



## Adsorption studies of molasse's wastewaters on activated carbon: Modelling with a new fractal kinetic equation and evaluation of kinetic models

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### ABSTRACT

Adsorption kinetic of molasses wastewaters after anaerobic digestion (MSWD) and melanoidin respectively on activated carbon was studied at different pH. The kinetic parameters could be determined using classical kinetic equations and a recently published fractal kinetic equation. A linear form of this equation can also be used to fit adsorption data. Even with lower correlation coefficients the fractal kinetic equation gives lower normalized standard deviation values than the pseudo-second order model generally used to fit adsorption kinetic data, indicating that the fractal kinetic model is much more accurate for describing the kinetic adsorption data than the pseudo-second order kinetic model.

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### 1. Introduction

The substitution of fossil fuels with biofuels is part of the strategy to mitigate greenhouse gas emissions from road transport, and to increase security of energy supply. One way of production of bioethanol is distillation of fermented sugarcane molasses, a sugar cane industry by-product. This process leads to large quantities of molasses wastewaters, known as either vinasse or molasses spentwash (MSW). The amount of vinasse produced can be up to 10 times larger than that of ethanol. Due to its dark-colour, typical odour, strong acidic character (pH 3.5) and high chemical oxygen demand (COD) [3], MSW is an effective water pollutant. Anaerobic digestion of MSW results, however, to only, 60–75% removal of COD [4,5]. Molasses spentwash after anaerobic digestion (MSWD) has a high COD content, up to 41 g/l and still contains a high amount of phenolic recalcitrant compounds such as melanoidin and tannic acid [7], accounting for 33% of its composition [6]. Like tannic acid, Melanoidins, which are brown polymers formed by the Maillard amino-carbonyl reaction [8] have antioxidant properties and are toxic to many organisms typically used in wastewater treatment process [8–13]. A secondary treatment is thus necessary in order to

obtain a wastewater that can be discharged in the natural waters according to the legislation. One possible post-treatment available for anaerobic wastewater treatment effluent can be the use of activated carbons (AC) for adsorption of pollutants from wastewaters [14,15]. It was recently, demonstrated that an AC with a significant distribution of both micropores and mesopores and a significant amount of macropores that are assumed to act as conduits providing access to micro- and mesopores, have a good adsorption efficiency for melanoidins and coloured compounds of MSWD [14].

Study of the adsorption equilibrium and kinetics is essential to supply the basic information required for the design and operation of adsorption on ACs. Many models have been used to describe the transport of solutes inside the AC [16]. The overall rate of adsorption of organics on AC can be interpreted by a first [17] or second order kinetics [18]. In these adsorption reaction models, it is considered that the rate of adsorption on an active site is the controlling step and this rate can be assumed to follow a first or second order reaction. It is, however, very well documented in the literature that the overall rate of adsorption in a porous adsorbent must not only take into account the adsorption rate on an active site but also the external mass transfer, and intra-particle diffusion [19]. Indeed, intra-particle diffusion in liquid-porous solid systems may be governed by pore volume diffusion or surface diffusion or a combination of both mechanisms [16]. Pore diffusion and intra-particle diffusion models such as respectively the Bangham and Burt [20] and intra-particle equation [19] models are readily used

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to describe such kinetics. The complex adsorption phenomenon may also involve chemical interactions between the solute and the chemical groups on the AC surface, which may involve electrostatic interactions, Van der Waals, hydrogen bonding, ligand exchange, hydrophobic interactions. The elovich model [21] has been applied satisfactorily to chemisorption of adsorbates on sorbents with heterogeneous surface. However, it has been recently shown that the adsorption process of a solute on an AC which takes place at the liquid–solid boundary is clearly an “heterogeneous” reaction, and the interface of the two phases represents a special environment under dimensional or topological constraints [1,2]. Therefore, these systems can be considered to belong to the class of complex systems, and adsorption kinetic can be described by a recently proposed fractal kinetic equation [1,2]. One of our previous work, clearly shows that the fractal kinetic which has been extensively applied to biophysical systems can be a useful theoretical tool for study adsorption processes of single compounds on AC [1].

The purpose of this work is to study adsorption kinetic on AC of molasses's wastewaters, a complex mixture of organic compounds, in order to be able to predict the rate at which the pollutant can be removed from the aqueous solution. For this purpose, classical adsorption kinetic models are tested and compared to the fractal kinetic equation in order to describe the adsorption kinetic of MSWD and melanoidin on ACs.

## 2. Experimental

### 2.1. Chemicals

Reagent grade, glucose, glycine and sodium bicarbonate were from Prolabo (VWR International, Fontenay-sous-Bois, France).

### 2.2. Sorbents

A commercial powder activated carbon, reported as a good adsorbent for MSWD and melanoidin [14], named PACV, from Prolabo (VWR International, Fontenay-sous-Bois, France) was used. The activated carbon was dried at 110 °C in an oven for 24 h, then cooled and stored at ambient temperature in a desiccator prior to use. PACV is a powder AC exhibiting a surface area of 909 m<sup>2</sup>/g, micropore and mesopore volumes of 0.21 and 0.53 cm<sup>3</sup>/g, respectively, and an average pore diameter of 3.2 nm, showing, that this carbon is principally mesoporous (Table 1).

