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Dyes removal from water using low cost adsorbents

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Abstract. In this study, the removal capacity of low cost adsorbents during the adsorption of Methylene Blue (MB) and Congo Red (CR) at different concentrations (50 and 100mg·L⁻¹) was evaluated. These adsorbents were produced from wood wastes (cedar and teak) by chemical activation (ZnCl₂). Both studied materials, Activated Cedar (AC) and activated teak (AT) showed a good fit of their experimental data to the pseudo second order kinetic model and Langmuir isotherms. The maximum adsorption capacities for AC were 2000.0 and 444.4mg·g⁻¹ for MB and CR, respectively, while for AT, maximum adsorption capacities of 1052.6 and 86.4mg·g⁻¹ were found for MB and CR, respectively.

1. Introduction

Dyes discharges to water bodies from different industrial sectors has led to the detriment of aquatic ecosystems by micro-toxicity. Due to this, the regulation related to the amount of dyes in water is every day more strict [1]. With the above mentioned, research related to new and efficient procedures to dyes removal from water is increasing. Biological and chemical methods are the most common to solve this problem. However, they generate high amounts of waste, have low selectivity and have high costs. Therefore, adsorption methods arise as suitable technologies because they are cost-effective and easy to operate. The most important challenge here is to find a selective, renewable and economical adsorbent material [2].

Agroindustry wastes become in a suitable source for the development of activated carbon to dyes removal. Some authors such as, Duman, D. *et. al.* [1] and Hameed, B. *et. al.*[3] produced activated carbon from wood and they found good porosity development and high adsorption capacities during dyes removal, with values of 370.37mg·g⁻¹ and 294,14mg·g⁻¹, respectively.

In this paper, we studied the removal of two typical dyes present in industrial water (MB and CR), using activated materials developed in our laboratory from wood wastes of cedar and teak [4]. To evaluate the removal rate of dyes on activated carbon, different kinetic models were used. Langmuir and Freundlich isotherms were evaluated to determine the interaction between the contaminants and the adsorbents.

2. Methodology

2.1. Adsorption experiments

To obtain the active carbon a methodology used and reported in our group was used [5] and the adsorption tests were carried out using low cost adsorbents produced from waste wood (cedar and teak) [4]. Adsorption experiments were carried out by batch methods using two different types of dyes (MB and CR), which included two different concentration of each 50 and 100mg·L⁻¹. By kinetic studies, the



optimum contact time was determined. And equilibrium studies allowed to find the adsorption capacity of each material. To determine the final dyes concentration, calibration curves were performed. The absorbance to determine the concentration was measured on a spectrophotometer (VIS-DR 3900) at a wavelength of 665nm and 490nm for MB and CR, respectively.

2.2. Kinetic experiments

Kinetic experiments were conducted at room temperature (22°C) by adding a fixed amount of activated carbon (0.05g) into a 250mL erlenmeyer flask that contained 50mL of the MB and CR solutions. The mixture was agitated at 150rpm, and samples were collected at different times as follow: between 5 and 240min for MB and between 5 and 1440min for CR. The final concentration of each dye was measured by using their absorbance. Adsorption kinetics experiments are important because they can predict the removal rate of a contaminant from aqueous solutions and provides data that facilitate the understanding of the adsorption mechanism [6]. To analyze the adsorption rates of dyes onto the activated materials and the amount of each dye adsorbed at time (t) a mass balance between initial concentration and concentration at time (t) should be done by using the follow equation (1).

$$q_t = \frac{(C_i - C_t)}{w} \times V \quad (1)$$

Where q_t is the adsorption capacity of the activated carbon ($\text{mg}\cdot\text{g}^{-1}$), C_i and C_t are the dyes concentrations in solution at initial and time t ($\text{mg}\cdot\text{L}^{-1}$), V is the solution volume (L), and w is the mass of the activated carbon (g). Through this experiments the optimal contact time can be determinate [6]. In this study, the kinetics models of pseudo first order, pseudo second order and the intra-particle diffusion were evaluated for the adsorption of MB and CR on low cost adsorbents. The kinetic model of pseudo first order assumes that the limiting step during the adsorption process is the physisorption. Dye mass transfer to the adsorbent surface is based on equation 12 in [7]. When plotting a $\log(q_e - q_t)$ as a time function, q_e y k_1 , can be determinate from the intercept and slope respectively [7]. The pseudo second order model is described by equation 14 in [7]. It assumes that chemisorption is the determining step of the adsorption process rather than mass transfer in solution. q_e and k_2 values can be determined from a plot of t/q_t Vs t using the slope and the intercept, respectively. Intra-particle diffusion model is useful to elucidate the diffusion mechanism, it assumes that the adsorption mechanism is developed by different steps: external diffusion, pore diffusion and adsorption at the pore surface, and it is described by equation 16 in [7]. The values of the intra-particle diffusion rate constant k_{di} y C_i can be calculated from the slope and intercept of q_t vs \sqrt{t} [6].

