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Proceedings of European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Kinetic and thermodynamic study of the adsorption of natural organic matter on granular activated carbon

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Abstract

Adsorption equilibrium and kinetics of natural organic matter (NOM) on two different granular activated carbons (GAC) were studied. Firstly physical and chemical properties of both carbons were evaluated and significant differences were observed. The influence of the initial concentration of NOM and adsorbent particle size were also investigated. The kinetic data were fitted using the pseudo-first-order equation (PPO), the pseudo-second-order equation (PSO), the intraparticle diffusion model (ID) and the modified pseudo-first-order equation (MPPO). The corresponding kinetic parameters for these models are presented. The results show that the PSO model generated the best agreement with the experimental data for the NOM/GAC A and NOM/GAC F system. Finally, the adsorption equilibrium data were correlated with Freundlich and Langmuir isotherms.

Keywords: Drinking water treatment; Natural organic matter; Granular activated carbon; Adsorption kinetics.

1. Introduction

During the disinfection of drinking water the reaction between disinfectant and natural organic matter generates disinfection by-products (DBPs). When chlorine is used as disinfectant, these harmful products include trihalomethanes (THMs) and haloacetic acids (HAAs) [1]. Nowadays, numerous rules make provisions for minimizing the formation of undesirable DBPs [2-4].

Although many technologies has been tested for the removal of dissolved contaminants such as natural organic matter from drinking water the United States Environmental Agency has designated GAC adsorption as a best available technology for removing NOM [5]. At the moment, NOM adsorption equilibrium data are available in the literature [6,7,9] but residence times at water treatment plants are not

long enough and the process seldom reaches equilibrium. So, the study of not only adsorption equilibrium but also kinetics is essential in supplying the fundamental information required for the design and operation of adsorption equipments for drinking water treatments. Therefore, both data were evaluated in this study, looking for the activated carbons with both high removal capacity and increased kinetics.
The kinetic data were fitted to the following models [10-13].

PPO $$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

PSO $$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2)$$

ID $$q_t = k_p t^{1/2} \qquad (3)$$

MPPO $$\frac{dq_t}{dt} = K_1 \frac{q_e}{q_t}(q_e - q_t) \qquad (4)$$

where q_t (mg g^{-1}) is the solid phase concentration at time t (h), q_e (mg g^{-1}) is the solid phase concentration at equilibrium, k_1 (h^{-1}) is the pseudo-first-order constant, k_2 (g mg^{-1} h^{-1}) is the pseudo-second-order constant, k_p (mg g^{-1} $h^{-0.5}$) is the intraparticle diffusion constant and K_1 is the modified pseudo-first-order constant, $k_1 = K_1 \frac{q_e}{q_t}$.
Moreover, the adsorption equilibrium data were correlated with two well-known models, Freundlich (5) and Langmuir (6) isotherms [12-14]:

$$q_e = K_F C^{n_F} \qquad (5)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (6)$$

where K_F (l mg^{-1}) is Freundlich constant signifies the adsorption capacity, and n_F is the adsorption efficiency or the heterogeneity factor. Q_0 (mg g^{-1}) is adsorption capacity and b (l mg^{-1}) is Langmuir adsorption constant related to energy of adsorption.
The scope of the study is to test the validity of the pseudo-first-order equation, the pseudo-second-order equation, the intraparticle diffusion model and the modified pseudo-first-order equation for the adsorption of NOM onto activated carbon. Moreover the parameters of Freundlich and Langmuir isotherm models will be test to find the best adequate model to describe the process for different initial concentration level.

2. Experimental methodology

Two different GACs were used for DBPs precursors elimination, one coconut based, AUXI, (GAC A) used in a Spanish Water Treatment Plant and one coal based, F400 produced by Chemviron Carbon (GAC F). Firstly the GACs were grounded and separated in adequate size. Then the adsorbents were oven-dried at 105 ºC to constant weight.

Various characterization methods have been used to determine physicochemical properties of activated carbon. Physical characteristics were determined by: (i) thermo gravimetric analysis in oxidant atmosphere (ii) from nitrogen adsorption isotherms at 77 K using: (a) BET equation for total surface area (b) nitrogen uptake at the relative pressure of 0.98 for total pore volume (c) Micromeritics´ density functional theory (DFT) software for pore size distribution. Chemical characteristics were determined by: (i) pH of point of zero charge (pH_{PZC}) [15], (ii) charge density [16,17], (iii) total NaOH and HCl uptakes [7].