### 2.3. Sorbates

Melanoidin was prepared by mixing 4.5 g of glucose, 1.88 g of glycine and 0.42 g of sodium bicarbonate with 100 ml of distilled water and then heated for 7 h at 95 °C [15]. After heating, 100 ml of water was added and dilute solutions of melanoidin were prepared. Melanoidins are known as brown nitrogenous polymers and co-polymers and their solutions also contain dehydration products of sugar [22]. MSW was obtained from an industrial distillery plant (Distillerie Bonne-mère, Sainte-Rose, Guadeloupe). Before being discharged, MSW was submitted to anaerobic digestion at industrial scale, in a 1700 m<sup>3</sup> tank, to obtain MSWD. The initial COD and

biological oxygen demand (BOD) values of MSW before anaerobic digestion were 92 and 25 g O<sub>2</sub>/l. COD and BOD values of MSWD were 41 and 2 g O<sub>2</sub>/l. 55% of the COD could be treated by anaerobic digestion. Although the resulting effluent, MSWD, has a much lower BOD, it still has a high COD value, greater than the discharge standards. MSWD contains melanoidins, proteins, several organic compounds such as gallic acid and, tannic acid, and phosphorus nutrients [6].

### 2.4. Kinetic study

Kinetics experiments were done at 27 °C in 1 l bottles containing MSWD and Melanoidin solutions. 0.3 ml aliquots were taken at predetermined time intervals during 8 days, until equilibrium is reached. The samples were analysed for UV–visible absorbance using a UV–visible spectrophotometer (Model Anthelie from Secomam). For concentration measurements, linear Beer–Lambert relationships between COD and absorbance were previously established using appropriate wavelengths; i.e. 297 and 290 nm for melanoidin and MSWD, respectively. The amount of solute adsorbed at time  $t$ ,  $q(t)$  was calculated as  $q(t) = (C_0 - C_t)V/W$ , where  $C_0$  and  $C_t$  are, respectively, the COD (mg l<sup>-1</sup>) at time  $t = 0$  and time  $t$  and  $V$  the volume of the solution in l,  $W$  the weight of the dry adsorbent in g. The pH of the solutions was adjusted using HCl or NaOH

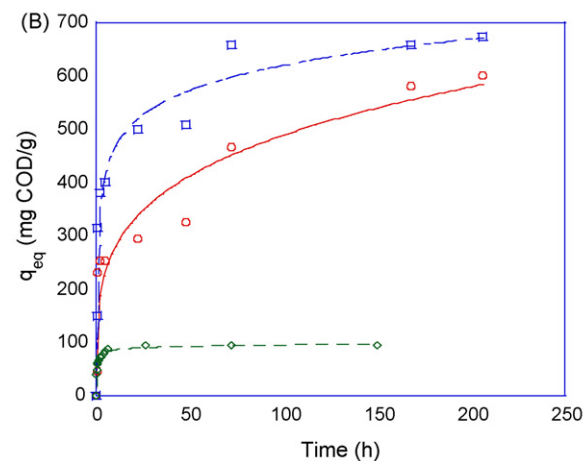
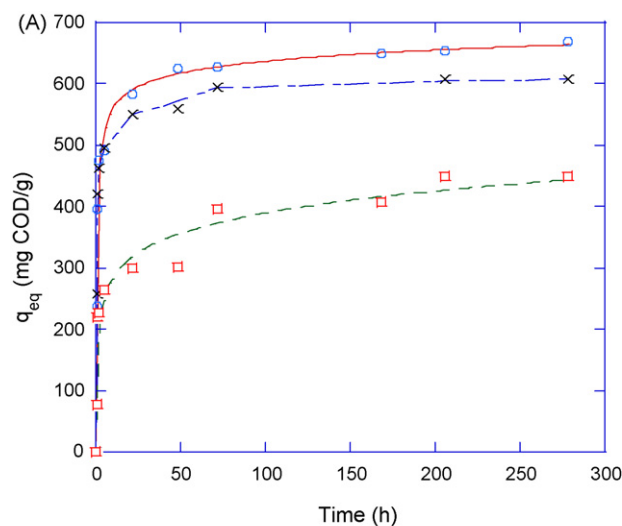


Fig. 1. Kinetic plots of adsorption on PACV at 27 °C of (A), MSWD (□) 51 mg/l, (×) 106 mg/l, (○) 134 mg/l and (B) melanoidin (◇) 34 mg/l, (○) 73 mg/l, (□) 152 mg/l.

Table 1  
Textural characteristics of powder activated carbon PACV

BET surface area (m <sup>2</sup> /g)	909
Pore Volume (cm <sup>3</sup> /g)	0.74
Micropore volume (cm <sup>3</sup> /g)	0.21
Mesopore volume (cm <sup>3</sup> /g)	0.53
Mean pore diameter (nm)	3.2

for experiments at a given pH. All the experiments were done in triplicate.

### 3. Results

#### 3.1. Influence of the initial wastewater concentration

Adsorption kinetic of MSWD and melanoidin respectively on PACV, were performed at three COD concentrations ranging from 51 to 134 mg/l for MSWD and from 34 to 152 mg/l for melanoidin (Fig. 1). Uptake of the solutes by the sorbent enhanced notably with increasing the initial effluent concentration tending to saturation at higher concentrations. The results presented in Fig. 1 show that raising the effluent concentration allows the carbon to increase its equilibrium adsorption capacity from 440 to 660 mg/g for MSWD and from 93 to 670 mg/g for melanoidin.