2.3. Equilibrium experiments

Langmuir and Freundlich isotherm models can describe the interaction between the contaminant and the adsorbent material and measure the adsorption capacity of the activated carbon, at equilibrium. The Langmuir model assumes homogeneous surfaces with a single interaction energy [5]. The Langmuir equation 3 in [5] is widely used to quantify adsorption capacity. When plotting C_e/Q_e vs C_e , straight lines are obtained, where K_L and Q_{max} can be calculated using the intercept and slope, respectively. From equation 4 in [5], the dimensionless separation factor, R_L , can be calculated. It allows to indicate if the adsorption process is favorable or unfavorable [8]. Freundlich model is used for heterogeneous adsorption and it is described by equation 3 in [5]. K_f y n can be determined from the intercept and slope of the linear relationship of $\log Q_e$ vs $\log C_e$, respectively.

3. Results and discussion

3.1. Effect of contact time and initial concentration on the adsorption process

Figure 1 shows the contact time effect and initial concentration (50 and $100\text{mg}\cdot\text{L}^{-1}$) of both dyes for the adsorption process on activated carbon (AC and AT). Results indicate fast adsorption at the beginning

which decreases over time until reaching equilibrium. This tendency could be related to the existence of high number of active sites (porosity and functional groups) available for the adsorption process. Then, the process begins to stabilize due to the saturation of the active sites. This trend is similar to some literature reports [9]. For the adsorption of MB on AC and AT (Figure 1(A) and (B)), it is observed that the process is strongly influenced by the initial concentration, since the adsorption capacity increases with the concentration, which is in agreement with other studies [5]. Authors reported that for a concentration of $150\text{mg}\cdot\text{L}^{-1}$ the adsorption capacity of MB removal was $884.5\text{mg}\cdot\text{g}^{-1}$, while for a lower concentration of $50\text{mg}\cdot\text{L}^{-1}$ its adsorption capacity decreased to $671.1\text{mg}\cdot\text{g}^{-1}$. The opposite case occurs when CR is used as an adsorbate on AC and AT (Figure 1(C) and (D)), where the adsorption capacity decreases with the increase of concentration. This behavior can be explained because CR molecule is larger than MB molecule. High concentrations of CR make a rapidly saturation of the adsorbent material, decreasing the adsorption capacity, which is similar to reports done by Lorenc-Grabowska, *et. al.*[9,10]. y Tor, *et. al.*[9,10].

