



Carbon – Science and Technology

ISSN 0974 – 0546

<http://www.applied-science-innovations.com>

ARTICLE

Received : 18/10/2008, Accepted : 3/11/2008

Adsorption of Remazol Black B dye on Activated Carbon Felt.

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The adsorption of Remazol Black B (anionic dye) on a microporous activated carbon felt is investigated from its aqueous solution. The surface chemistry of activated carbon is studied using X-ray microanalysis, "Boehm" titrations and pH of PZC measurements which indicates that the surface oxygenated groups are mainly acidic in nature. The kinetics of Remazol Black B adsorption is observed to be pH dependent and governed by the diffusion of the dye molecules. The experimental data can be explained by "intra-particle diffusion model". For Remazol Black B, the Khan model is best suited to simulate the adsorption isotherms.

1. Introduction :

Azo dyes are of our interest since they represent nearly half (> 50 %) of the dyes commercially used in textile industry. Within the class of azo dyes, a lot of different types can be distinguished : acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulfur dyes. Particularly, the Azo's *reactive* dyes are more resistant to the usual water purification treatment. However, treatment methods based on adsorption [1], biological treatment [2], coagulation, electrochemical techniques [3], membranes process [4] or oxidation-ozonation are known to be effective for the removal of this type of dye from polluted water. Among all these methods the cheapest and simplest is the physical-chemical adsorption. The adsorption performed on the Granular Activated Carbon was extensively studied in past [5]. In order to obtain cheaper sorbents, numerous biomass based porous materials have also been tested [6, 7]. Only in the last decades, activated carbons fibers (ACF) have been developed in the form of fabric or felt that can reach specific surface area comparable to granular carbon [8]. The most important aspect of these new forms of activated carbon materials is their ability to be used in adsorption or electrosorption filters devices [9]. Electrosorption is widely used for the removal of metals in water [10]. Several studies have focused on hydrocarbons [11] and more recently on dyes [12]. The main benefits of electrosorption are an increase of the adsorption capacity and rate, and also an enhancement of the regeneration efficiency [13]. For such applications, the sorbent must have good textural properties (high surface area and porous volume), but also needs to have good conductivity. The aim of the present work was to investigate the removal of Azo reactive dye

[Remazol Black B (RB5)] from aqueous solutions by adsorption onto Activated Carbon Felt (ACF) [14].

2. Materials and methods :

2.1 Dye Material :

The schematic of the molecular structure of Remazol Black B [C₂₆H₂₁N₅Na₄O₁₉S₆] (Molecular Weight : 991) (DYSTAR Company) used in the present study is shown in Figure (1).

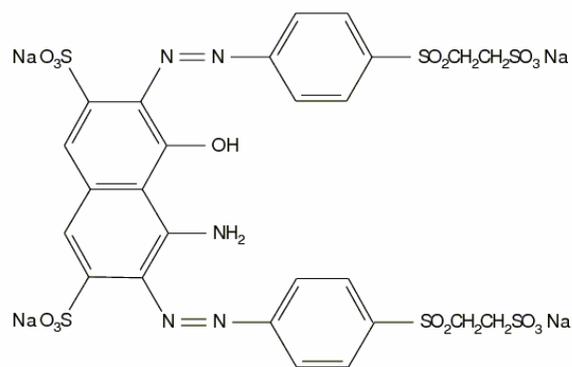


Figure (1) : Schematic of the Molecular Structure of Remazol Black B dye.

The pKa (3.8 and 6.9) of the dye were determined by acidobasic titrations of 50 mg/L with 0.01 M HCl and NaOH standard solutions.

