

## Adsorption of Remazol Black 5 and Indigo Carmine on Corn Cobs Activated Carbon: Kinetic, Equilibrium, and Thermodynamic Studies

Abo Essis Armand<sup>1</sup>, Kouakou Yao Urbain<sup>2\*</sup>, Yobouet Yao Augustin<sup>3</sup>, Trokourey Albert<sup>1</sup>

<sup>1</sup>UFR SSMT, Laboratoire de Chimie Physique, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire, <sup>2</sup>UFR Sciences et Technologies, Université de Man, BP 20 Man, Côte d'Ivoire, <sup>3</sup>Ecole Normale Supérieure (ENS), Laboratoire de Chimie des Eaux (LCE), 08 BP 10, Abidjan 08, Côte d'Ivoire

### ABSTRACT

In the present work, the study of the adsorption of Indigo Carmine (IC) and Remazol black 5 (RB5) dyes on activated carbon produced from corn cobs (corn cob activated carbon [CCAC]) was performed. The adsorption kinetics of each dye followed a pseudo-second-order kinetic model with high correlation coefficients ( $R^2 > 0.99$ ) with 30 min as equilibrium time. Parameters such as the initial dye concentration, the initial pH of the solution and the temperature were well investigated. The amount of dyes adsorbed increases with the initial concentration and decreases with the increase of pH. The optimal pH is therefore 2. For an initial concentration of 25 mg/L, the rate of elimination at pH = 2 is 99.96% and 96.92%, respectively, for IC and RB5 at 25°C. The adsorption of these dyes also increases with temperature. With an initial concentration of 100 mg/L, the percentage dye uptake increased from 62.14% at 25°C to 99.99 % at 70°C for IC and from 47.12% at 25°C to 99.93 % at 70°C for RB5. These adsorption processes are spontaneous and endothermic. The Freundlich and Langmuir models well describe the phenomenon of adsorption which is physisorption in nature. When IC and RB5 are mixed, the adsorption capacity of CCAC decreases.

**Key words:** Corn cobs activated carbon, Adsorption, Thermodynamics, Kinetics, Indigo carmine, Remazol black 5.

### 1. INTRODUCTION

Dyes are widely used in various fields of activity, particularly in the textile industry, paper, and plastics industries, and in the food industry to color their final products. This massive use is not without consequences for the environment. Indeed, dyes induce several types of pollution. Apart from its messy and unwanted appearance, the presence of dyes in water is a source of problems for fish and aquatic animals due to the reduction of light penetration and their toxicity [1]. Many of these dyes are toxic, non-biodegradable, carcinogenic and mutagenic for aquatic systems, and human health [2]. The difficulty of eliminating dyes is one of the major issues in their use. A variety of methods have been used for removing dyes from wastewater, such as coagulation, precipitation, oxidation, electrochemical process, and adsorption [3,4]. Among these techniques, adsorption is widely used due to its efficiency and ease of implementation. The successful removal of dyes with activated carbon [5], bentonite [6], and nontronite mineral [7] has been carried out by several researchers. However, one of the major problems with this process remains the relatively high production cost of adsorbent. The use of agricultural waste is one of the possibilities for reducing the cost of production. Thus, activated carbons from coconut shells [8], ricinodendron heudelotii shells [9], walnuts shells [10], and banana peels [11] were produced.

The main aim of this study is to remove two dyes, remazol black 5 (RB5) and indigo carmine (IC) from an aqueous solution using corn cobs activated carbon as a new low cost adsorbent. For this reasons, the kinetic study was carried out as well as the study of the influence of pH, temperature, amount of adsorbent, and dyes concentration. In addition, we determined the thermodynamic parameters and modeled the adsorption phenomenon.

### 2. MATERIALS AND METHODS

#### 2.1. Adsorbent

The adsorbent used in this work is the best activated carbon obtained from the optimization of the production of activated carbon from corn cobs by chemical activation using KOH and H<sub>3</sub>PO<sub>4</sub> following a plan of experience [12]. The characteristics of this activated carbon are given in Table 1.

#### 2.2. Chemical Agents and Equipment

IC and RB5 were chosen as organic anionic dyes in this study. Their chemical structures and general characteristics are shown in Table 2. The dyes were supplied by Chimtec Textile Company (Cote d'Ivoire) and of 100% purity

All reagents were of analytical grade and were used as received without any purification.

