

## The Removal of Organic Pollutant from Aqueous Solution by Modified Activated Carbon Surface

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### Abstract

The removal of organic pollutant from aqueous solution was carried out by using modified activated carbon surface. Activated carbon was modified using chemical and physical treatment, such as using oxidizing agent ( $\text{HNO}_3$ ) and air oxidation, respectively. In this study, Rhodamine B was used as the organic pollutant. The results showed that activated carbon modified with air oxidation treatment rapidly attained the Rhodamine B adsorption after 30 minutes of contact time. Adsorption data are used for modelling, from the pseudo-first-order and pseudo-second-order kinetic equation and intra-particle diffusion models. The isotherm adsorption of Rhodamine B was fitted with Freundlich isotherm indicating that adsorption occurs on a heterogeneous surface through a multilayer adsorption mechanism. In addition, the intra-particle diffusion suggests that there were two stage mechanisms which contributed to the adsorption efficiency of Rhodamine B.

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## 1. Introduction

Organic matter as in synthetic dyes discharged from industries generate destructive characteristic such as toxic, carcinogenic and mutagenic [1]. The usage of Rhodamine B as one of synthetic cationic dye are vary, namely as a fluorescent material for water tracer [2], a biological stain in the lab [3] and as colorant for textile [4], printing and photographic industries [5]. In contrary, exposure of Rhodamine B causing some effect on our health, from irritation to chronic toxicity [6-8]. As a persistent organic matter, removal of dye is challenging task owing to their complex structure and high molecular weight [9]. Existing methods on removal of dye are separation process, including adsorption [3, 10-14] and degradation process [15]. Adsorption has gained its reputation as a significant, effective and efficient yet simple method [16-17]. Activated carbon (AC), known for its versatile usage as an adsorbent, can be enhanced its properties and activities by modification or activation [18-19]. Modification or activation are meant to accommodate alteration in physical (i.e. surface area and pore volume) and chemical (i.e. defect and functional groups) characteristics. There have been a lot of studies reported on preparation of modified or activated carbon, both via gasification and chemical agents [18-21]. However, most of the works used CO<sub>2</sub>, ozone or steam for the physical activation. Thus, here in we are reporting the utilization of air and acid as oxidizing agent for Rhodamine B adsorption with kinetic aspects being discussed.

## 2. Experimental

### 2.1. Materials

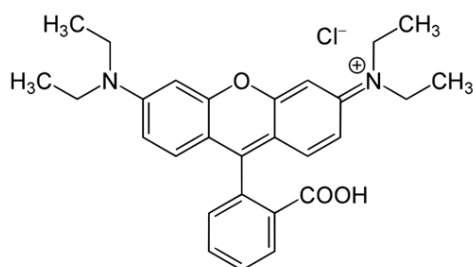
The chemicals required for this work were purchased from Wako Pure Chemical Industries, Ltd and Rhodamine B was obtained from Sigma-Aldrich. All chemicals were used without purification.

### 2.2. Preparation of Modified Activated Carbon Surface

Air and HNO<sub>3</sub> were utilized for preparation of the modified activated carbon surface. The preparation of air oxidized carbon was conducted according to Lina et al. (2018) [22]. As for chemical functionalized carbon: in typical carbon synthesis, 2.0 g of dried carbon was placed into round bottom flask and mixed with 20 mL of HNO<sub>3</sub> for 3h at 90 °C. The mixture was filtered and washed to neutralized the pH using distilled water and further dried at 110 °C overnight. HNO<sub>3</sub>-Carbon was obtained.

### 2.3. Adsorption of Rhodamine B in Aqueous Solution

A stock solution at a concentration 100 mg L<sup>-1</sup> was prepared. Absorption efficiency for Rhodamine B was performed by contacting 0.01 g of activated carbon with 20 mL of organic dye pollutant solutions. Samples were collected at interval times and filtered using filter paper (Whatman Grade 42), then analyzed using Uv-Vis spectrophotometer used wavelength of 554 nm. The chemical structure of Rhodamine B is shown in Figure 1.