2.2. Activated Carbon Felt (ACF) :

Before adsorption tests, the Activated carbon felt (ACTITEX FC 1201 from PICA Company MI, ITA) was washed in a Soxhlet extractor with distilled water for ten days in order to eliminate the impurities. Subsequently, the felt was degassed for 12 hours at 150 °C and 1×10^{-6} torr and stored in a desiccator until adsorption measurements. The washed ACF was characterized by Scanning Electron Microscopy (SEM) in the backscattered electron mode using a Leo microscope coupled with an energy dispersive X-ray analysis spectrometer. The pH-PZC of washed ACF was determined by the method of Noh and Schwarz [15].

The surface oxygenated groups have been titrated by means of the so-called ‘Boëhm’ method [16]. The ACF was characterized by Nitrogen adsorption measurements at the liquid nitrogen temperature (77.4 K), using an Autosorb 1 LP apparatus (Quantachrome) after degassing at 200 °C for 15 hours. From this isotherm, the BET specific surface area (S_{BET}) was determined, and, as the carbon material is mainly microporous, the relative pressure range [0.01 to 0.05] was used [17]. The total pore volume (V_{tot}) was measured at a relative pressure of 0.95. The microporous volume (V_{micro}) was computed by applying the Dubinin - Radushkevich equation and the mesoporous volume (V_{meso}) was obtained by difference between the total pore volume and the microporous volume. In addition, the pore size distribution (PSD) was computed by using the DFT method.

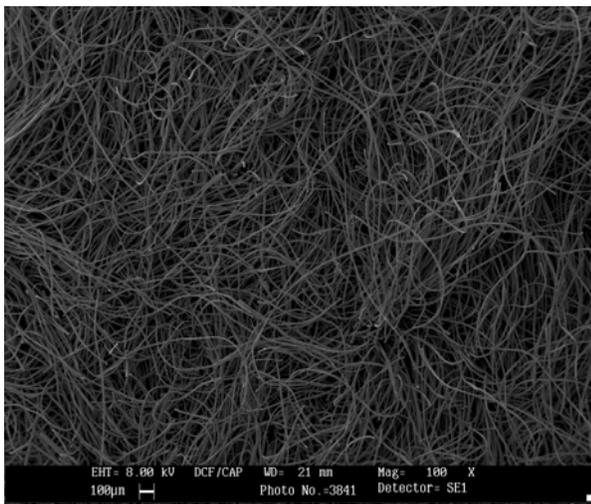


Figure (2) : SEM image of Actitex FC 1201 surface.

2.3. Dye Adsorption measurements :

The amount of dye adsorbed was determined by the depletion method. A Shimadzu 160 A UV-Visible spectrophotometer was used for optical absorbance measurements to determine the concentrations of remaining dye after adsorption by ACF. The amount of adsorbed dye per unit mass of ACF at equilibrium (q_e) was calculated by equation (1) :

$$q_e = (C_0 - C_e)V / W_s \text{ -----(1)}$$

where V is the volume of dye solution (in L), C_0 and C_e are the initial and equilibrium concentrations, respectively, of the dye solutions (in mg/L) and W_s is the mass of ACF (in g).

3. Results and discussion :

3.1. Characteristics of ACF :

On the SEM image presented in Figure (2), the felt carbon on the surface after washing treatment is shown. The X-rays elemental microanalysis reveals mainly the presence of elemental carbon but also oxygen and phosphorous are detected. The oxygen content originates from the oxygenated surface groups. The phosphorous impurities are due to the phosphoric acid activation of the ACF precursor. The amount of oxygenated functional groups was obtained from acid-base titrations and is presented in Table (1). This shows that the ACF is rich in phenol, carbonyl and lactones acid groups.

Chemical Groups	Concentration (meq/g)
Carboxyls	0.027
Lactones	0.139
Phenol	0.677
Carbonyls	0.238
Bases	0.060

Table (1) : Concentration of surface groups on ACF as determined by the Boëhm method.

The amount of water trapped in the ACF was quantified by thermo-gravimetric analysis (TGA) and is close to 20 wt. %. This confirms that ACTITEX FC 1201 is very hydrophilic due to its high amount of acidic surface groups. The pH-PZC by Noh and Schwarz method is presented in Figure (3).