Sodium hydroxide (99%) was purchased from Scharlau (European Union) and hydrochloric acid (37%) from Carlo Erba (France).

The Hach 3900 spectrophotometer was used to determine the concentrations of dyes in solution.

#### \*Corresponding author:

E-mail: [urbainyk@gmail.com](mailto:urbainyk@gmail.com)

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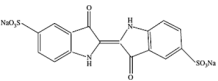
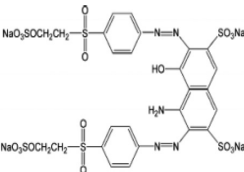
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**Table 1:** Characteristics of corn cob activated carbon.

Parameters	Values
Ash content	6%
Surface area (m <sup>2</sup> /g)	613
Iode number (mg/g)	674
pH <sub>ZC</sub>	5.3
Carboxyl (mmol.g <sup>-1</sup> )	1.48
Lactonic (mmol.g <sup>-1</sup> )	1.90
phenolic (mmol.g <sup>-1</sup> )	2.02
Acidic (mmol.g <sup>-1</sup> )	5.40
Basic (mmol.g <sup>-1</sup> )	2.05

**Table 2:** Characteristics of two used dyes.

Characteristics	Indigo carmine	Remazol black 5
Structure		
Formula	C <sub>16</sub> H <sub>8</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>8</sub> S <sub>2</sub>	C <sub>26</sub> H <sub>21</sub> N <sub>5</sub> Na <sub>4</sub> O <sub>19</sub> S <sub>6</sub>
Molecular weight (g.mol <sup>-1</sup> )	466.3	991.8
λ <sub>max</sub> (nm)	610	596

### 2.3. Effect of Contact Time and Initial Dye Concentration

In this study, the relationship between contact time and dye removal efficiency at different initial concentrations of solution was conducted. The study is performed by varying the initial concentration of each dye from 25 mg/L to 100 mg/L. A mass of 0.25 g of activated carbon was mixed with 25 mL of the dye solution (RB5; IC) of different concentrations in a 100 mL conical flask. The pH was adjusted to 2 at 25°C. These mixtures were shaken on magnetic agitator at 150 rpm for intervals time of 5 and 60 min. Centrifugation for the separation of activated carbon and adsorbate is carried out for 15 min in a centrifuge. The residual concentrations of the filtrates are determined using a Hach 3900 spectrophotometer.

The amount of dye adsorbed onto carbon is calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)}{m} x V \quad (1)$$

Where  $q_t$  is the amount of dye (RB5; IC) adsorbed by activated carbon (mg/g);  $C_0$  and  $C_t$  are, respectively, the initial and the final concentration of dye at time after filtration (mg/L);  $V$  is the initial solution volume (L);  $m$  is the mass of the activated carbon (g).

### 2.4. Effect of Activated Carbon Dose and pH

To determine the influence of the mass of activated carbon, 25 mL of IC and remazol solution of 25 mg/L concentration at pH = 2 were mixed with different masses of activated carbon. The mixture is stirred at the speed of 150 rpm using a mechanical stirrer for 30 min at a temperature of 25°C. The mixture is separated as in the previous process and analyzed.

For the influence of the pH, the study was carried out at 25°C with a concentration of 25 mg/L of dyes by varying the pH from 2 to 12 by adjusting with hydrochloric acid or with sodium hydroxide, for a time

of 30 min following a protocol similar to the study of the effect of the carbon dose.

### 2.5. Adsorption Kinetic and Equilibrium of IC and RB5 and Thermodynamic Studies

To model the kinetics and isotherm of adsorption of IC and RB5 dyes on activated carbon, a series of experiments were carried out. Thus, the study of the influence of temperature in interaction with the initial concentration of dyes at different contact times was carried out under the following conditions. A 0.25 g mass of activated carbon is brought into contact with 25 mL of dye solution (IC or RB5) of different concentrations (25 mg/L; 50 mg/L; 75 mg/L; and 100 mg/L) in Erlenmeyer flasks. The pH of the mixture is maintained at pH = 2. The Erlenmeyer flasks are then closed, placed in a thermostatic bath (SHZ88-1 China), at temperatures between 28 and 70°C (28°C, 40°C, 50°C, 60°C, and 70°C) and stirred regularly for predetermined times (5 min, 10 min, 20 min, 30 min, and 60 min). After the equilibrium time, samples were filtered and analyzed by spectrophotometer Hack 3900. The amount of IC and RB5 adsorbed per unit mass of activated carbon at equilibrium,  $q_e$ , was calculated by:

$$q_e = \frac{(C_0 - C_e)}{m} x V \quad (2)$$

Where  $C_0$  and  $C_e$  are the concentrations of dye at initial and equilibrium times, respectively;  $V$  is the volume of the (L); and  $m$  is the mass of activated carbon used (g).

