Kinetics and Mechanism of *p*-toluidine Adsorption onto Granular Activated Carbon

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In this work the kinetics and mechanisms of p-toluidine adsorption from aqueous solution onto mesoporous granular activated carbon were studied for 100, 1000 and 2000 mg L^{-1} *initial concentrations, at constant 22°C temperature. Three models, i.e., pseudo-first order, pseudo-second order, and Avrami fractionary order were tested to fit the kinetic data. In order to evaluate the kinetic parameters, the nonlinear regression has selected as robust algorithm. The adsorption processes were found to follow Avrami fractionary order model with values of* $n < 1$ *meaning that the adsorption is more approximated to the pseudo-first order kinetic. The adsorption mechanism was determined from intra-particle diffusion model. Weber–Morris plots indicate that the intra-particle diffusion is not the rate-limiting step for the whole adsorption process.*

Keywords: adsorption, activated carbon, p-toluidine, kinetics, mechanism

Aniline compounds are very toxic to human and animal life and resistant to biodegradation [1]. Unfortunately, they are common pollutants of wastewaters derived from from manufacture of polymers, rubber, plastic, dyes and pigments, paper and textile industries, etc [2, 3]. Because of the wide prevalence of organic compounds in wastewaters and their toxicity, it is essential to remove them before discharge into the environment. Various treatment methods have been applied to remove pollutants from industrial waters, including chemical oxidation, membrane techniques, chemical coagulation, solvent extraction and adsorption [4]. Adsorption is preferred due to its simplicity in design, low cost and applications for a large spectrum of undesirable and removable compounds. Among many available adsorbents, the activated carbon is most widely used because of their high adsorption capacity and fast adsorption kinetic.

The adsorption process of phenol and its derivates on activated carbon are generally well known, but very limited informations are currently available regarding the adsorption of anilinic compounds. Duman and Ayranci (2005) [2] investigated the adsorption of anilinic compounds (aniline, *p*-toluidine, 1-napthylamine and sodium salt of diphenylamine-4-sulfonic acid) onto high-area carbon-cloth by first-order kinetic model and the adsorption isotherms were evaluated by Langmuir and Freundlich models. The adsorption equilibrium of aniline, 4-methylaniline, and 4-nitroaniline onto hydrophilic bifunctional polymeric resin (LS-2) with sulfonic groups and onto the commercial Amberlite XAD-4 has been investigated by pseudo-first order and pseudo-second order kinetic models, as show Jianguo et al. [3] in their work. As authors reported, the adsorption of the aniline compounds on LS-2 is the result of coexistence of physisorption and chemisorption and was well fitted by the pseudo-second order model, while the adsorption of the compounds on XAD-4 was governed by physical adsorption and follows the pseudo-first order kinetic model.

In this paper, the kinetic of p-toluidine onto granular activated carbon is investigated. The overall kinetic of the adsorption process is analysed by pseudo-first-order, pseudo-second-order, and Avrami fractionary order kinetic models. The parameters of the models are estimated using nonlinear regression. Afterwards, in order to determine whether or not intraparticle diffusion is the only rate-determining step, the intraparticle diffusion model based on the theory of Weber and Morris was employed for to analyze the adsorption mechanism.

Experimental part

Adsorbent and adsorbant charaterization

The *p*-toluidine is analytical grade and was purchased from Merck Romania SRL and used without further purification.

A mesoporous granular activated carbon (GAC) for which the physical properties have been determined in previous studies was supplied by Ecopur System SRL, Romania [5, 6].

The surface of the GAC was chemically characterized by Boehm titration [7-9]. A known mass of 1.0 g activated carbon sample was placed in 50 mL of 0.1 N of the following solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The vials were sealed and shaken for 24 h and then filtered; 10 mL of the filtrate was pipetted, and the excess base or acid was titrated with HCl (0.1 N) or NaOH (0.1 N), respectively. The number of acidic sites was determined under the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups, Na_2CO_3 neutralizes carboxylic and lactonic groups and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites was calculated from the amount of hydrochloric acid that reacted with the activated carbon.