#### 3.2. Influence of the temperature on wastewater adsorption

The effect of temperature on the equilibrium sorption capacity was investigated in the temperature range of 25–35 °C. As shown in Fig. 2, the adsorption of MSWD and melanoidin respectively enhanced with raising the temperature up to 35 °C indicating that a higher temperature favored the organic compounds removal by adsorption onto PACV. The enhancement in adsorption could be due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. This may also be a result of an increase in the mobility of the solutes molecule with an increase in their kinetic energy, and the enhanced rate of intra-particle diffusion of sorbate with the rise of temperature. The sorption of MSWD and melanoidin is an endothermic process that may involve not only physical but also chemical sorption.

#### 3.3. Adsorption kinetic modelling studies

In two recent papers [1,2] it was shown that a fractal kinetic equation which has been extensively applied to biophysical problems can also be a useful theoretical tool for study adsorption processes, and to describe the dynamics of adsorption

phenomena on AC:

$$q_{n,\alpha}(t) = q_e [1 - (1 + (n-1)(t/\tau_{q,\alpha})^\alpha)^{-1/(n-1)}] \quad (1)$$

This equation was developed in reference [1] and [2], from the general fractional differential equation:

$$-\frac{dq}{dt^\alpha} = K_{\alpha,n} q^n$$

$q(t)$  being the mass of solute adsorbed per gram of AC,  $q_e$ , the maximum adsorbed quantity,  $n$ , the reaction order and  $\alpha$  a fractional time index. When  $n$  and  $\alpha$  are different from 1, one can no longer define a time independent rate constant and the relevant quantity characterizing the time evolution of the process is the characteristic time  $\tau_{q,\alpha}$ . One can define a “half-reaction time”  $\tau_{1/2}$  which is the time necessary to adsorb half of the equilibrium quantity by solving the equation:

$$\left(1 + (n-1) \left(\frac{t}{\tau_{q,\alpha}}\right)^\alpha\right)^{-1/(n-1)} = 1/2 \quad (2)$$

Different cases can occur:

(a) if  $n = 1$ ,  $\alpha = 1$  and  $-(dq/dt) = K_1 q$ , the solution of this equation is

$$q_t = q_e \exp(-k_1 t) \quad (3)$$

which is a first order kinetics with  $k_1$ , the first order rate constant.

(b) In the case where  $n \rightarrow 1$  and  $\alpha \neq 1$ , it can be written as a Weibull distribution:

$$q_\alpha(t) = q_e \left[1 - \exp\left(-\frac{t}{\tau_\alpha}\right)^\alpha\right] \quad (4)$$

with  $\tau_{1/2} = (\ln(2))^{1/\alpha} \tau_\alpha$

(c) If  $\alpha = 1$ ,  $n = 2$ , we have,  $-(dq/dt) = K_2 q^2$  leading to:

$$\frac{1}{q_e - q_t} = K_2 t + \frac{1}{q_e}, \quad (5)$$

with  $K_2$ , the second order constant.

This is the second order kinetics, corresponding to the very popular pseudo-second order kinetic [18]. This equation can be rearranged into the very convenient form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

If  $\alpha \neq 1$ ,  $n = 2$  (1) becomes

$$q(t) = q_e \left[1 - \frac{1}{1 + (t/\tau_{n,\alpha})^\alpha}\right] \quad (7)$$

and  $\tau_{1/2} = \tau_{n,\alpha}$

In order to study the adsorption kinetic of MSWD and melanoidin respectively on PACV at pH 3, 7 and 10, low initial COD concentrations of 34 and 41 mg/l for melanoidin and MSWD, respectively were used in order to avoid the use of high amounts of HCl and NaOH for pH adjustment. Classical models presented in Table 2, generally used to fit adsorption data have been tested.

The Lagergen equation [17] fits of adsorption data of MSWD and melanoidin, respectively, on PACV at the different pH are presented Figs. 3A and 4A. The correlation coefficients values obtained,  $R^2$ , were between (0.6555) and (0.9541), indicating that this pseudo-first order rate expression could not fit properly those experimental data.

The intra-particle model [19],  $q_t = k_{id} t^{1/2} + C$ , where  $k_{id}$  is the intra-particle rate constant and  $C$  a constant, was tested. The plot of

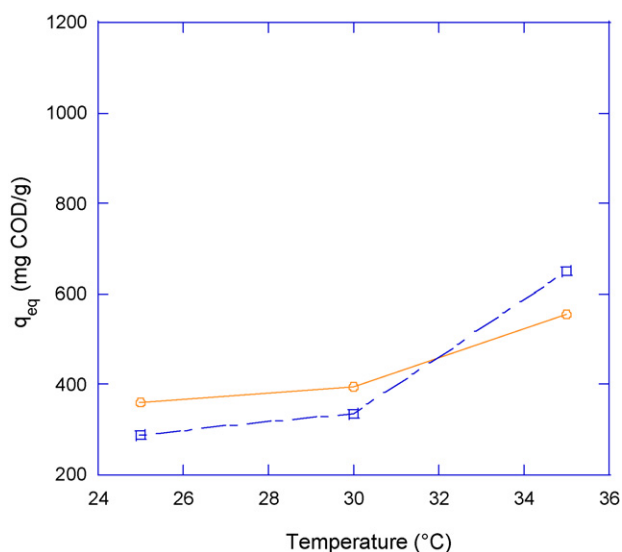


Fig. 2. Equilibrium adsorption capacity,  $q_{eq}$  for adsorption of (○) VMM and (□) MSWD as a function of the temperature.