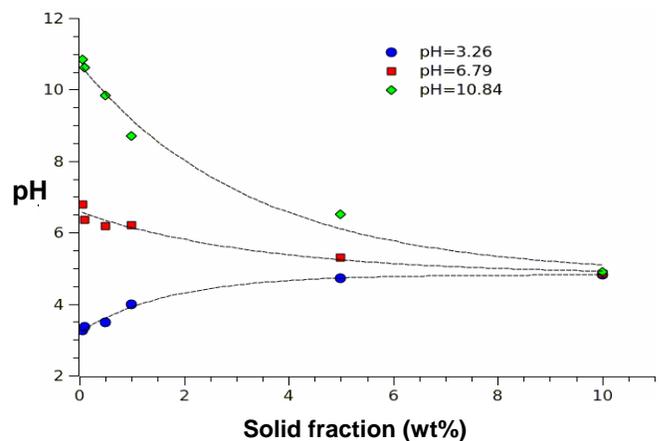


Figure (3) : Determination of the pH-PZC of Actitex FC 1201 : evolution of the pH of solution as a function of weight fraction for three initial pH values. All pH curves tend to the pH-PZC value.

The value obtained is 4.8 which is in agreement with the rather acidic surface chemistry of the carbon materials.

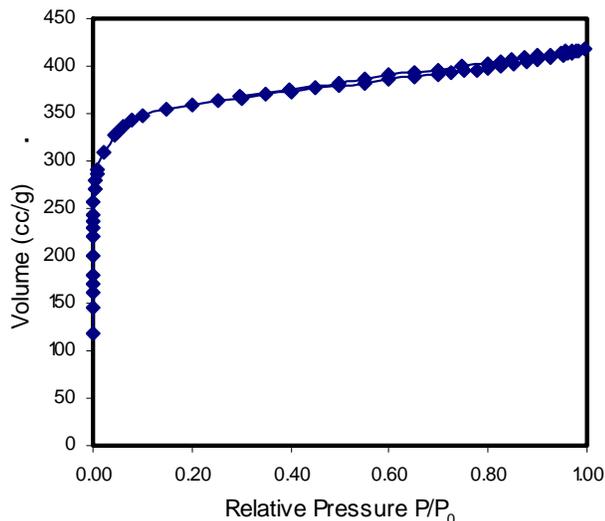


Figure (4) : Nitrogen adsorption isotherm at 77.4 K of ACF.

The isotherm of nitrogen adsorption at 77.4 K of the ACF [Figure (4)] is of type I and typical of a microporous materials [9]. The specific surface area of ACF according to method of Brunauer-Emmet-Teller [18] (S_{BET}) calculated from the isotherm in the conventional P/P_0 range [0.05-0.30] is 1112 m^2/g . As previously reported, the BET model is not adapted to microporous materials, but in this case S_{BET} is rather an indication of the microporous volume. For such microporous materials, the S_{BET} is generally measured in the relative pressure range [0.01 - 0.05]. In this range, the S_{BET} value obtained for the Actitex tissue is 1405 m^2/g . The total volume of pores (V_{tot}) is equal to 0.64 m^3/g . These values are typical of activated carbon fibers [19]. The pore size distribution (PSD) for mesopores and micropores was estimated by density functional theory (DFT) method [20] is shown in Figure (5).

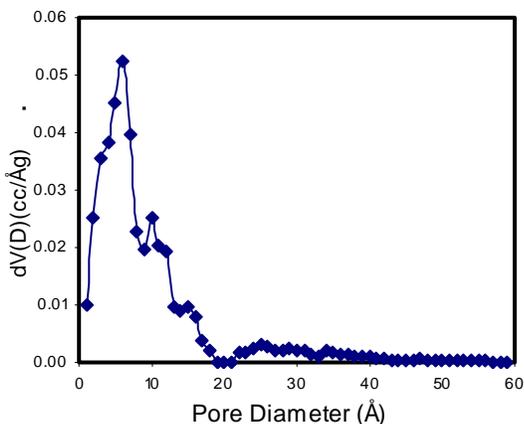


Figure (5) : Pore size distribution of ACF according to DFT.