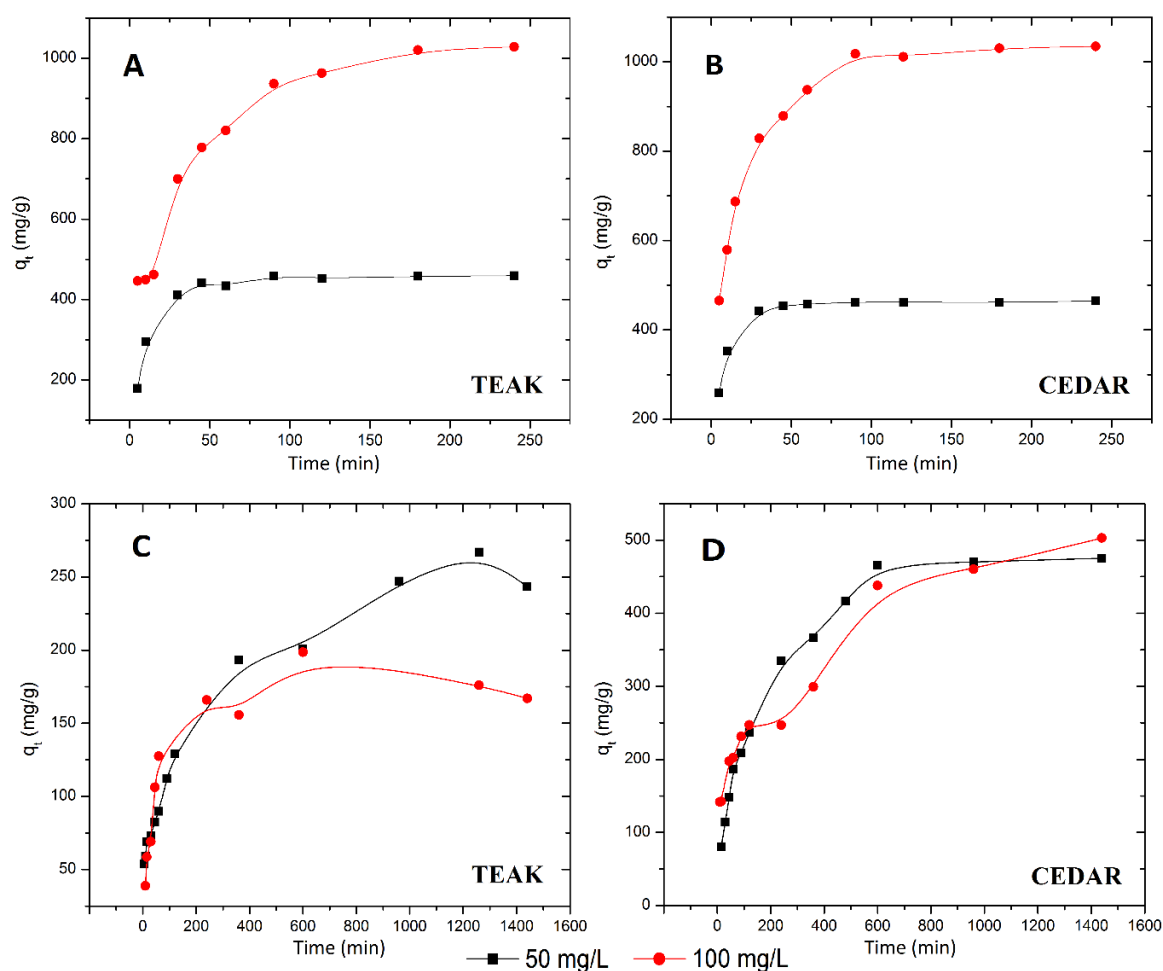


Figure 1. Effect of contact time and initial concentration (50 and $100\text{mg}\cdot\text{L}^{-1}$) during the adsorption on MB (A) and (B) and CR (C) and (D).

3.2. Kinetics experiments

Table 1 shows kinetic parameters for pseudo first order, pseudo second order and intra-particle diffusion models. For the two activated carbons (AC and AT) it was found that the optimal contact time for CR was 10h for both concentrations (50 and $100\text{mg}\cdot\text{L}^{-1}$), while for MB it was 1.5h for $50\text{mg}\cdot\text{L}^{-1}$ and 2 h for $100\text{mg}\cdot\text{L}^{-1}$. Observing the correlation coefficients, $R^2 \geq 0.970$ (Table 1), for the adsorption of dyes (MB

and CR) on each adsorbent material (AC and AT), these processes can be well represented by the pseudo-second-order kinetic model. This infers that chemisorption is the determining step of the adsorption process rather than mass transfer in solution. Similar kinetics results have also been reported by different authors using a variety of adsorbents [5,6].

In order to study a possible mechanism of MB and CR adsorption on the two activated materials, the intra-particle diffusion model was evaluated. A good adjustment of the experimental data was found. These plots present multilinearity, which indicates that two or more steps occur and that they are limiting the overall rate of adsorption. For the adsorption of MB and CR on AC, the value of k_{1d} is greater than the value of k_{2d} , indicating that surface adsorption is faster than adsorption into the pores, which is driven by the difference in the initial dyes concentration. Conversely, it occurs with AT, where the value of k_{1d} is lower than the value of k_{2d} . C_1 y C_2 values indicate the effects of the boundary layer. For AC, C_2 values are greater than the values of C_1 , whereas for AT the opposite occurs. Larger values for C_i , indicate that surface adsorption contribution is greater to the rate-limiting step [6].

