UPTAKE OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTIONS ONTO CHEMICAL ACTIVATED CARDOON (*CYNARA CARDUNCULUS*)

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ABSTRACT

A new adsorptive material was prepared from the chemical modification of cardoon (*Cynara cardunculus*) appropriate for dye removal. Cardoon was used either as pellet or powder (300μm) form during the experiments. It was activated with acid solutions of HCL or H_2SO_4 at different initial concentrations (1-5 M). Activated cardoon adsorbents were characterized through FTIR analysis. Kinetic and equilibrium studies of dye uptake onto the activated cardoon were also examined. According to the results, the FTIR analysis of the activated cardoon has shown the presence of different functional groups such as –C=O, -C-O, -C-H and –OH. Dye adsorption ability on activated cardoon depends on the shape of cardoon and the type of acid used for activation and increases according to the order: HCL, Powder (300 μm) > H_2SO_4, Pellet > HCL, Pellet > H_2SO_4, Powder (300 μm). Methylene blue adsorption percentage onto the cardoon depends on the acid concentration following the same order (1M < 4M < 3M < 5M < 2M) for both acids. The results have shown that the cardoon in powder form activated with HCL 2M presented the highest MB adsorption ability (97.9%) from the first 60 min. The kinetic models that were applied to MB adsorption data indicated that the adsorption process follows pseudo-second order kinetic model and the overall rate is controlled by chemisorption. Equilibrium studies of MB adsorption on cardoon has shown that dye solution concentration in equilibrium decreased by the increase in the dose of adsorbent due to the increase in the availability of surface active sites. In conclusion, activated cardoon either in pellet or powder form, is a very promising material in water purification as filter, so it is useful to be investigated thoroughly in the future.

Keywords: cardoon, pellet, chemical activation, methylene blue dye, kinetic analysis

1. Introduction

Industries, such as textile, paper and plastics, use a substantial amount of dyes and water to color their products. Methylene blue (MB) is a cationic dye that is used extremely for dying cotton, wool and silk. It is a dangerous pollutant, because it can be harmful for human and other living pieces. Therefore many methods such as chemical coagulation, ion exchange, electrolysis, biological treatments and adsorption (Gupta *et al.*, 2004) have been developed for dye pollution removal from wastewater before being discharged into the environment. Among these methods, adsorption through activated adsorbents is highly effective, cheap and eco-friendly for the removal of dyes and pigments as well as other organic and inorganic polluters (Acemioğlu, 2005).

The general process to produce activated lignocellulosic adsorbents is based on the carbonization and activation process of the raw materials of agricultural origin. Plant-based materials such as *cynara cardunculus*, can be applied as raw materials for adsorption purposes. The procedure of carbonization takes place in furnaces with a gradual increase of temperature under a continuous flow of an inert gas such as nitrogen. An activation process is an independent stage, which either follows the carbonization process leading to activated carbons or is applied directly to the raw lignocellulosic materials leading to activated adsorbents. In both

cases the pore volume and porosity are ameliorated. Activation process may be achieved either physically (thermal process) by using carbon dioxide, steam or chemically by using solutions of $ZnCL_2$, H_3PO_4, KOH (Ioannou *et al.*, 2015).

The purpose of the present paper is the development of a novel type of adsorbent for MB adsorption. Specifically, a chemical activated cardoon (*Cynara cardunculus*) has been successfully synthesized through a chemical method with either HCL or H_2SO_4. Kinetic and equilibrium studies of dye uptake onto the activated cardoon were also examined using different kinetic models.

2.   Materials & methods
2.1 Preparation of chemical activated adsorbents

Cardoon was prepared in pellet form using a hammer mill. In the experiment, it was used either as pellet or was crushed and sieved up to 300 μm (powder form). An amount of 0.4 g of cardoon raw material was added to 20mL of hydrochloric acid (1-5M) or sulfuric acid (1-5M) into 50mL falcon tubes. Then, the samples were placed in an orbital shaker for 24 h in order to establish complete contact between hydrochloric acid - biomass and sulfuric acid - biomass, at 24°C. They were filtered and washed several times with distilled water, to remove hydrochloric or sulfuric acid residues until the filtrate pH remained neutral (~7). After that, the samples were dried in an oven at 110°C for 24 h (Hayashi *et al.*, 2000; Açikyildiz *et al.*, 2014).