## 3. RESULTS AND DISCUSSION

### 3.1. Adsorption of Dyes

#### 3.1.1. Kinetic study of adsorption

The study of the kinetics of adsorption of dyes on activated carbon was carried out with different concentrations. The curves in Figure 1 show that the concentrations of IC and RB5 decrease as a function of time. It was found that more than 75% removal of dyes concentration occurred in the first 10 min, and thereafter the rate of adsorption was found to be slow. There is a rapid saturation of the active sites of the carbon by these dyes. The rate of adsorption was fast due to the higher availability of vacant surfaces. After saturation of these active sites, the dyes entered the pores of the adsorbent with a slower rate to reach the equilibrium time. The equilibrium time is 30 min for the RB5 and for the IC. This carbon has an excellent affinity with these dyes.

To determine the mechanism of adsorption, three kinetic models were applied under different experimental conditions. In this purpose, several kinetic models including the pseudo-first-order equation, the pseudo-second-order equation, and intraparticle diffusion model [13,14] were tested here to find out adsorption mechanism,

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$q_t = k_i t^{1/2} + c \quad (5)$$

Where  $q_t$  is the amount of dye adsorbed at time  $t$  in (mg/g),  $q_e$  is the amount of dye adsorbed at equilibrium in (mg/g),  $t$  is the contact time in (min),  $k_1$  is the first-order reaction rate constant of adsorption of dye on activated carbon in (min<sup>-1</sup>),  $k_2$  is the rate constant of the pseudo-second-order model,  $k_i$  is the intraparticle diffusion constant (mg/g min<sup>1/2</sup>), and  $c$  is the intersection of the line with the axis of ordinates provides information on the thickness of the boundary layer of intraparticle diffusion model.

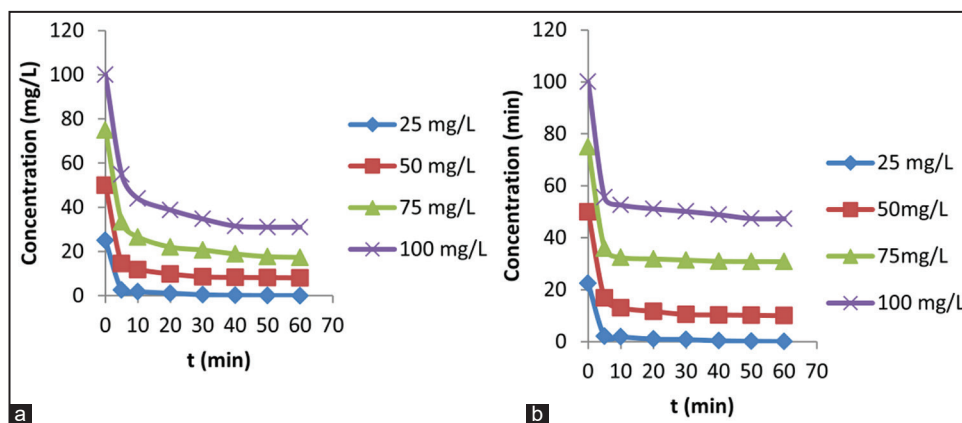
To evaluate the applicability of these models, we have plotted  $\ln(q_e - q_t)$  versus  $t$  for the pseudo-first-order reaction,  $\frac{t}{q_t}$  versus  $t$  for the pseudo-second-order reaction and  $q_t$  versus  $t^{1/2}$  for the intraparticle diffusion reaction. The representations of the curves are shown by Figure SM1. The values of  $k_1$ ,  $q_{e,cal1}$ ,  $R_1^2$  (correlation coefficient for pseudo-first order adsorption kinetics),  $k_2$ ,  $q_{e,cal2}$ ,  $R_2^2$  (correlation coefficient for pseudo-second order adsorption kinetics), and  $k_i$ ,  $c$ ,  $R_i^2$  (correlation coefficient for intraparticle diffusion model) were calculated and summarized in Table 3. According the values from this table, the model of pseudo-second order (Figure SM1) with a good correlation coefficient ( $R_2^2$  between 0.9996 and 1.000) is suitable to describe the adsorption kinetic of IC and RB5 onto corn cob activated carbon (CCAC). In addition, it can be seen that the adsorbed quantities calculated by this model are closer to the quantities adsorbed experimentally. Similar results were obtained by adsorption of IC on rice husk ash [15] and adsorption of RB5 onto biosorbent based on canola stalks [16].

