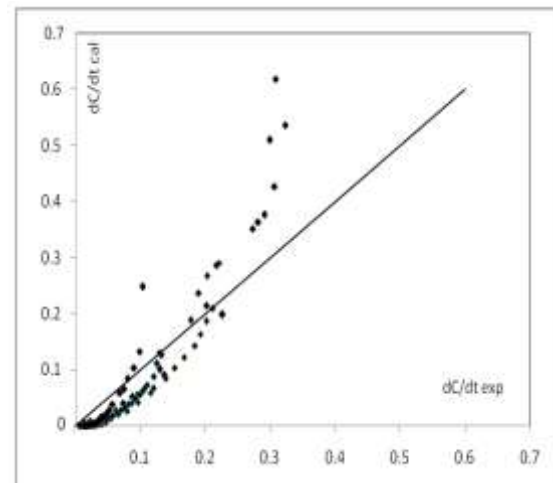

Figure 7. *Correlation diagram between, experimental and calculated kinetic data(the pseudo-second-order model (eq11)).*

Table 7 gives the variance for the three models, it can be clearly seen that surface reaction model was the most suitable to represent kinetics data of OTC adsorption onto ECA08 activated carbon. In addition, kinetic parameters given by this model did not vary with the operating conditions, showing its relevance for subsequent scale-up

The adsorption kinetic of OTC onto activated carbon ECA08 can be therefore represented by the following equation at 22°C±1(mg.L^{-1}.min^{-1}):

$$r = 0.00003\left[C(152.63 - C_0 + C) - \frac{1}{0.15}(C_0 - C)\right]$$

Table 7.Statistical analysis of different models

Model	variance
Modified surface reaction Eq.2	0.0069
Modified pseudo-first-order Eq.4	0.0164
Pseudo-second order linear form Eq.11	0.0580

V. Conclusion:

The reaction kinetics is the most important factor which controls the design of a liquid-solid reactor. The kinetics of adsorption must be known to satisfactorily design equipment to perform these reactions on a technical scale. If the reaction is too slow, design becomes complicated and the kinetic information is needed with high accuracy.

For adsorption of OTC on activated carbon ECA08, kinetic data obtained from closed loop fixed bed adsorber showed that AC was very effective in removing OTC from an aqueous solution with yields up to 98%. The equilibrium time varied with the initial concentration, e.g. 1260 min are needed to reach equilibrium for 150 mg/L, and 410 min. for 30 mg/L.

The test of various equation kinetics showed that the differentiate rate equation allowed to obtain the adsorption parameters with high accuracy for various initial adsorbate concentrations. The differentiate approach modeling appeared therefore more successful than the integrated modeling approach, and the surface reaction was probably a limiting step of the sorption reaction between AC and OTC.

VI. References

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