Synthetic water was prepared from humic and fulvic commercial acids (Fluka Products and Fredricks Research Products). Then, solution was filtered using 0.45 µm filter. The pH was adjusted using NaOH and HCl at 8.0 units. Finally the synthetic water was added sodium bicarbonate and calcium chloride in order to adjust the alkalinity and hardness to 100-150 mg HCO_3 l^{-1} and 25-50 mg Ca l^{-1}, average data in Basque country. The DOC and UV were measured by Total Organic carbon Analyser (Shimadzu TOC-5050A) and Helios Gamma Ultraviolet and Visible Spectrophotometer at 200-500 nm with a 1 cm path length. Studies have demonstrated that removal of UV absorbance can provide a good indication of THMs producing organic precursors [8]. The obtained results were 50 mg l^{-1} DOC and 3.4 cm^{-1} at 254 nm.

3. Results

Firstly, physical and chemical properties were evaluated for GAC A and GAC F. The results are tabulated in Table 1. Significant differences were observed between both carbons.

Table 1. Texture parameters of the studied activated carbons.

			GAC A	**GAC F**
Inorganic content		*%*	0.6	5.7
SA_{BET}		*m^2 g^{-1}*	808	852
V_{micro}		*cm^3 g^{-1}*	0.312	0.272
V_{total}		*cm^3 g^{-1}*	0.341	0.483
$V_{meso+macro}$		*cm^3 g^{-1}*	0.029	0.211
DFT **Surface area distribution**	**0.7-1 nm**	*%*	87	75
	1-2 nm	*%*	15	20
	2-50 nm	*%*	3	5
pH_{PZC}			9.5	10.5
Charge density		*µC cm^{-2}*	0.28	1.55
Acidic groups		*meq g^{-1}*	0.014	0.098
Basic groups		*meq g^{-1}*	0.172	0.286

According to the literature the adsorption of NOM is controlled predominantly by the compatibility between the molecular size distribution of NOM mixture and the pore size distribution of the carbon pores [7,[18]. So, GAC F with larger pore sizes than GAC A and slightly higher surface area will be able to provide better removal efficiencies. Moreover, it is known that NOM in natural waters is typically a heterogeneous mixture of acidic macromolecules that are negatively charged. For these reasons carbon F with basic surface properties shows a high affinity for NOM adsorption [5]. As well, carbon F with a high net positive charge will show also greater adsorption due to the electrostatic forces between the carbon surface and NOM [17]. Then, GAC F according to our investigations seems to be the most efficient carbon towards NOM adsorption.

Preliminary bench scale experiments demonstrated that the NOM initial concentration and adsorbent particle size (Figure 1) were the most significant factors on adsorption rate. This behaviour was attributed to mass transfer phenomena. In this figures can be also observed greater adsorption for GAC F.