**3.2. Study of the Influence of Some Factors on the Removal of IC and RB5**

**3.2.1. Effect of pH solution**

The influence of pH on the removal of IC and RB5 by the activated carbon is shown in Figure 2. As can be seen in the figure, the

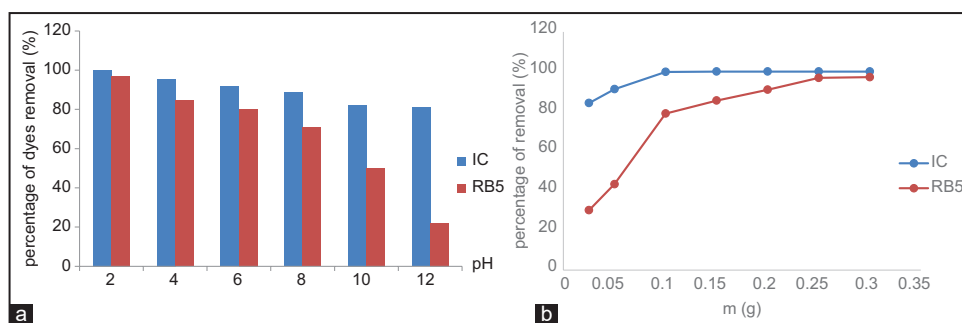
percentages of IC and RB5 removal increase respectively to 99.96% and 96.92% at pH = 2, and decreases slightly with increasing pH and reaches the limit values of 80.89% and 22.03% at pH = 12, respectively, for IC and RB5. These results show that the adsorption is strongly pH-dependent. The maximum elimination of these two dyes is obtained at pH 2. The  $pH_{PZC}$  value for CCAC which is 5.3 confirms the ranges of optimal pH values for dyes removal. At a solution pH lower than  $pH_{PZC}$ , the surface charge of the activated carbon is positively charged, while at a higher solution pH, the surface charge of the activated carbon becomes negative. Therefore, at a lower pH, an excess of proton ( $H^+$ ) in solution will be available, thus increasing the electrostatic attraction between the positively charged adsorption sites of CCAC and the coloring anions thus causing an increase in the capacity of adsorption of IC and RB5 dyes [5,15]. When the pH of the solution increases, that is, to say higher than the  $pH_{PZC}$ , the number of negatively charged sites increases and the number of positively charged sites of CCAC decreases. A negatively charged surface site on the adsorbent does not promote adsorption of coloring anions due to electrostatic repellency [17]. The significant decrease in the adsorption rate of RB5 and IC in the alkaline pH zone could be justified by the presence in excess of  $OH^-$  ions which compete with anionic dyes at the adsorption sites. In addition, the decrease in the adsorption rate of dyes with increasing pH could also be attributed to competitive adsorption



**Figure 1:** Evolution of (a) indigo carmine and (b) Remazol black 5 concentration as a function of time (Conditions: mass of IC = mass of RB5= 0.25 g; pH = 2; T = 28°C).