**Table 2**  
Classical kinetic models used in this study

Model	Equation
Pseudo-first order	$\text{Log}(q_e - q) = \text{Log}(q_e) - \frac{k_1}{2.303} t$ (8)
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$ (5)
Intra-particle diffusion	$q_t = k_{id} t^{1/2} + C$ (9)
Bangham	$\text{Log} \left( \frac{C_0}{C_0 - q_t \times m} \right) = \text{Log} \left( \frac{k_b m}{2.303 V} \right) + a \text{Log}(t)$ (10)
Elovich	$q_t = \left( \frac{1}{b} \right) \ln(ab) + \left( \frac{1}{b} \right) \ln t$ (11)

$q_t$  versus  $t^{1/2}$  may present a multilinearity indicating the few steps taking place:

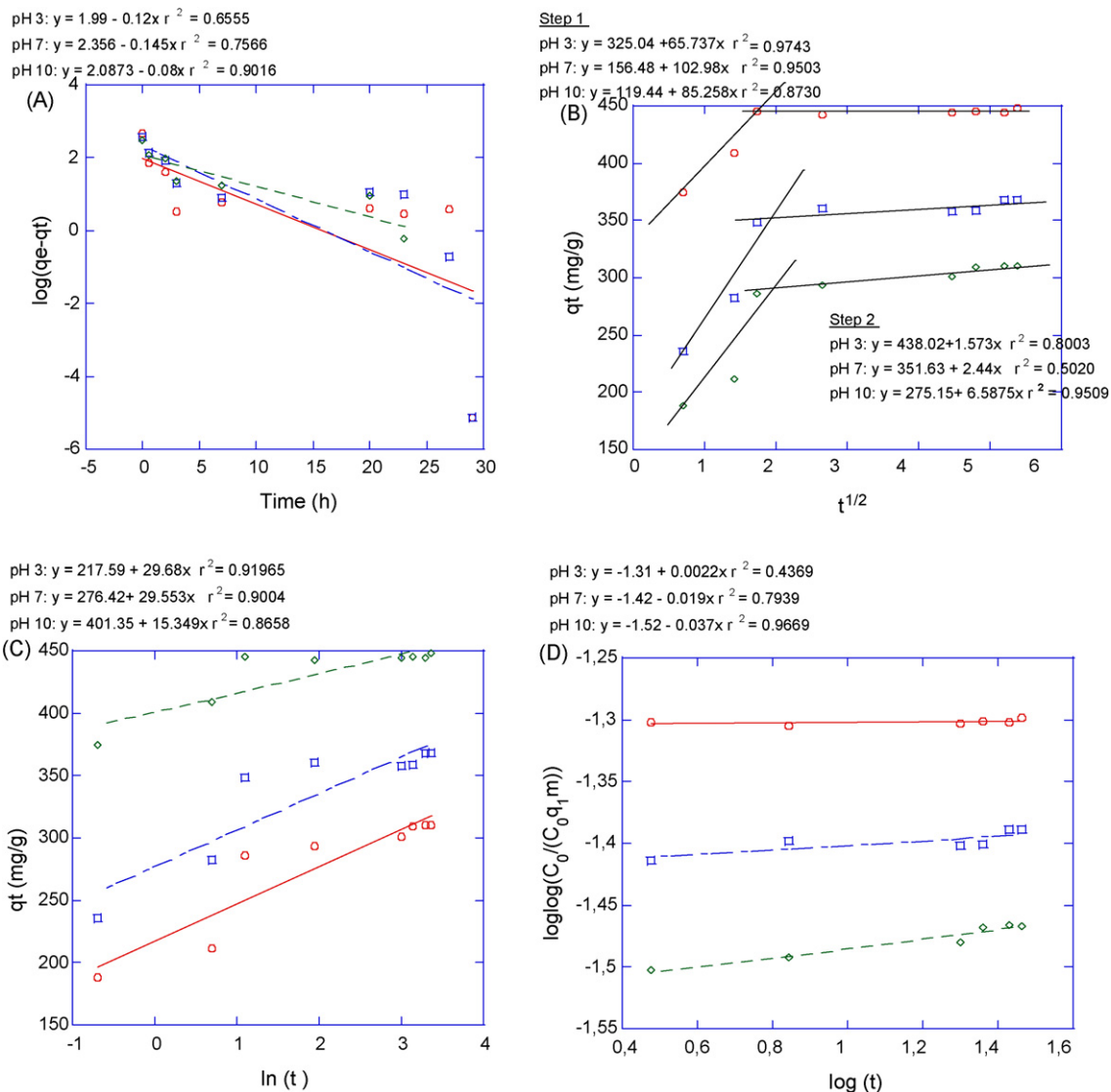
- (i) The first sharper portion is attributed to the diffusion of adsorbate through the solution to the outer toward the interface space, so-called external diffusion.
- (ii) The second portion describes the gradual adsorption stage, corresponding to diffusion of sorbate molecules inside the pore of the adsorbent, where intra-particle diffusion is rate limiting.