3.2. Adsorption kinetics of dye :

The kinetic of adsorption have been studied for RB5 at pH = 2.5 up to 5000 min [Figure. (6)].

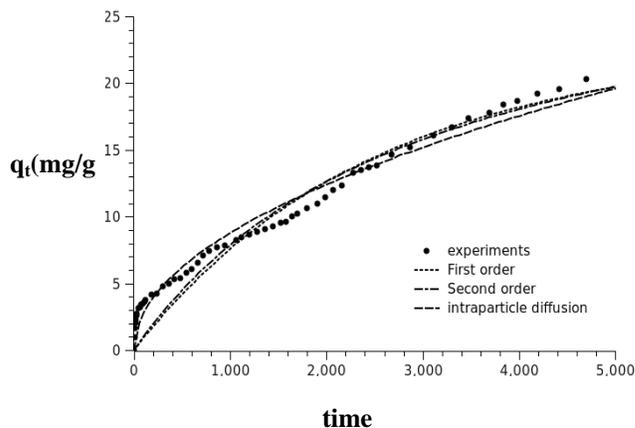


Figure (6) : Experimental data of the kinetic of adsorption of Remazol Black B at pH = 2.5 and the simulated plots with first order, second order and diffusion models.

Three kinetic models were applied to adsorption kinetic data in order to investigate the behavior of adsorption process of Remazol Black B dye onto ACF : the pseudo-first-order [21], the pseudo-second-order [22] and the intraparticle diffusion models [23].

The first-order equation is the simplest one and is the most widely used for the adsorption of a solute from a liquid solution. The rate law is :

$$dq_t / dt = k_1 (q_e - q_t) \quad \text{-----(2)}$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and q_e and q_t (mg/g) denote the amounts of adsorbed dye at equilibrium and at time (t , min), respectively. After integrating equation (2), we get :

$$q_t = q_e (1 - e^{-k_1 t}) \quad \text{-----(3)}$$

The values of k_1 and q_e were evaluated from the non-linear regression of q_t versus t for the dye, and are tabulated in Table (3). In several studies on adsorption of metals or dyes on porous materials, it has also been observed that the evolution of the adsorbed amount with time follows a second order law [22].

This pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the following form :

$$dq_t / dt = k_2 (q_e - q_t)^2 \quad \text{-----(4)}$$

where k_2 (g/mg.min) is the rate constant of pseudo-second order adsorption process. Integrating equation (4) gives :

$$q_t = (k_2 q_e^2 t) / (1 + k_2 q_e t) \quad \text{-----(5)}$$

The values of k_2 and q_e were also evaluated from the non-linear regression of q_t versus t data for each dye and are tabulated in Table (3). In addition to the adsorption of molecules on the sites of the sorbent material, the diffusion

of the molecules in the boundary layer around the particle and in the porosity of the sorbent can be limiting processes [24, 25]. Several models have been proposed to take this into account. In many cases, the diffusion of molecules in the boundary layer is not a limiting step. In the simplest way, intraparticle diffusion can be formulated by the Weber and Morris equation as :

$$q_t \approx k_i t^{1/2} \text{-----(6)}$$

where k_i ($\text{mg g}^{-1} \text{min}^{-1/2}$) is an intraparticle diffusion rate constant which is also reported in Table (2).