**Table 3:** Values of parameters of the three applied kinetics models for dyes.

	IC				RB5			
Concentration (mg/L)	25	50	75	100	25	50	75	100
$q_{e,exp}$ (mg/g)	2.4832	4.2810	6.1265	7.5211	2.3425	4.1211	4.7225	5.6215
Pseudo-first order								
$k_1$ ( $min^{-1}$ )	0.0936	0.0951	0.0776	0.1403	0.0637	0.0792	0.0913	0.0953
$q_{e,cal1}$ (mg/g)	0.5206	1.0012	2.4065	7.2062	0.3315	0.7682	0.6458	1.7805
$R_1^2$	0.9767	0.9914	0.9517	0.8921	0.951	0.9657	0.9683	0.9315
Pseudo-second order								
$k_2$ (g/mg.min)	0.4331	0.2098	0.0668	0.0418	0.4699	0.2246	0.3387	0.1257
$q_{e,cal2}$ (mg/g)	2.5368	4.2771	5.9916	7.3099	2.5169	4.0733	4.4683	5.3937
$R_2^2$	0.9999	1.0000	0.9998	0.9996	0.9999	1.0000	1.0000	0.9998
Intraparticle diffusion								
$k_i$ ( $mg/g \ min^{1/2}$ )	0.0482	0.1122	0.2709	0.4112	0.0381	0.1086	0.0775	0.1483
$c$	2.1610	3.4261	3.8516	4.0583	2.2087	3.2544	3.8951	4.2097
$R_i^2$	0.9351	0.8596	0.8956	0.8873	0.9785	0.8027	0.7283	0.9448



**Figure 2:** Effect of solution pH on RB5 and IC adsorption (a) and effect of adsorbent dose on RB5 and IC removal (b).

between anionic dyes and excess  $\text{OH}^-$  ions in solution. Indeed, the high concentration and the high mobility of  $\text{OH}^-$  ions would promote their adsorption compared to dyes. The negatively charged surface of the carbon would not promote the adsorption of anionic molecules of RB5 and IC due to electrostatic repulsion [18]. There is, thus, a decrease in the quantity of dyes adsorbed on CCAC at alkaline pH.

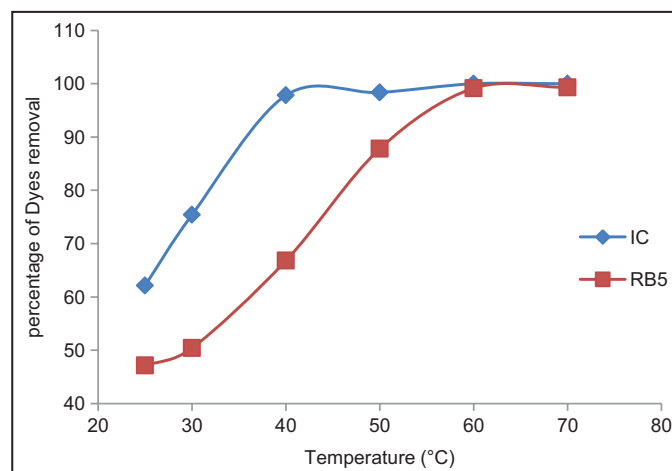
This indicates that adsorption is mainly due to a physical process. Some authors have made the same observation [19,20]. The adsorption of these dyes is better in an acidic environment ( $\text{pH} = 2$ ) and whatever the pH value, IC adsorbs more than RB5. This could be due to the size of the dye molecules. In fact, the surface area occupied by an IC molecule is  $197 \text{ \AA}^2$  and that of RB5 is  $462 \text{ \AA}^2$ . Thus, several molecules of IC can be absorbed than RB5.

### 3.2.2. Effect of adsorbent dose

The effect of activated carbon dose on the elimination of IC and RB5 was studied by varying the mass of CCAC (from 0.025 to 0.3 g). The results obtained are shown in Figure 2. Experimental results show that the removal percentages of the two dyes increase as the amount of activated carbon increases. We have an almost total elimination of IC when the quantity of activated carbon goes from 0.025 g to 0.2 g. Indeed, the adsorption rate drops from 84.12 to 100% for IC. As for the RB5 dye, the removal rate goes from 30.15 to 97.18% for an amount of added activated carbon ranging from 0.025 g to 0.3 g. The increase in the adsorption percentage of IC observed as a function of the amount of CCAC is due to the availability of free adsorption sites (the area of the available surface) which increases with the amount of adsorbent until the mass 0.15 g [21]. At low doses of CCAC, anions of the IC dye readily access carbon adsorption sites, resulting in the amount adsorbed rapidly increasing with the mass of activated carbon. Beyond this mass, the number of accessible free sites becomes stable. The addition of CCAC adds the number of free sites, but these additional additions result in the formation of agglomerations of the activated carbon particles, and exclude some CCAC particles from the adsorption process; the adsorption percentage thus remains constant up to 0.3 g of added CCAC [22]. The main factor explaining this characteristic is that the adsorption sites remain unsaturated during the adsorption reaction while the number of sites available for the adsorption site increases with increasing the dose of activated carbon. This result is similar to that of Wang (2018) [23]. In addition, we note that regardless of the mass of activated carbon, the rate of adsorption of IC is relatively faster and greater than that of RB5. This could be explained by the mechanisms involved in the adsorption of each dye. Indeed, it has been noted that IC has the advantage of involving two adsorption mechanisms probably favoring its retention and therefore higher absorption rates