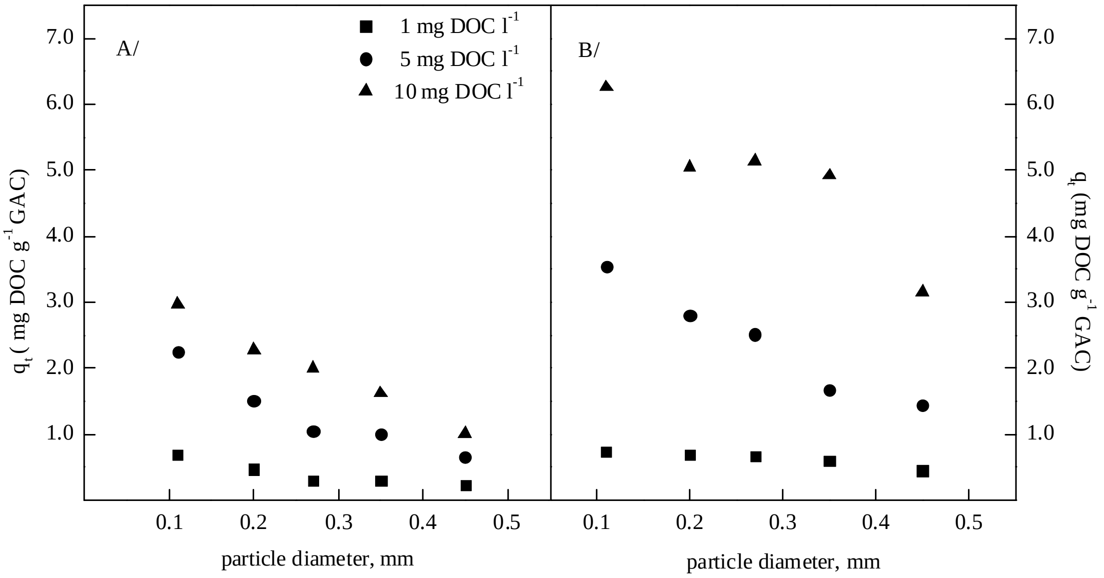

Figure 1. Influence of particle size and initial DOC concentration on NOM adsorption: A/ GAC A; B/ GAC F.

Next the adsorption kinetic of NOM shown in Figure 2 was carried out. It were evidenced significant differences in removal for both carbons, so pore size distribution, point of zero charge (pH_{pzc}) and superficial basicity and acidity controlled the NOM adsorption process.

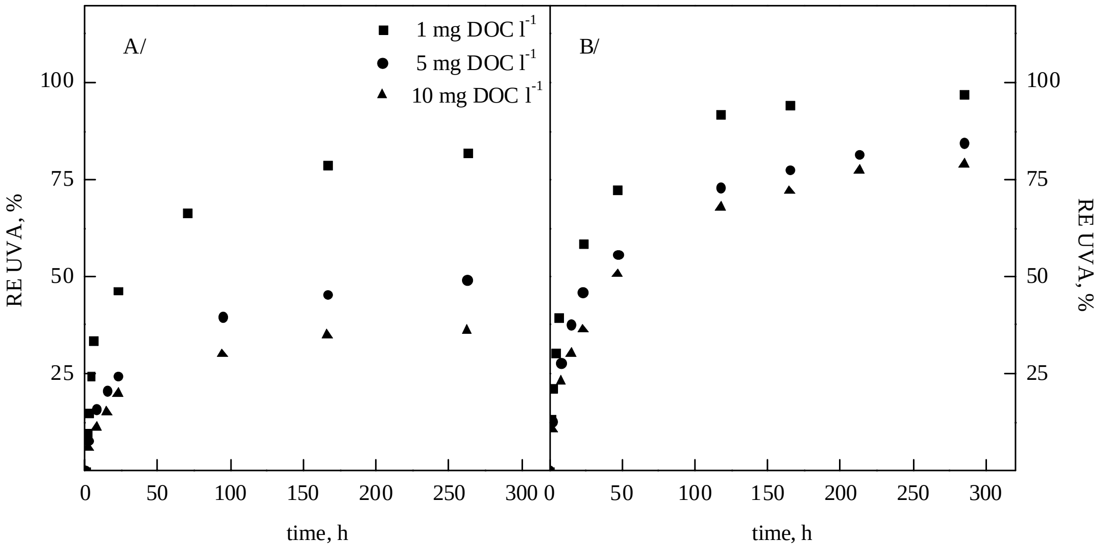

Figure 2. NOM adsorption kinetics for initial concentrations of 1, 5 and 10 mg DOC l^{-1} on: A/ GAC A; B/ GAC F.

After that, obtained kinetic data indicated in Figure 2 were fitted to the adsorption models. The parameters are shown in Table 2 and Table 3. Among the four kinetics models, the PSO equation generates the best fit to the experimental data of the investigated adsorption NOM/GAC A and NOM/GAC F systems throughout all adsorption curve. All the correlation coefficients obtained are bigger than 0.995. In addition, the rate constant of the PSO has been found to decrease with increasing initial concentration due to mass transfer phenomena. Moreover, PSO generates the best agreement with the experimental equilibrium data. This behaviour was maintained regardless of the initial NOM concentration.

Table 2. Kinetic parameters of NOM adsorption on the GAC A. (pH 8.0, 30 ºC, 200 rpm, 0.25-0.3 mm).