**Figure 1:** Chemical structure of Rhodamine B

## 2.4. Characterization of Surface Chemistry

The numbers of acidic functional groups on the adsorbent can be identified using Boehm's titration [23]. For each analysis, 100 mg of catalyst was pretreated in 20 mL  $\text{NaHCO}_3$  and NaOH solution for 24 h at room temperature. Filtrate obtained from filtration of pretreated sample were used for back titration. Two drops of pH indicator (methyl orange) was added to a mixture of 5 mL of sample and 10 mL of HCl standard solution, turning them pinkish-red color and sonicated for one minute to remove dissolve  $\text{CO}_2$  generated by the decomposition of  $\text{NaHCO}_3$ . The samples were titrated with NaOH standard solution until all excess acid in the sample was consumed indicated by color changed from pinkish-red to yellow. The quantity of acidity of various type were determined from the assumption that  $\text{NaHCO}_3$  reacts with carboxylic groups and NaOH reacts with carboxylic, lactonic and phenolic groups.

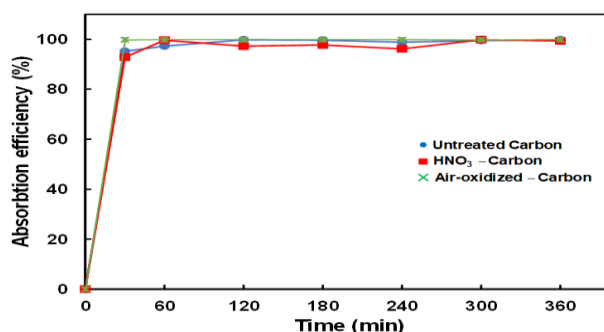
## 3. Results and discussion

### 3.1. Surface Functional Groups

The surface of AC gained considerable amount of oxygenated functional groups through modification using oxidizing agent, i.e. air [24] and  $\text{HNO}_3$  [16, 25]. This oxygenated groups give the acidity of carbon increased. Number of acidic functional groups such as phenols, carbonyls, carboxylic acid, lactones and anhydrates can be detected and quantified using Boehm titration [25]. The results of Boehm titration showed that surface functional groups increased greatly compared to untreated activated carbon, that was 2.64 and 3.38  $\text{mmol g}^{-1}$  for air-oxidized carbon and  $\text{HNO}_3$ -carbon, respectively, compared to 0.35  $\text{mmol g}^{-1}$  for untreated carbon [22]. The increased of oxygenated functional group due to modification or activation by gasification showed different results with some reported works. Gasification which involving two steps namely carbonization and activation are reported to enhance the porosity of AC [20] and destroyed oxygen surface functional groups since it is unstable at high temperatures [26]. Meanwhile, result of the treated AC with  $\text{HNO}_3$  as oxidizing agent agrees with most of other studies. That is the acidic treatment increased the density of oxygen complexes which is weakly acidic functional groups [27].

### 3.2. Removal of Rhodamine B

A study of the effect of contact time on the adsorption of Rhodamine B in solution by carbons was performed and the results are shown in Figure 2. The adsorption of dyes on various carbons is rapid at the initial period of contact time and then becomes slow and stagnate with the increase in contact time. It took about 30 min for the uptake of the dye before reaching equilibrium state where the amount of dye adsorbed was negligible [28]. It is worth to notice that air-oxidized carbon showed comparable adsorption capacity with  $\text{HNO}_3$ -carbon and untreated carbon. This phenomenon might be due to the electronic interaction between active site of activated carbon which mostly like more negatively charge (carboxyl and epoxy) with the organic dye contaminant.



**Figure 2:** Adsorption of Rhodamine B on activated carbon. (●) Untreated carbon, (■) HNO<sub>3</sub>-carbon and (x) Air-oxidized carbon

As shown in Figure 1, the Rhodamine B are more likely positively charge so that it will have strong attraction to the negatively charge of the active site of AC, resulting high adsorption capacity. In addition, the results of this study suggested that AC obtained from gasification with air and chemical activation posses weakly acidic functional groups are excellent adsorbent. This result is in contrast with other studies that showed declining in AC adsorption capacity. Their adsorbent lost the active adsorption sites after 2 h when the equilibrium state attained [11-12].