### 3.2.3. Effect of temperature on adsorption

The influence of temperature on the adsorption of IC and RB5 on activated carbon was evaluated. As shown in Figure 3, percentage dye uptake increased from 62.14% at  $25^\circ\text{C}$  to 99.99% at  $70^\circ\text{C}$  for IC and from 47.12% at  $25^\circ\text{C}$  to 99.93% at  $70^\circ\text{C}$  for RB5. For temperatures



**Figure 3:** Percentage of indigo carmine (IC) and Remazol black 5 (RB5) removal as a function of temperature (Conditions: mass of IC = mass of RB5 = 0.25 g;  $\text{pH} = 2$ ;  $C = 100 \text{ mg/L}$ ).

below  $60^\circ\text{C}$  and under the same operating conditions, IC adsorbs more than RB5. From  $60^\circ\text{C}$ , we see the same adsorption rate of dyes which is almost 100%. Hence, the adsorption of these different dyes increases with temperature.

This characteristic may be attributed to the decrease in viscosity of the solution at higher temperature that caused rapid diffusion of the dye molecules from the liquid phase to the external boundary layer and surface cavities of the adsorbent particles. Moreover, change in temperature alters the saturation capacity of the adsorbent for a particular adsorbate [24]. This designates that the adsorption of IC and RB5 by CCAC was endothermic process [25].

### 3.3. Study of Adsorption at Equilibrium

The study of the adsorption of IC and RB5 on activated carbon was carried out at  $25^\circ\text{C}$ . The amount of dye adsorbed at equilibrium per mass of carbon is given in Figure SM2. The amount of dyes adsorbed increase with the concentration at equilibrium.

This isotherm appears to be type I according to the IUPAC classification, justifying the microporous aspect of the carbon used.

To study the adsorption phenomenon, two models were used namely the Freundlich model and the Langmuir model [26].

The empirical Freundlich equation is written:

$$q_e = K_F C_e^{1/n} \quad (6)$$

$C_e$  (mg/L) is the concentration of adsorbate at equilibrium in the residual solution,  $K_F [(\text{mg/g})(\text{L/mg})^n]$  and  $n$  (unitless) are

Freundlich's constants depending on the adsorption capacity, the bodies present and the temperature.

The linear form of the Freundlich model is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

The Langmuir equation is:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{8}$$

With  $b$  the Langmuir thermodynamic constant linked to the free energy of adsorption,  $q_e$  (mg/g) the quantity of solute adsorbed per unit mass of adsorbent at equilibrium, and  $q_m$  (mg/g) the quantity of solute adsorbed per gram of solid required to cover the surface of the adsorbent with a monomolecular layer or maximum adsorption capacity.  $C_e$  (mg/L) represents the residual concentration of the solute at equilibrium.

There are several linear forms of the Langmuir model, one of the most frequently used is:

$$\frac{1}{q_e} = \frac{1}{b q_m} \frac{1}{C_e} + \frac{1}{q_m} \tag{9}$$

The application of the linear form of the Freundlich model made it possible to draw the curve

$\ln q_e = f(C_e)$  (Figure SM2). The values of the parameters of this curve are grouped together in Table 4. The linear correlation coefficient is  $>0.97$  and  $n$  is close to 1. The adsorption is favorable. The Freundlich model can be used to describe the adsorption of IC and RB5 on this carbon, reflecting the heterogeneity of the surface of this carbon [27].

In Figure SM2, we have represented  $\frac{1}{q_e} = f\left(\frac{1}{C_e}\right)$ . The Langmuir

linear correlation coefficient is  $>0.98$  (Table 4). Langmuir's model can, therefore, be used to describe the adsorption of these dyes onto this carbon.