		PSEUDO-FIRST-ORDER			**MODIFIED PSEUDO-FIRST-ORDER**		
C_0 *(mg DOC l^{-1})*	**qexp**	**k_1** *(h^{-1})*	**qe**	**R^2**	**K_1** *(h^{-1})*	**qe**	**R^2**
1	0.803	0.0184	0.632	0.9795	0.0134	0.810	0.9978
5	2.460	0.0146	1.978	0.9818	0.0098	2.511	0.9968
10	3.647	0.0199	3.105	0.9849	0.0149	3.966	0.9655
		PSEUDO-SECOND-ORDER			**INTRAPARTICLE DIFFUSION**		
C_0 *(mg DOC l^{-1})*	**qexp**	**k_2** *(g mg^{-1} h^{-1})*	**qe**	**R^2**	**k_p** *(mg g^{-1} $h^{-0.5}$)*	**qe**	**R^2**
1	0.803	0.1002	0.831	0.9978	0.0492	-	0.9059
5	2.460	0.0182	2.607	0.9960	0.1497	-	0.9461
10	3.647	0.0131	3.905	0.9974	0.2267	-	0.9307

Table 3. Kinetic parameters of NOM adsorption on the GAC F. (pH 8.0, 30 ºC, 200 rpm, 0.25-0.3mm).

		PSEUDO-FIRST-ORDER			**MODIFIED PSEUDO-FIRST-ORDER**		
C_0 (mg DOC l^{-1})	**qexp**	**k_1** (h^{-1})	**qe**	**R^2**	**K_1** (h^{-1})	**qe**	**R^2**
1	0.930	0.0296	0.771	0.9906	0.0225	1.005	0.9784
5	4.257	0.0116	3.140	0.9823	0.0087	4.305	0.9972
10	8.365	0.0125	6.621	0.9549	0.0100	9.035	0.9378
		PSEUDO-SECOND-ORDER			**INTRAPARTICLE DIFFUSION**		
C_0 (mg DOC l^{-1})	**qexp**	**k_2** (g mg^{-1} h^{-1})	**qe**	**R^2**	**k_p** (mg g^{-1} $h^{-0.5}$)	**qe**	**R^2**
1	0.930	0.0970	0.980	0.9959	0.1683	-	0.9388
5	4.257	0.0101	4.442	0.9980	0.2164	-	0.9101
10	8.365	0.0043	8.834	0.9987	0.4006	-	0.8948

In Figure 3 is shown the simulation for the kinetics model for carbon A and carbon F. It was observed that the PSO equation generates the best fit throughout all adsorption curve with the experimental data for both systems.

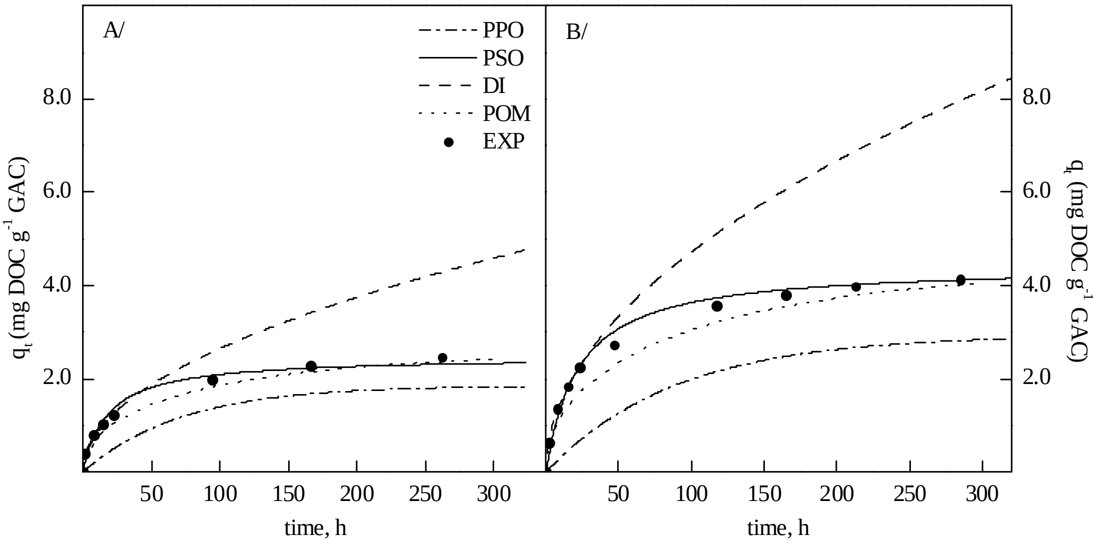

Figure 3. Kinetics of NOM adsorption on GAC A and GAC F. (pH 8.0, C_0 =5 mg DOC l^{-1}, 30 ºC, 200 rpm, dp = 0.25-0.3 mm).