### 3.3. Adsorption Kinetics

Pseudo-first-order, pseudo-second-order and intraparticle diffusion were applied to analyze the adsorption behavior of Rhodamine B onto various activated carbon. The non-linear form of the pseudo-first-order equation is expressed as follows [29]:

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

where the  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) are the sorption capacities at equilibrium and at time  $t$  (min), respectively,  $k_1$  (min<sup>-1</sup>) is the rate constant of the pseudo-first-order model. The non-linear form of the pseudo-second-order equation is expressed as:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of the pseudo-second-order model.

According the adsorption results, Rhodamine B adsorption followed the pseudo-second-order model with  $R^2$  value is 1 for three different activated carbon. The parameters of adsorption kinetics are presented in Table 1.

**Table 1:** Pseudo-first-order and pseudo-second-order kinetic parameters

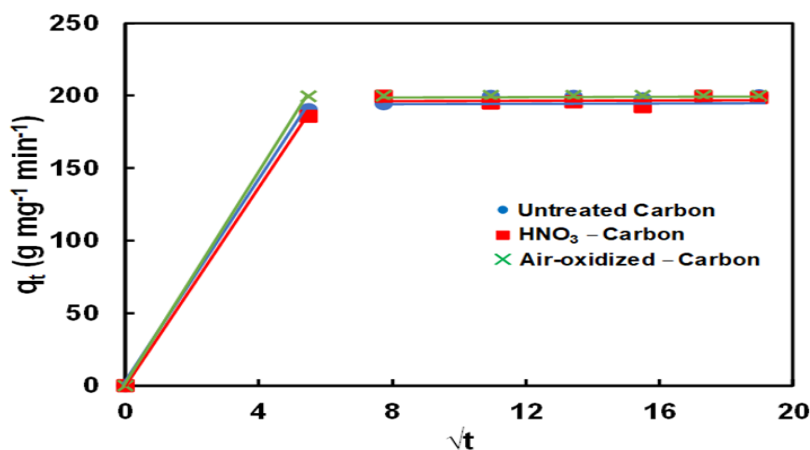
Adsorbent	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
	Rhodamine B							
	$q_e$ , exp (mg	$q_e$ , cal (mg	$k_l$	$R^2$	$q_e$ , exp (mg	$q_e$ , cal (mg	$k_2$	$R^2$
	g <sup>-1</sup> )	g <sup>-1</sup> )	(min <sup>-1</sup> )		g <sup>-1</sup> )	g <sup>-1</sup> )	(g mg <sup>-1</sup> min)	
Untreated Carbon	199.726	2.845	0.007	0.186	199.726	200	0.003	0.999
HNO <sub>3</sub> -Carbon	198.706	1.197	0.001	0.044	198.706	200	0.002	0.999
Air-oxidized Carbon	199.758	41.286	0.025	0.160	199.760	200	0.500	1.000

The overall adsorption process may indeed be controlled either by one or more steps, namely film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [30] which is described:

$$q_t = k_{id} \sqrt{t} + C \quad (3)$$

where,  $q_t$  is the amount of ion/dye molecule adsorbed per unit mass of adsorbent (mg g<sup>-1</sup>) at a time  $t$  and  $k_{id}$  the intra-particle diffusion rate constant (mg/g.min<sup>-1/2</sup>) [31]. The intra-particle diffusion of Rhodamine B adsorption is

presented in Figure 3. The adsorption process was occurred in two stage mechanisms. First is the external mass transfer surrounding the particles which happened at the early stage of adsorption. This first stage is represented by the first sharp line of the Figure 3 indicated the macropore and mesopore diffusion. The second stage which also depicted as the second linear portion (Figure 3) is the gradual adsorption stage with controlling intra-particle diffusion.



**Figure 3:** The intra-particle diffusion model for Rhodamine B

## 4. Conclusion

Surface modification using the oxidizing agent, HNO<sub>3</sub> and air oxidizing on carbon increased the acidity of the surface by forming more oxygenated functional group. These modified carbons were successfully removed dye, Rhodamine B, within first 30 min. Dynamic adsorption of Rhodamine B adsorption was followed the pseudo-second-order kinetic model and the two stages of adsorption mechanism were involved according intra-particle diffusion model.

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