### 3.4. Determination of Thermodynamic Parameters

The main criterion for knowing the nature of the adsorption phenomenon is the determination of the thermodynamic parameters. For the determination of the free energy ( $\Delta G^\circ$ ), the enthalpy ( $\Delta H^\circ$ ) and the entropy ( $\Delta S^\circ$ ) of adsorption of IC and RB5 on activated carbon, the following equations were used [28]:

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{T} \tag{10}$$

$$\Delta G^\circ = -RT \ln\left(\frac{q_e}{C_e}\right) \tag{11}$$

Where  $q_e$  (mg/g) is the amount of dyes adsorbed at equilibrium,  $C_e$  (mg/L) is the concentration of dyes at equilibrium,  $T$  is the temperature, and  $R$  ( $8.314 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ ) is the ideal gas constant.

The curve  $\ln\left(\frac{q_e}{C_e}\right)$  as a function of  $1/T$  is represented in Figure SM3.

The use of the data of these lines made it possible to determine the thermodynamic parameters of adsorption and grouped together in Table 5.

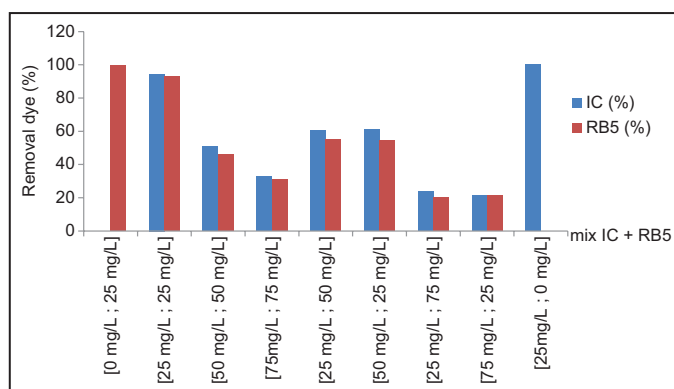
**Table 4:** Equilibrium adsorption isotherm parameters for dyes sorption onto CCAC.

Model Dyes	Langmuir			Freundlich		
	R <sup>2</sup>	qm (mg/g)	b	R <sup>2</sup>	lnk	1/n
IC	0.9726	6.917	0.4033	0.9855	3.6438	0.2508
RB5	0.993	5.761	0.2343	0.9925	3.0135	0.2685

**Table 5:** Values of the thermodynamic parameters of the adsorption of IC and RB5 on activated carbon.

Dyes	Concentration	Temperature (K)	$\Delta G^\circ$ (KJ. mol <sup>-1</sup> )	$\Delta H^\circ$ (KJ. mol <sup>-1</sup> )	$\Delta S^\circ$ (J.mol <sup>-1</sup> . K <sup>-1</sup> )
IC	25 mg/L	301	-5.45	9.43	281.11
		313	-10.92		
		323	-12.36		
		333	-14.67		
	50 mg/L	301	-1.38	19.34	528.97
		313	-4.34		
		323	-10.53		
		333	-15.33		
	75 mg/L	301	-3.53	18.47	495.24
		313	-0.37		
		323	-5.11		
		333	-12.75		
100 mg/L	301	-0.88	14.13	366.71	
	313	-4.17			
	323	-5.72			
	333	-6.64			
RB5	25 mg/L	301	-1.32	7.21	195.30
		313	-1.97		
		323	-3.27		
		333	-4.44		
	50 mg/L	301	-4.06	8.40	216.04
		313	-2.78		
		323	-1.21		
		333	3.25		
	75 mg/L	301	-0.23	7.12	177.66
		313	-1.96		
		323	-3.63		
		333	-5.49		
100 mg/L	301	-3.90	6.68	156.06	
	313	-4.56			
	323	-6.77			
	333	-8.58			

The enthalpy ( $\Delta H^\circ$ ) is positive. The adsorption process is, therefore, endothermic. The positive values of  $\Delta S$  indicated that the randomness of the solid/solution interface increased during the adsorption process [29]. The free energy ( $\Delta G^\circ$ ) is negative, which reflects the spontaneity of the adsorption phenomenon. There is, therefore, a good affinity between



**Figure 4:** Influence of the mixture of dyes on the adsorption process (Conditions: mass of indigo carmine = mass of Remazol black 5 = 0.25 g; pH = 2; T = 28°C).

activated carbon and IC and RB5 [30]. For  $\Delta G^\circ > -20 \text{ kJ.mol}^{-1}$ , we have physisorption, while a value below  $-40 \text{ kJ.mol}^{-1}$  means that we have chemisorption. Furthermore, a free energy value between  $-40$  and  $-20 \text{ kJ.mol}^{-1}$  suggests that physisorption and chemisorption are both responsible for the adsorption phenomenon [28,31]. All the values of the free energy being  $> -20 \text{ kJ/mol}$ , the phenomenon is, therefore, of the physisorption type. This result is in agreement with the applicability of the Freundlich model seen in the adsorption models section.