- (iii) The third portion is attributed to the final equilibrium stage for which the intra-particle diffusion starts to slow down due to low adsorbate concentration left in the solution.

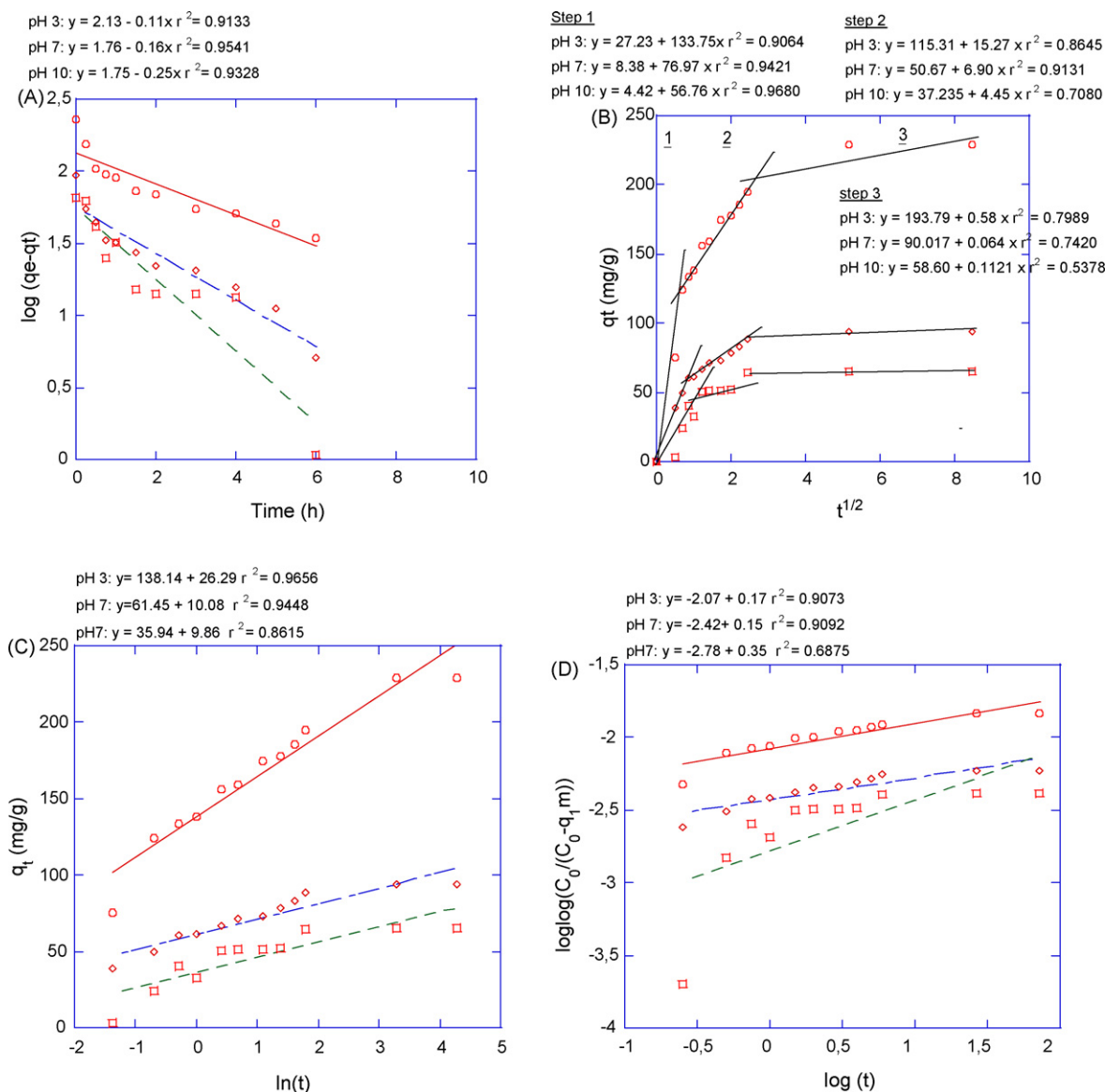
For adsorption of MSWD on PACV (Fig. 3B), at pH 3, 7 and 10, two steps can be observed. The linear fit gives correlation coefficients values,  $R^2$ , between (0.8738) and (0.9743), for the first sharper portion and between (0.8003) and (0.9509) for the second portion.

For adsorption of melanoidin on PACV (Fig. 4B), three steps can be observed for pH 3, 7 and 10, the linear fit gives correlation coefficients values obtained,  $R^2$ , were between (0.9064) and (0.9680), for the first sharper portion, between (0.7080) and (0.9131) for the second portion, and between (0.5378) and (0.7989) for the third portion, indicating a poor fit using this model.

The Elovich equation is widely used to describe the chemisorptions of gases on solid surfaces [21] and some authors have successfully applied the Elovich equation to simulate the sorption kinetics in liquid-phase adsorption and/or ion exchange such as Tseng et al. [23] who successfully used the Elovich equation to interpret the adsorption kinetic of dyes and phenol onto activated carbons in aqueous phase. The Elovich equation fits of adsorption



**Fig. 3.** Kinetic plots of MSWD adsorption on AC at 27 °C for: (○) pH 3, (◇) pH 7, (□) pH 10, (A) Langmuir fit, (B) intra-particle diffusion fit, (C) Elovich fit and (D) Bangham's fit.