Finally, it can be said that adsorption of MB and CR on activated carbon is a process involving multiple steps (adsorption on the outer surface and diffusion within the pores). Similar results have been reported in the literature for the removal of MB and CR using different activated materials [5,9,11,12].

Table 1. Pseudo first order kinetic, Pseudo second order kinetic and intra-particle diffusion model constants for the adsorption of MB and CR by the activated carbon (AC and AT).

Material	Cedar				Teak			
	Dye		MB	CR	MB	CR		
C_i (mg L ⁻¹)	50	100	50	100	50	100	50	100
q_e exp. (mg g ⁻¹)	462.34	1010.88	466.00	437.77	458.32	963.2	200.89	198.58
Pseudo first order								
q_e (mg g ⁻¹)	222.79	594.02	386.81	273.02	229.35	754.57	167.65	-
k_1 (min ⁻¹) x 10 ⁻²	6.91	3.5	-0.41	0.18	-3.48	3.39	0.83	-
R^2	0.972	0.987	0.989	0.858	0.976	0.957	0.988	-
Pseudo second order								
q_e (mg g ⁻¹)	461.7	1075.3	512.82	523.56	471.7	1098.9	265.25	176.06
k_1 (min ⁻¹) x 10 ⁻⁴	4.49	0.86	3.8	3.65	4.49	0.83	14.2	32.26
R^2	0.999	0.999	0.995	0.970	0.999	0.998	0.988	0.995
Intra-particle diffusion								
k_{d1} (mg g ⁻¹ min ^{1/2})	5.29	13.48	2.07	1.49	6.73	0.92	0.62	1.19
C_1 (mg g ⁻¹)	15.98	16.09	1.23	9.08	5.11	42.40	4.08	0.57
R^2	0.934	0.996	0.925	0.966	0.942	0.842	0.953	0.856
k_{d2} (mg g ⁻¹ min ^{1/2})	0.29	4.78	1.65	-	-	5.80	0.89	0.61
C_2 (mg g ⁻¹)	43.47	56.37	5.84	-	-	38.17	2.59	7.23
R^2	0.997	0.997	0.983	-	-	0.994	0.989	0.939

MB: methylene blue; CR: congo red; C_i : initial concentration; q_e : adsorption capacity at equilibrium; exp.: experimental; k_1 : Adsorption rate constant; R^2 : correlation coefficient; k_{di} : intra-particle diffusion rate constant; C_i : constant

3.3. Equilibrium experiments

Isotherms analysis allows to describe the interaction between the dye and the adsorbent material, and to know the adsorption capacity of the material in the equilibrium. Kinetics parameters are shown in Table 2. For AC, maximum adsorption capacities (q_m) of 2000.0 and 444.4mg·g⁻¹ for the adsorption of 100mg·L⁻¹ of MB and CC, respectively were found. For AT, maximum adsorption capacities (q_m) are 1052.6 and 86.4mg·g⁻¹ para MB (100mg·L⁻¹) and CR (50mg·L⁻¹), respectively. Langmuir correlation coefficients are $R^2 \geq 0.942$, indicating that adsorption process for both AC and AT have homogeneous sites on the surface which can interact with dyes (MB and CR). For AC and AT, the R_L values for both dyes are in the range of $0 < R_L < 1$, indicating that the adsorption process is favorable. The adsorption of

MB on AC can be well represented by Freundlich model (Figure 2(A)), which indicates that in this process there are different types of interactions between adsorbent and adsorbate. That is, the MB can be adsorbed on AC by interaction with functional groups and by diffusion through the pores [4], which could explain the high adsorption capacity of AC to remove MB.

Table 2. Calculated parameters for the two different adsorption models tested during this study.

Material	Cedar				Teak			
Dyes	MB		CR		MB		CR	
C_i (mg L ⁻¹)	50	100	50	100	50	100	50	100
Langmuir								
q_m (mg g ⁻¹)	1369.86	2000.00	381.68	444.44	416.67	1052.63	86.43	-
K_L (L g ⁻¹)	0.23	0.28	0.84	0.12	1.75	0.63	0.13	-
R_L	0.09	0.04	0.03	0.08	0.01	0.02	0.14	-
R^2	0.988	0.997	0.991	0.995	0.999	0.992	0.948	-
Freundlich								
K_F (mg g ⁻¹)	27.03	59.96	25.27	20.72	-	55.96	48.47	-
n (g L ⁻¹)	2.02	3.10	9.58	6.55	-	6.30	2.53	-
R^2	0.935	0.925	0.884	0.821	-	0.890	0.805	-

MB: methylene blue; CR: congo red; C_i : initial concentration; q_m : maximum adsorption capacity; K_L : Langmuir constant; R_L : dimensionless separation factor; R^2 : correlation coefficient; K_F : Freundlich; constant; n : constant.