### 3.5. Mixing and Selectivity of Dyes

Since wastewater containing dyes is usually dye mixtures, we investigated the influence of mixing RB5 and IC dyes on the adsorption capacity of CCAC. To do this, the aqueous solutions of dyes of different concentrations are brought into contact with a fixed mass of carbon of 0.25 g, at pH = 2, for 60 min and at a temperature of 27°C. The results obtained are presented in Figure 4.

By analyzing this figure, we can see that the presence of another dye causes a decrease in the adsorption of each dye. Indeed, under the same experimental conditions, when moving from a single dye to two in solution, the adsorption rate drops from 99.99% to 21.53% and from 99.6% to 21.12%, respectively, for the IC and for the RB5. This result can be explained by the fact that the presence of another dye causes an increase in the initial concentration of dye to be adsorbed by the fixed mass of carbon, thus causing a reduction in the retention of each dye. We can also cite other factors involved in this phenomenon such as: The interaction between the dyes in solution, modification of the surface charge of the adsorbent due to adsorption and competitive adsorption between the dyes for the active sites on the adsorbent surface, causing displacement effects to replace other dyes at adsorption sites. A similar phenomenon has been observed in some studies of the adsorption of mixed dyes to activated carbons [32,33]. Moreover, regardless of the composition of the mixture, IC remains relatively better adsorbed. In addition, the results confirm that when the initial concentration of both IC and RB5 increases, the adsorption rate decreases, confirming the results previously obtained. It is noted that the composition which gives the best levels of adsorption is that in which there is 25 mg/L of IC and 25 mg/L of RB5. The removal rate of dyes is 94.45% and 92.75%, respectively, of the rate of elimination of IC and RB5.

## 4. CONCLUSION

In the present study, activated carbons from corn cobs prepared by chemical activation (CCAC) have been used as an adsorbent for the removal of IC and RB5 from aqueous solutions. CCAC shows promising adsorption capacity for IC and RB5. Adsorption was

influenced by various parameters such as initial pH, temperature, and adsorbent dose. The maximum uptake of IC and RB5 by CCAC occurred at an initial pH of 2.0. At 60°C, the elimination of dyes is almost total for a concentration of up to 100 mg/L. The kinetics studies indicated that the adsorption of IC and RB5 on this adsorbent follows a pseudo-second-order model better than a pseudo-first-order model and intraparticle diffusion. The interlayer diffusion is not the rate-determining step in the IC and RB5 adsorption mechanism. The adsorption isotherm data fits reasonably well for Freundlich and Langmuir isotherm models with good correlation coefficient. The surface of the carbon is heterogeneous with non-uniform adsorption. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  of adsorption. The results confirmed those of the adsorption models and Kinetics study. The moderate uptake of dyes and values of free energy ( $-20 \text{ kJ.mol}^{-1} < \Delta G^\circ < 0$ ) indicates that the rate determining step could be physisorption in nature. The thermodynamic parameters show that the adsorptions process are endothermic and a spontaneous nature. The presence of one of the two dyes in the same solution as the other influences the adsorption of the latter. An optimal composition for simultaneous removal of IC and RB5 from wastewater is 25 mg/L for each dye with the same volume for a mass of 0.25 g of CCAC. Thus, continuous adsorption using activated carbon obtained from Corn Cobs may be considered an inexpensive and environmentally friendly process for the elimination of IC and RB5 from wastewater.

## 5. COMPETING INTERESTS

The authors have declared that no competing interests exist.

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#### \*Bibliographical Sketch



Dr. Kouakou Y. Urbain, obtained Baccalaureate in Mathematics and Physical Sciences at the Lycée Classique de Bouaké. He obtained a master's degree in Physical Sciences from the University of Cocody in 2007 and a Diploma of Advanced Study in Physical Chemistry in 2010. He completed his doctorate in Physical Chemistry from the University Félix Houphouët Boigny in 2015. He has published 10 research articles internationally. His main areas of research are the study of surface phenomena, theoretical chemistry, the synthesis and research of adsorbents and water treatment. He is an Assistant Professor in the Chemistry Department at the University of Man in Ivory Coast.