**Fig. 4.** Kinetic plots of melanoidin adsorption at 27 °C for: (○) pH 3, (◇) pH 7, (□) pH 10 on AC, (A) Langergen fit, (B) intra-particle diffusion fit, (C) elovich fit and (D) Bangham's fit.

data of MSWD and Melanoidin, respectively, on PACV at the different pH are presented Figs. 3C and 4C. The correlation coefficients values obtained,  $R^2$ , were between (0.8658) and (0.9656), indicating that the Elovich expression could not fit properly those experimental data.

Kinetic data can further be used to check whether pore-diffusion was the only rate-controlling step or not in the adsorption system using Bangham's equation [20]. The Bangham model fits of adsorption data of MSWD and melanoidin respectively on PACV at the different pH are presented Figs. 3D and 4D. The correlation coefficients values obtained,  $R^2$ , were between (0.6875) and (0.9669), indicating that the Bangham expression could as well, not fit properly those experimental data.

The pseudo-second order model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange electrons between sorbent and sorbate. It is assumed that the sorption capacity is proportional to the number of active sites occupied on the sorbent [24–27]. Among the classical models tested only

the pseudo-second order equation could fit perfectly the kinetic adsorption data of MSWD and melanoidin respectively on PACV, giving correlation coefficient values  $R^2 \geq 0.998$  both for adsorption data of MSWD and Melanoidin, respectively, on PACV and at all pH values tested (Fig. 5, Table 3). Indeed, the pseudo-second order kinetic equation is known to generally give very good fit to adsorption data over the whole adsorption curve [18].

The fractal kinetic Eq. (1) was also used in order to fit the adsorption kinetic data of MSWD on PACV. With  $n=2$ , the second order Eq. (6) allows us to fit properly the experimental data and  $R^2$  values of 0.9975, 0.9866 and 0.9771 were obtained for pH 3, 7 and 10, respectively (Fig. 6A, Table 3). For adsorption data of melanoidin on PACV, it was difficult to distinguish between a first or a second order kinetic and finally the fractal kinetic Eq. (1) could properly fit the adsorption data for a value  $n=1.5$ , and  $R^2$  values of 0.9885, 0.9922 and 0.9460 were obtained for pH 3, 7 and 10, respectively (Fig. 6B, Table 3).

The correlation coefficient is generally not a sufficient criterion for selection of a kinetic model. Consequently, to compare the valid-

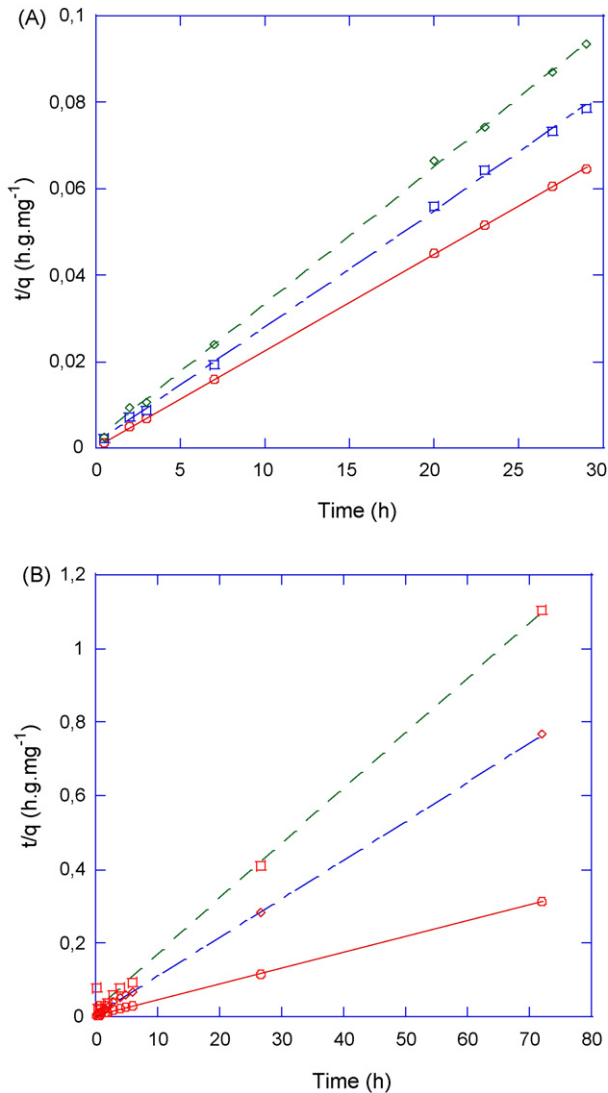


Fig. 5. Pseudo-second order kinetic plots of (A) MSWD and (B) melanoidin adsorption on AC at (○) pH 3, (◇) pH 7 and (□) pH 10.

ity of the two former models, a normalized standard deviation  $\Delta q$  was also calculated:

$$\Delta q(\%) = 100 \sqrt{\frac{\sum [(q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}}]^2}{N - 1}}$$

where  $N$  is the number of data points.