The point of zero charge (pH_{PZC}) was determined using a pH/Ion/Conductivity/DO meter CyberScan PCD 6500 [10]. The initial pH (pH_i) for 25 mL of 0.1 M KNO_3 aqueous

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Table 1
PHYSICAL AND CHEMICAL PROPERTIES OF THE ADSORBENT (GAC)

Physical properties	
BET surface area, $m^2\ g^{-1}$	1376
Micropores area, $m^2\ g^{-1}$	594
Average pore diameter, nm	2.96
Micropores volume, $cm^3\ g^{-1}$	0.27
Chemical properties	
Acidic groups, $mmol\ g^{-1}$	1.545
Carboxylic groups, $mmol\ g^{-1}$	1.270
Lactonic groups, $mmol\ g^{-1}$	0.055
Phenolic groups, $mmol\ g^{-1}$	0.220
Basic groups, $mmol\ g^{-1}$	0.496
pH_{PZC}	7.5

solutions were adjusted in the range of 4–10 by using 0.1 M of HCl or NaOH. Then, an amount of 0.05 g of GAC was added to each sample. The resulting materials were stirred at 25°C for 24 h and filtered. The final *pH* of the solutions (pH_f) was then measured. The point of zero charge was calculated based on (pH_i - pH_f) versus pH_i. According to Reffas et al. [11], at $pH < pH_{PZC}$, the activated carbon surface is positively charged while at $pH > pH_{PZC}$, the surface is negatively charged, that could influence the adsorption of the *p*-toluidine on activated carbon due to electrostatic interactions.

The physical and chemical properties are presented in table 1.

Batch kinetic experiments

Batch kinetic experiments were carried out at 22 ± 0.1°C. The experiments were performed using 2 g of activated carbon with 100 mL of aqueous *p*-toluidine solutions in 250 mL glass bottles of different initial concentration (100, 1000, and 2000 mg/L, respectively). The flasks were shaken at presettled temperature under 200 rpm until equilibrium reached. All adsorption data were determined without adding any buffer to control the pH to prevent introduction of any new electrolyte into the system. The *p*H of the solution throughout the experiment was found at *p*H 7.30 to 7.46 in *p*-toluidine solution after filtration. For the kinetics study, samples by 5 mL aliquots were collected at regular time intervals and the concentration of *p*-toluidine was spectrophotometrically measured at wavenumber of 233 nm (*Jenway V550* UV/Visible spectrophotometer).

The amount of p- toluidine adsorbed by activated carbon at time *t*, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t)\cdot V}{W} \qquad (1)$$

Table 2
NONLINEAR KINETIC MODELS
USED FOR ANALYSIS OF EXPERIMENTAL DATA

Kinetic models	Equation	Equation no.	Parameters	Ref.
Pseudo-first order	$q_t = q_e[1 - \exp(-k_1 t)]$	(2)	k_1 is the pseudo first order rate constant (min^{-1}).	[12]
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + q_e k_2 t}$	(3)	k_2 is the rate constant of pseudo-second-order model ($mg^{-1}\ min^{-1}$).	[13]
Avrami	$q_t = q_e\left[1 - \exp(-k_{AV} t)\right]^n$	(4)	k_{AV} is the Avrami kinetic constant (min^{-1}), *n* is a fractionary order which can be related to the posible changes of the adsorption mechanism	[14]

where:

C_0 and C_t are the initial and at time *t* concentration of *p*-toluidine ($mg{\cdot}L^{-1}$),

V is the volume of the solution (L) and *W* is the GAC mass (g).

Results and discussions

The overall kinetic of the adsorption process was evaluated by the pseudo-first order, pseudo-second order, and Avrami fractionary order kinetic models. The mathematical expression (nonlinear forms) of these kinetic models is presented in table 2.

In order to evaluate the goodness-of-fit of the kinetics to the experimental data, the Levenberg–Marquardt (*LM*) methods are used. The *LM* algorithm starts with a set of trial values for the parameters to be estimated. Then, these parameters are iteratively adjusted and improved until the sum of squares errors *SSE* achieves a global minimum. *SSE* is the sum of squared deviations of the experimental points from the regression curve. Along with values of *SSE*, another four statistical functions are employed in evaluations of goodness-of-fit of *LM* algorithm. In table 3 are presented the forms of all statistical functions.