Therefore, the PSO equation is potentially a generalized kinetic model for NOM adsorption study.

Subsequently, adsorption equilibrium data in Figure 4 were correlated with two well-known empirical isotherm models, Freundlich and Langmuir equations. Regression analysis of the linearized isotherms of Freundlich (log q_e versus log C_e) and Langmuir (1/qe versus 1/Ce), using the slope and the intercept, gave the sorption constants revealed in Table 4.

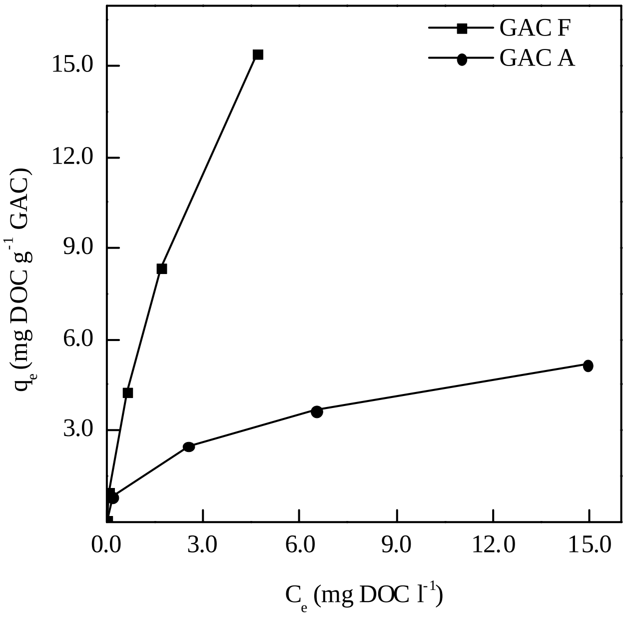

Figure 4. Adsorption Isotherms of GAC A and GAC F. (pH 8.0, 0.25-0.3mm, 30ºC).

Table 4. Parameters from Freundlich and Langmuir fitting for GAC A and GAC F.

Langmuir	**Q_0**	**b**	**R^2**	**Freundlich**	**K_F**	**n_F**	**R^2**
GAC A	5.8	0.39	0.9615	GAC A	1.66	0.42	0.9999
GAC F	21.2	0.49	0.9087	GAC F	5.79	0.64	0.9998

Although the Langmuir isotherm model does not correspond well to the NOM adsorption phenomena, it is used in this study in order to evaluate their adsorption capacity. Thus, GAC F was revealed to possess a highest NOM uptake of 21.2 mg DOC g^{-1}. Low b values indicate a high affinity between the NOM and the carbons. Regarding Freundlich isotherm according to the literature, for both carbons the adsorption process is favourable because of the fact that $0.1 < n_F < 1.0$. Nevertheless, it was revealed greater value for K_F for GAC F, indicative of higher adsorption capacity [12]. Therefore, NOM adsorption process is favoured for GAC F.

4. Conclusions

The adsorption equilibrium and kinetic of two adsorption systems, NOM/ GAC A and NOM/ GAC F, have been carried out in this study. The adsorption has been demonstrated to be controlled by the pore size distribution of the carbon pores and by carbon superficial chemical properties. Moreover, NOM initial concentration and adsorbent particle size has significant influence in this process due to intraparticle diffusion phenomena. The pseudo second order kinetic model generates the best fit to all the experiment data, indicating it is potentially a generalized kinetic model for NOM adsorption study. Moreover the rate constant of the PSO has been found to decrease with increasing initial concentration due to mass transfer phenomena.

Although rate constant NOM/ GAC A system is higher, equilibrium data is lower, so both parameters are necessary in order to study these systems.
The results obtained indicate that the two carbons can be fitted by the parameters of Freundlich isotherm model. It was demonstrated that GAC F shows higher adsorption capacity than GAC A.

5. References

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