Although the correlation coefficient calculated using the pseudo-second order fit were all much closer to 1 than those calcu-

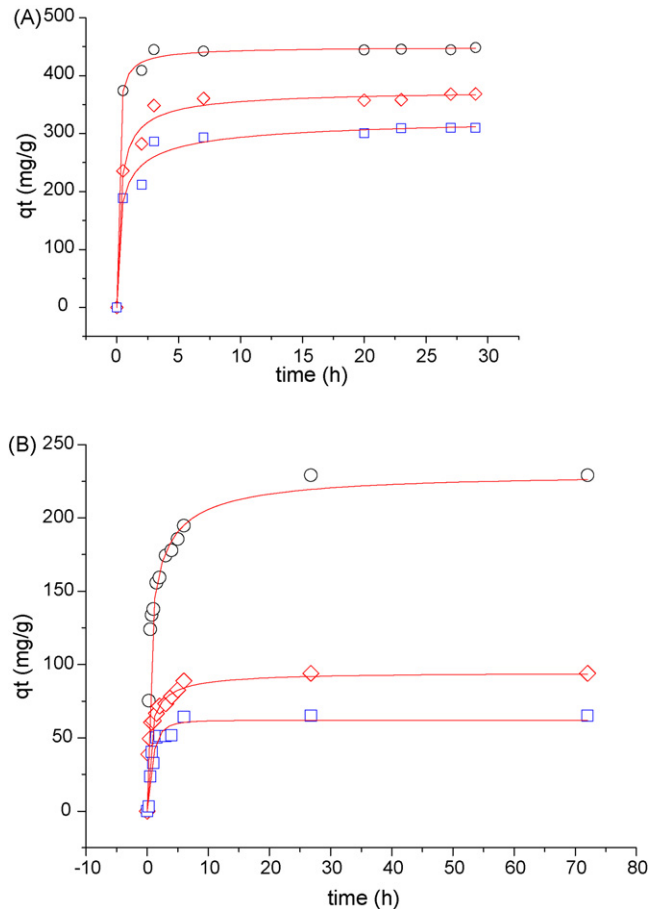


Fig. 6. Fractal kinetic fit of (A) MSWD and (B) melanoidin adsorption on PACV.

lated using the fractal kinetic equation, similar and even slightly lower  $\Delta q$  values (Table 3) could be calculated from the fractal kinetic fit of both MSWD and melanoidin adsorption data, i.e. the pseudo-second order fit of adsorption data of MSWD on PACV at pH 10 gives a  $R^2$  value of 0.9997 and a corresponding  $\Delta q$  value of 10.47, whereas the fractal kinetic fit gives a  $R^2$  of 0.9866 and the corresponding  $\Delta q$  value is 7.31. As previously observed [18], the pseudo-second order equation fits of kinetic adsorption data generally give very good correlation coefficients ( $\geq 0.99$ ), that is due to its very convenient form  $t/q$  versus  $t$ , in which  $q$  generally increases with  $t$ , and  $t/q$  is then obviously proportional to  $t$ . One can, however, observe (Table 3) that similar  $q_e$  and  $\tau_{1/2}$  values are obtained from the simple pseudo-second order model and the fractal kinetic model, and for lower  $\Delta q$  values, closer  $q_e$  and  $\tau_{1/2}$  values are obtained from both models.

Table 3

Kinetic parameters obtained from the pseudo-second order equation for adsorption of melanoidin and MSWD respectively, at pH 3, 7 and 10

	Kinetic parameters from pseudo-second order					Kinetic parameters from the fractal kinetic equation					
	$q_e$ (mg/g)	$K_2$	$t_{1/2}$ (h)	$R^2$	$\Delta q(\%)$	$q_e$ (mg/g)	$\alpha$	$\tau_\alpha$ (h)	$\tau_{1/2}$ (h)	$R^2$	$\Delta q(\%)$
	MSWD					MSWD					
pH 3	448.01	$2.06 \times 10^{-6}$	0.11	0.99948	1.95	455	0.86	0.09	0.09	0.9975	2.09
pH 7	370.08	$7.27 \times 10^{-3}$	0.37	0.99975	6.021	370	0.87	0.28	0.28	0.9866	5.02
pH 10	315.40	$5.66 \times 10^{-2}$	0.56	0.99971	10.47	325	0.68	0.37	0.37	0.9771	7.31
	Melanoidin					Melanoidin					
pH 3	232.08	$5.35 \times 10^{-3}$	0.81	0.99989	11.53	231	0.52	0.91	0.74	0.9885	8.58
pH 7	94.80	$1.86 \times 10^{-2}$	0.57	0.99995	6.16	94.6	0.60	0.93	0.43	0.9922	3.98
pH 10	66.64	$1.27 \times 10^{-2}$	1.15	0.99823	16.78	62	0.9	1.15	0.76	0.9460	15.35

Overall, the results presented here, clearly show that even with lower correlation coefficients the fractal kinetic equation gives similar or even lower  $\Delta q$  values, indicating that this complex model is more accurate for describing the kinetic adsorption data and may provide better  $q_e$  and  $\tau_{1/2}$  values. Indeed, the adsorption process on AC is clearly a heterogeneous process taking place at the liquid–solid boundary, and the diffusion process occurs in a complex matrix with a fractal architecture as recently demonstrated [1], and these systems belong to what has been called “complex systems”. Our data are in agreement with the observation of Ho and McKay [18]. Analyzing literature adsorption data of various compounds on different solid materials they reported that complex mechanisms were generally observed in sorption reactions. Even if it might be incorrect to apply simple kinetic models such as first or second order rate equations to sorption with solid surfaces which are rarely homogeneous and because the effects of transport phenomena and chemical reactions that are often experimentally inseparable [28], high correlation coefficients could be obtained using the pseudo-second order kinetic model [18]. Moreover, the pseudo-second order model is very convenient and attractive to use due to its simplicity for kinetic data fitting procedure.