The statistical functions (table 3) adopted to solve kinetics equations requires few explanations. These are in the following:

-*N* denotes the number of experimental data

-Y_{calc} is the regression-predicted value of the dependent variable

-Y_{exp}s the experimental value of dependent variable

-w_i is the weighting coefficient or a measurement of errors. In the regression analysis performed in this work was selected the direct weighting method where is the value from the *i*th row of *yErr* column

-*DF* is the degree of freedom of regression model. The number of degrees of freedom is simply the number of experimental data points (*N*), minus the number of model parameters (*P*)

Table 3
STATISTICAL FUNCTIONS AND THEIR EQUATION FORMS

Statistical functions	Equation form	Equation no.
Sum of squares errors (*SSE)*	$SSE = \sum_{i=1}^{N} w_i (Y_{exp} - Y_{calc})^2$	(4)
Reduced sum of the squares of the errors (*Red-SSE)*	$Red\text{-}SSE = \frac{SSE}{DF}$	(5)
Coefficient of determination (R^2)	$R^2 = \frac{SS_{reg}}{SS_T} = 1 - \frac{SSE}{SS_T}$	(6)
Adjusted R^2 (Adj- R^2)	$Adj\ R^2 = 1 - \frac{SSE/DF}{SS_T/DF_T}$	(7)

-SS_T is called the „total sum of squares" and represents the variation between data points and the mean. The SS_T can be divided into two parts: the variation explained by regression and that is not explained by regression:

$$SS_T = SS_{Reg} + SSE = \sum_{i=1}^{N}\left(Y_{calc} - \bar{Y}\right)^2 + \sum_{i=1}^{N}\left(Y_{exp} - Y_{calc}\right)^2 \qquad (2)$$

whereY is the mean of the experimental data.

- DF_T is the total degree of freedom of regression model and is assigned as the number of experimental data points (*N*), minus one.

The results of the kinetic regressions which are expressed as the plots of adsorption capacity against the adsorption times are presented in figure 1. As previously mentioned, the aim of this study was to select the best descriptive kinetics model.

Table 4 shows the calculated parameters of the kinetic models, the *qe* values and the corresponding statistical function values. The regression analysis of experimental data shows that the correlation coefficients R^2 and $Adj\text{-}R^2$ for the Avrami model obtained for almost all experimental data (exception makes the initial concentration of 2000 mg/L *p*-toluidine) were relatively high and the error functions *SSE*, *Red-SSE* are relatively low (table 4). This finding indicated that almost the adsorption process of *p*-toluidine follows the Avrami model. In the case of Avrami models, it was observed that the *qe* values obtained from these equations were very close to the experimental *qe* values. Values of the correlation coefficients R^2 and $Adj\text{-}R^2$ of the Avrami model are around of 0.98, suggesting that this model give a goodnest of fit. Furthermore, when the values of the *SSE* and *Red-SSE* error functions were analyzed (table 4), it was observed that the values of the error functions were generally lower than other evaluated kinetics model. Also, the values of $n < 1$ in Avrami model suggest that the adsorption is more approximated to the pseudo-first order kinetic. It is well know that pseudo first-order model presumes that the adsorption occurs due to a gap of concentration between adsorbate surface and solution, and this happens when the external mass transfer controls the adsorption process [15]. In table 4 it can been observed that *qe* values obtained from pseudo-first order model were in good agreement with the experimental *qe* values and these confirm that *p*-toluidine adsorption follow the pseudo-first order kinetic. Similarly, Jianguo et al. [3] and Duman and Ayranci [2] have been used pseudo-first-order kinetic model in order to express the adsorption of *p*-toluidine and of other anilinic compounds onto different adsorbents.