Kinetic		RB5
Pseudo-first-order	k_1 (min^{-1})	4.07×10^{-4}
	q_e (mg/g)	22.6
	R^2	0.935
	SSE	115
Pseudo-second-order	k_2 (g/mg.min)	1.04×10^{-7}
	q_e (mg/g)	31.7
	R^2	0.942
	SSE	103
Intraparticle diffusion	k_i ($\text{mg.g}^{-1} \text{min}^{-1/2}$)	0.277
	R^2	0.977
	SSE	42
	k_i (min^{-1})	4.07×10^{-4}

Table (2) : Fitted data of the adsorption kinetic of Remazol Black B (RB5) at pH = 2.5.

The values presented in Table (2) shows that all three models allow for a relatively good fitting with the experimental values. This is not surprising since it is known that even diffusion limited processes can be fitted with first-order models. The only way to separate diffusion from adsorption is to change some geometric parameters of the sorbent. Nevertheless, for the dye, the intraparticle diffusion model gives better agreement with experiments. This is consistent with the textural properties of the carbon material, which exhibits only micropores with a size below 2 nm. The diffusion of the relatively large dye molecules in such pores is therefore slow as indicated by the relatively low values of k_i , significantly lower than the ones observed on some biomass based sorbents [6].

3.3. Adsorption isotherms :

Following the classification of Giles [26], the isotherms are of type H_2 . The maximum adsorption capacities are close to 20 mg/g for RB5. The influence of the pH on the uptake is very important for the adsorption of RB5 dye. This was already observed for adsorption on biomass based materials [27]. For the dye, we have measured the pKa values almost close to 3.8 and 6.9. The pKa of the sodium sulfonate groups ($-\text{SO}_3\text{Na}$ i. e. sulfonic groups) attached to the dye molecules are known to be very low (lower than 1) and can reach negative values (for example : the pKa of toluene-para-sulfonic acid is -2.8), thus it was not determined experimentally in our studied pH window. The pKa value of 3.8 is close to the pKa of aniline (i.e. 4.6) and can be attributed to the $-\text{NH}_2$ groups of the dye molecules. This

means that at pH lower than 3.8 and higher than the pKa of the sulfonate groups, the dye molecules are in their anionic forms and have got the highest negative charge. From the pH-PZC values equal to 4.8, the ACF surface is positively charged at pH lower than this value. Thus, in acidic medium : $0 < \text{pH} < 3.8$, the electrostatic attractions between the anionic dyes and the positively charged surface of ACF are maximized, so that the pH dependent adsorption isotherms of the dye [Figure (7)] show higher maximum adsorption capacities at acidic pH (close to pH = 1). Numerous models have been used to describe the adsorption isotherms of organic molecules on carbon materials. This is the consequence of the complexity of the phenomena which are involved in the adsorption process.

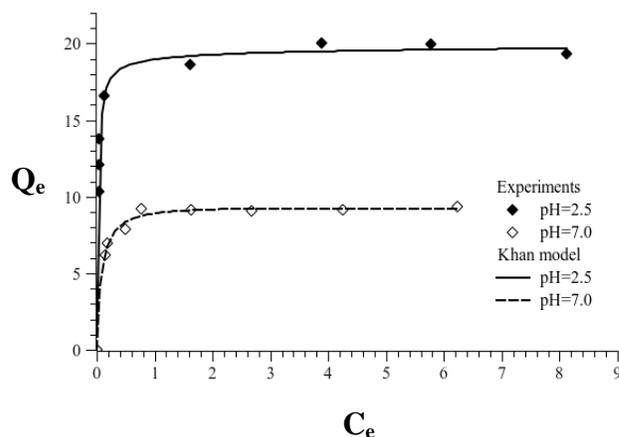


Figure (7) : Adsorption isotherms at room temperature of Remazol Black B onto Actitex FC1201 at pH = 2.5 and 7.0. Fits of the same isotherms using the Khan empirical model. Q_e (mg/g) and C_e (mg/l).