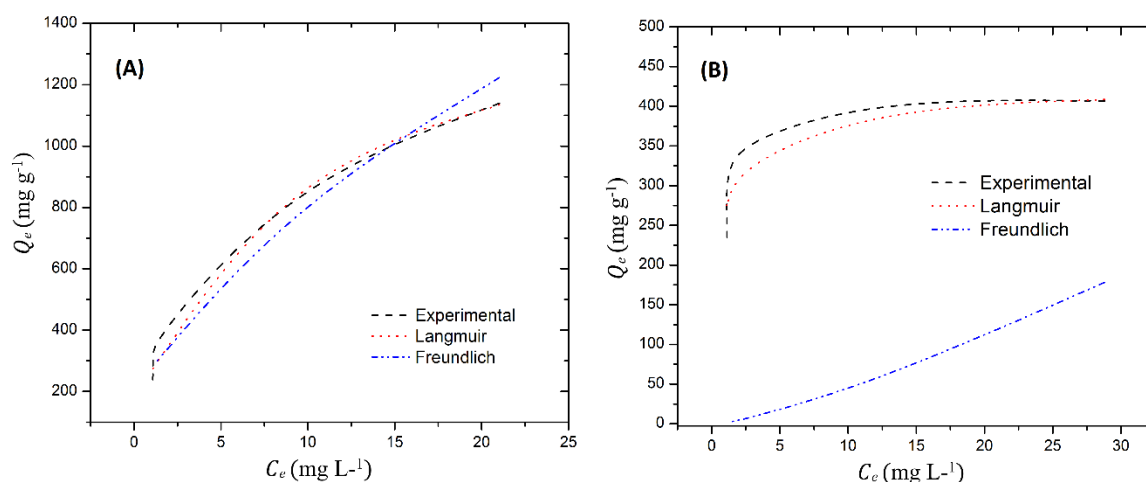


Figure 2. Langmuir and Freundlich Isotherms for MB adsorption with a concentration of 50mg·L⁻¹ using: (A) Activated Cedar (AC) and (B) Activated Teak (AT).

3.4. Comparison with other adsorbents

To illustrate the potential in the use of these activated materials as MB and CR adsorbents a comparative evaluation of the adsorption capacities of various types of adsorbents is provided in Table 3. The high adsorption capacity of the materials evaluated in this study, compared with those reported by other authors suggests that our materials have great potential to be applied as adsorbents in the removal of dyes from aqueous solutions.

Table 3. Comparison of the activated materials (AC and AT) with other adsorbents for MB and CR.

Adsorbent	Type of dye	Q_m (mg·g ⁻¹)	Reference
AC	MB	2000.0	This study
AC	CR	444.4	
AT	MB	1052.6	
AT	CR	86.4	
Oil Palm Fiber	MB	763.4	[5]
Oil Palm Peel	MB	724.6	[5]
Potato wastes	MB	540.0	[13]
m-Cell/Fe ₃ O ₄ /ACCs	CR	66.1	[14]
BAF	CR	11.9	[15]
Sodium Bentonite	CR	19.9	[16]

4. Conclusions

Two activated carbon (AC and AT) were evaluated for the removal of different concentration of MB and CR. The kinetic and equilibrium studies showed that the pseudo second order kinetics model provided the best correlation with the experimental data ($R^2 \geq 0.970$), which indicates that the adsorption was controlled by a chemisorption process. Using the regression coefficient values, both the Langmuir and the Freundlich isotherms models fit MB and CR adsorption behavior on AC materials, from which the maximum adsorption capacities were calculated. For AC the capacities were 2000.0 and 444.4 mg·g⁻¹ for MB y CR, respectively. For AT the capacities were 1052.6 y 86.4 mg·g⁻¹ para MB and CR, respectively. This study demonstrate that the materials produced in our group are viable materials to remove dyes from natural aquatic environments.

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