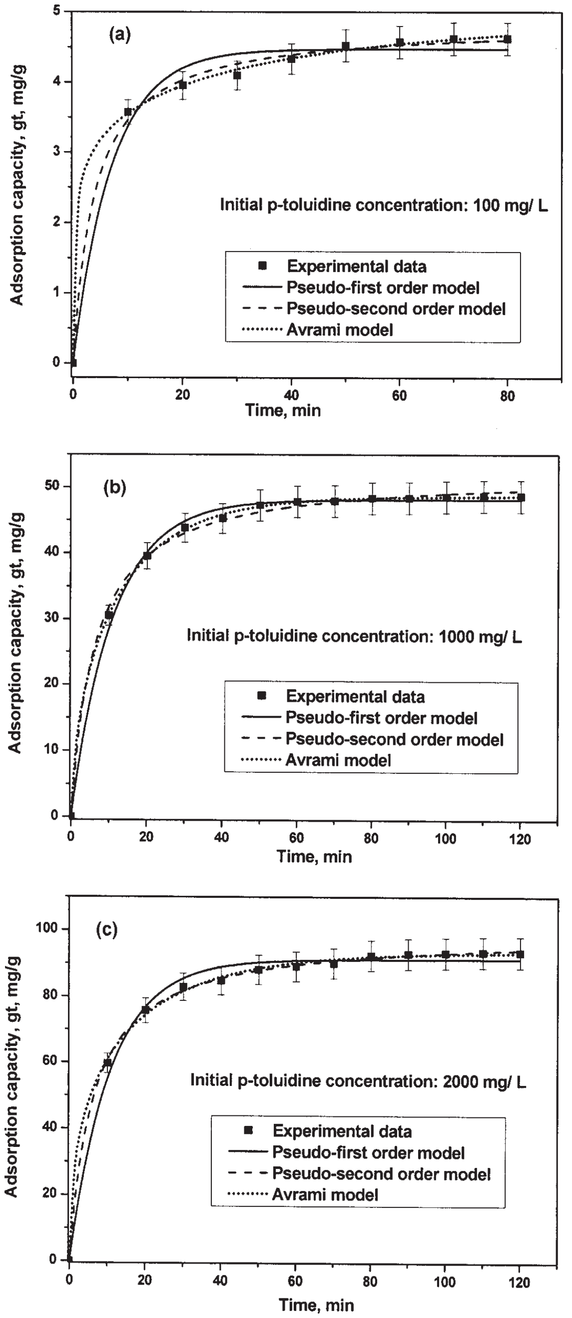

Fig. 1. Effect of contact time on *p*-toluidine adsorption on GAC. Experimental conditions: GAC 2 g; shaking speed: 200 rpm; and temperature: 22°C.

Table 4

KINETICS PARAMETERS AND STATISTICAL FUNCTIONS VALUES

	C_0 (mg L^{-1})	100	1000	2000
	q_e (exp)	4.62	48.6225	93.35
Pseudo-first order model	q_e (mg g^{-1})	4.47079	48.0624	91.1806
	k_1 (min^{-1})	0.14021	0.09008	0.0922
	SSE	0.05519	16.8536	289.1305
	Red-SSE	0.00788	1.53215	26.28459
	R^2	0.72599	0.96966	0.92201
	Adj-R^2	0.68684	0.96691	0.91492
Pseudo-second order model	q_e (mg g^{-1})	4.82252	52.07755	98.9046
	k_2 (mg^{-1}	0.05268	0.00303	0.0016
	SSE	0.00167	11.57765	20.602
	Red-SSE	0.01171	1.05251	1.87291
	R^2	0.94184	0.97916	0.99444
	Adj-R^2	0.93353	0.97727	0.99394
Avrami model	q_e (mg g^{-1})	**4.93884**	**48.57759**	**93.33112**
	k_{AV} (min^{-1})	0.01584	0.05795	0.04142
	n	0.17115	0.56011	0.39597
	SSE	0.00339	1.24803	40.19044
	Red-SSE	$5.652x10^{-4}$	0.1248	4.01904
	R^2	0.98316	0.99775	0.98916
	Adj-R^2	0.97755	0.9973	0.98699

The adsorption mechanism were analyzed by the intraparticle diffusion model of Weber-Morris:

$$q_t = k_{id} t^{0.5} + C \qquad (3)$$

where:

C is the intercept;

k_{id} is the rate constant of intraparticle diffusion.

Figure 2 show the intraparticle diffusion plots for the adsorption of *p*-toluidine onto GAC for different initial feed concentrations.