Isotherms	parameter	pH	
		pH=2.5	pH=7
Langmuir	$q_{\text{max}}(\text{mg/g})$	19.54	9.454
	$b_L(\text{L/m}^2\text{g})$	50.35	13.5
	R^2	0.9449	0.9335
	SSE	5.577	0.6675
Freundlich	K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	17.21	8.281
	n_F	11.63	11.13
	R^2	0.8599	0.7563
	SSE	14.17	2.523
Khan	$q_{\text{max}}(\text{mg/g})$	18.04	10.27
	b_K	60.86	11
	a_K	0.9852	1.022
	R^2	0.9479	0.9408
	SSE	5.27	0.6133

Table 3 : Fitted data of the adsorption isotherm of Remazol Black B at pH = 2.5 and pH = 7 using the Langmuir, Freundlich and Khan models.

In this work, adsorption isotherm data of Remazol Black B dye were fitted with the Langmuir and Freundlich models, which are the most widely used. In addition, the Khan model, which is an extension of the Langmuir equation, has

also been tested to reproduce the experimental data. The various isotherm fits were compared through the coefficient of correlation (R^2), the sum of error squared (SSE) and were reported in Tables (3).

3.3.1. Langmuir model :

The Langmuir model assumes uniform energies of adsorption onto the surface and no migration of the adsorbed material on the surface [28]. The Langmuir equation may be written as :

$$q_e = (q_{\max} b_L C_e) / (1 + b_L C_e) \quad \text{-----}(7)$$

where q_{\max} is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e the equilibrium concentration of the solute in the solution (mg/L), q_{\max} the maximum adsorption capacity (mg/g), and b_L is the constant related to the free energy of adsorption (L/mg).

3.3.2. Freundlich model :

The Freundlich [29] equation can be written as :

$$q_e = K_F C_e^{1/n_F} \quad \text{-----}(8)$$

where K_F is a constant indicative of the relative adsorption capacity of the adsorbent ($\text{mg}^{1-1/n_F} \text{L}^{1/n_F} \text{g}^{-1}$) and n_F is a constant indicative of the intensity of the adsorption. The Freundlich expression is an exponential equation and therefore it assumes that, as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases.

3.3.3. Khan model :

In many cases, the two simple isotherms presented above are not able to fit the experimental adsorption capacities over a large range of concentration. To overcome this, several equations have been proposed such as the ones of Toth [30] or of Radke and Prausnitz [31]. In the same way, Khan and co-workers have proposed a new equation which is expressed in the form [32] :

$$q_e = (q_{\max} b_K C_e) / (1 + b_K C_e)^{a_K} \quad \text{-----}(9)$$

This equation reduces to Langmuir isotherm or Freundlich isotherms when $a_K = 1$ or $b_K C_e \gg 1$ respectively.

4. Conclusions :

The adsorption of anionic dye 'Remazol Black B' on a microporous activated carbon felt (Actitex FC 1201) has been studied. The characterization of the surface chemistry of activated carbon fibers (ACF) by TGA and by the 'Boehm' method has shown the presence of oxygenated groups at the surface of the ACF which are mainly phenol groups.

The rates of adsorption of the dye on the ACF were measured, and it was observed that the process is controlled by intraparticle diffusion. In this case, about 10 % of the total adsorption capacity was reached in a very short time (less than 1 hour), then the adsorption uptake increases very slowly. This behavior was correlated with the textural properties of the carbon materials. A DFT analysis of the pore size distribution showed that the mean pore size is around 1 nm; this narrow pore size explains that a slow intraparticle diffusion process controls the adsorption.

The equilibrium adsorption isotherms of RB5 dye onto ACF were measured as a function of pH. The total adsorption capacity obtained was 20 mg/g for Remazol Black B dye. The Khan model gives the best agreements between experimental and computed values.

Thanks to the low pH-PZC of the ACF (4.8) and to the acido-basic properties of the dye, the adsorption of the anionic dyes is optimized in acidic conditions ($0 < \text{pH} < 3.8$) where the electrostatic attractions are stronger.

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