Comparison of data obtained from experiments done at the different pH shows that higher amounts of both MSWD and melanoidin respectively are adsorbed at lower pH, which may be due to the effect of predominating non-electrostatic interactions [14].

Where  $n \neq 1$ , it is also possible to write Eq. (1) in a linear form [2], using the definition of the deformed exponential:  $\exp_n(x) = [1 - (n-1)x]^{-1/(n-1)}$  if  $1 - (n-1)x > 0$  and

$$\text{with } r(t) = q_t/q_e = 1 - \exp_n(-(t/\tau_{n,\alpha})^\alpha)$$

$$R_n(t) = \frac{(1 - r(t))^{1-n} - 1}{n - 1}$$

$$\text{Log } R_n(t) = \alpha \text{Log}(t) - \alpha \text{Log}(\tau_{n,\alpha}) \quad (12)$$

This expression (12) allows us to use a linear curve in order to fit our experimental data. Fig. 7 shows the linear fit that could be obtained for adsorption kinetic of melanoidin on PACV at pH 3 and 7. The  $q_e$  values is determined graphically as the  $q(t)_{\text{max}}$  value. Considering that it was difficult to distinguish between a first or a second order kinetic, taking  $n = 1.5$  we could calculate a value of  $\alpha = 0.53$  and of  $\tau_{1/2} = 0.74$  at pH 3 and  $\alpha = 0.56$  and of  $\tau_{1/2} = 0.57$  at pH 7. There is a quite good agreement between the values found by fitting Eq. (1) and the linear fit. The higher value found for  $\tau_{1/2}$  with the linear fit at pH 7 may be explained by the choice of the theoretical  $q(t)$  max value.

#### 4. Summary

From the results presented in this paper, we can conclude that the fractal kinetic proposed for describing adsorption kinetic of solutes on ACs [1,2] can also be a useful theoretical tool to study adsorption of industrial effluents contaminated with various compounds. The kinetic data can either be fitted using the kinetic Eq. (1),  $q_{n,\alpha}(t) = q_e [1 - (1 + (n-1)/(t/\tau_{q,\alpha})^\alpha)^{-1/(n-1)}]$  to determine the parameters,  $q_e$ ,  $n$ ,  $\alpha$  and  $\tau_{1/2}$ , or a linear Eq. (12),  $\text{Log } R_n(t) = \alpha \text{Log}(t) - \alpha \text{Log}(\tau_{n,\alpha})$ , can also be used, for that, the  $q_e$  value being determined from the experimental curve. Furthermore, the results presented here, clearly show that even with lower correlation coefficients the fractal kinetic equation gives lower normalized standard deviation values than the pseudo-second order model, indicating that the fractal kinetic model is more accurate for describing the kinetic adsorption data than the pseudo-second order kinetic model. It follows, from a recent published paper [1] and from the above results that the fractal analysis performed in terms of adsorption measurements from liquid phases, seems to be an important tool for characterizing surface irregularities in porous materials.

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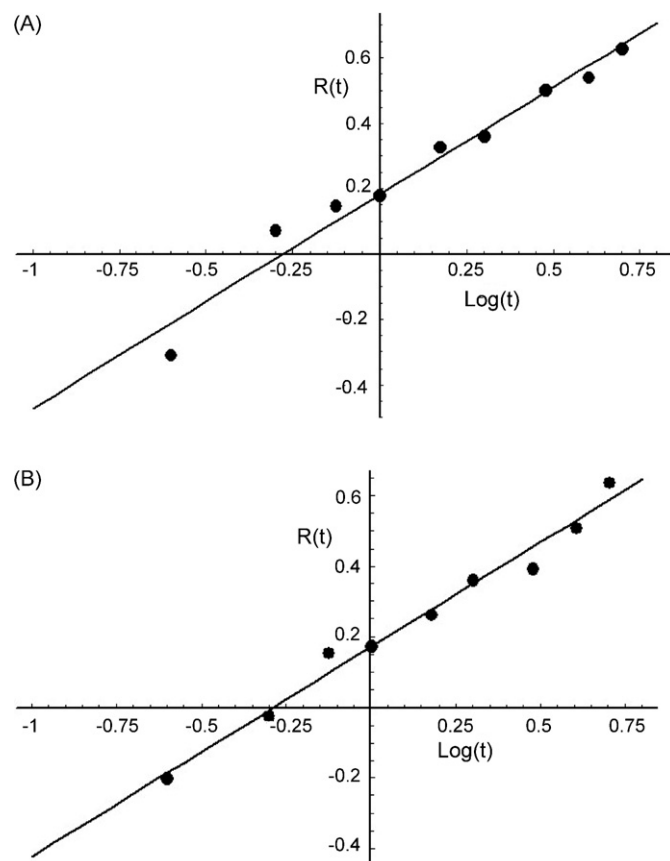


Fig. 7. Linear fit of the fractal kinetic equation for adsorption of melanoidin on PACV at (A) pH 3 and (B) pH 7.

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