Figure 2 shows the adsorption profiles by plotting q_t versus $t^{0.5}$ for all initial concentrations of *p*-toluidine on GAC. By analyzing the data in figure 2, two or three linear segments are depicted, according to *p*-toluidine initial concentrations. At 1000 and 2000 mg L^{-1} *p*-toluidine initial concentration, q_t versus $t^{0.5}$ indicates that intra-particle diffusion was not the only process involved in solute adsorption, and there coexist another process which may be involved in the rate controlling step. Firstly occurs the very fast transport of adsorbate molecules due to the greater concentration driving force from bulk solution to the external surface of adsorbent and then the adsorption step slows down when the external transport (diffusion) through the boundary layer of *p*-toluidine start-up. The second stage (the bold line in fig. 2) shows the gradual where the adsorbate is transferred to the interior of the particle by diffusion of *p*-toluidine molecules through macropores, mesopores and micropores. In this stage, the intra-particle diffusion was the rate limiting step. Finally, the third step shows the formation of plateau which indicate the equilibrium stage and maximum adsorption. On the other hand, at 100 mg L^{-1} *p*-toluidine concentration in feed solution, the plots q_t versus $t^{0.5}$ show only two stage. The first stages can be explained as gradual adsorption where intra-particle diffusion can be one of the rate limiting step. In other words, these first stages do not exclude the involvement of the film diffusion in adsorption rate controlling. The second stages are described as equilibrium stages where intra-particle diffusion becomes limited due to the depletion of the solution *p*-toluidine.

Table 5

INTRA-PARTICLE DIFFUSION RATE OBTAINED FROM WEBER–MORRIS MODEL FOR DIFFERENT INITIAL CONCENTRATIONS OF *P*-TOLUIDINE AND VALUES OF THE ERROR FUNCTIONS

C_0 (mg L^{-1})	100	1000	2000
k_{id} (mg g^{-1} $min^{0.5}$)	0.22889	1.81984	2.47344
C (mg g^{-1})	2.87547	33.94521	69.75955
SSE	0.00472	0.2796	1.33853
R^2	0.96767	0.92293	0.91371
Adj-R^2	0.93535	0.84587	0.87056

Figure 2 also illustrate that the plots did not pass through the origin, and consequently the intercepts C do not equal zero values. This further support the idea that the intra-particle diffusion is involved in the adsorption process, but is not the only rate-controlling step. The rate parameter k_{id} corresponding to the intra-particle diffusion stages and the intercept C values are reported in table 5 together with the error function values.

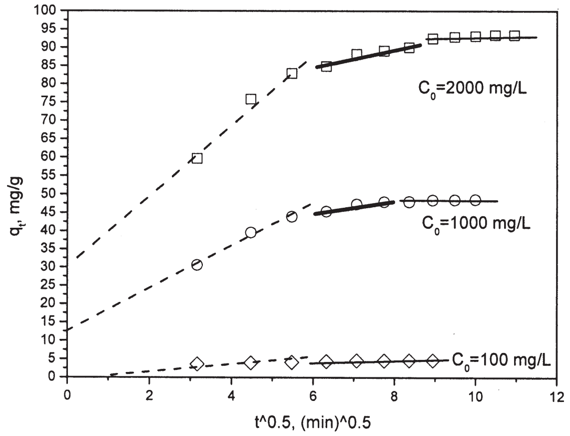

Fig. 2. Intra-particle diffusion plots for the adsorption of *p*-toluidine onto GAC for different initial feed concentrations

Due to the *p*H value it can be assumed that no electrostatic interactions between GAC and *p*-toluidine considering the neutral surface of the adsorbent (*p*H ≅ *p*H_{PZC}) and molecular form of *p*-toluidine (*p*H < pK_b). Given the higher concentration of the GAC surface acidic groups compared with basic groups, the first one will promote the adsorption of the basic *p*-toluidine. According to Duman et al. [2] the adsorption of *p*-toluidine on carbonaceous materials with graphitic structure (as GAC is) is physical, of dispersion forces type, between the π electrons of aromatic rings in the *p*-toluidine and p electrons in the GAC surface.

Conclusions

The present study shows that granular activated carbon (GAC) is a good adsorbent for the removal of *p*-toluidine from aqueous solution. Batch kinetic studies show that the pseudo-first order kinetic equation can adequately predict the adsorption of *p*-toluidine on the GAC surface. The Boehm titration confirms the acidic groups on GAC surface and these promote the adsorption of the *p*-toluidine. Intra-particle diffusion model was applied to identify the adsorption mechanism. Weber–Morris plots indicate that the intra-particle diffusion is not the only rate-limiting step for the whole concentration range of *p*-toluidine.

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