2.2. Preparation of dye solution

An aqueous methylene blue (MB) solution with a concentration of 0.03 g L^{-1} at 24°C was prepared. An amount of the chemical activated adsorbent was placed in 14mL-plastic tubes in an adsorbent – to – MB solution ratio equal to 10 g L^{-1} under continuous stirring using an orbital shaker. At specific time intervals, an amount of the solution was centrifuged for 2 min at 2,000 rpm and the respective MB concentration was determined by using a Perkin Elmer Lamda 25 UV-Vis spectrophotometer at 664nm. The batch experiments were done twice. The adsorbed amount (X_t) of MB was deduced from the difference between the initial amount of adsorbate (X_o) in the solution and the measured amount of the adsorbate in every solution sample. Equilibrium studies of MB adsorption onto the activated cardoon were also examined.

2.3. Characterization of adsorbents

The infrared spectra (FTIR) of cardoon samples in powder form, which were activated with HCL or H_2SO_4 in a concentration of 5M, were obtained using a Perkin Elmer spectrophotometer. Moreover, the FTIR spectra of activated cardoon samples after MB adsorption were also obtained. All FTIR images were taken and collected in transmission mode in the region of 4000-500 cm^{-1} at a resolution of 4 cm^{-1}.

2.4. Adsorption kinetic analysis

Four different kinetic models were used to investigate the mechanism of adsorption (McKay and Ho, 1999).

The pseudo-first-order kinetic model is given by the following equation:

$$\log(X_e - X_t) = \log X_e - \frac{k_1}{2.303}t \qquad (1)$$

where X_e and X_t refer to the amounts, of dye adsorbed per unit mass of adsorbent (μmoL g^{-1}) at equilibrium and at time t, respectively and k_1 is the equilibrium rate constant (min^{-1}). The slope and the intercept of the plot of $\log(X_e - X_t)$ versus *t* was used to determine *k_1* and *X_e*, which can be expressed as the theoretical adsorbed dye at equilibrium, i.e. *$X_{e,theor.}$*

The pseudo – second order kinetic model can be expressed as follows:

$$\frac{t}{X_t} = \frac{1}{k_2 X_e{}^2} + \frac{t}{X_e} \qquad (2)$$

where k_2 (µmoLg^{-1}min^{-1}) is the equilibrium rate constant of pseudo-second-order adsorption. The slope and the intercept of the plot of t/X_t versus t was used to determine k_2 and X_e. This model predicts the behavior over the whole range of adsorption if chemical adsorption mechanism is the rate-controlling step.

Kinetic adsorption data were further treated with the Elovich equation:

$$X_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t \qquad (3)$$

In this case the slope and the intercept of the straight line obtained by plotting X_t versus ln$t$, is used to determine $1/\beta$, and the adsorption quantity, $\ln(\alpha\beta)/\beta$.
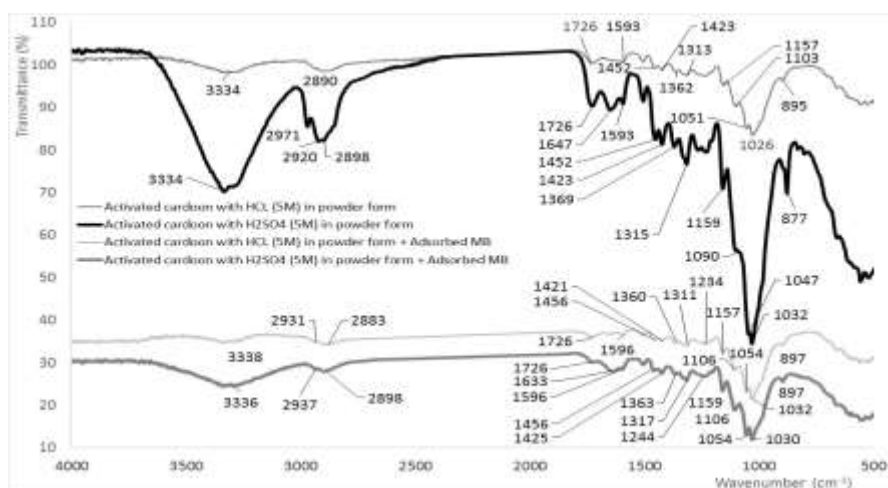
Another model such as intraparticle diffusion model can be defined as:

$$X_t = k_{id}t^{0.5} + C \qquad (4)$$

where X_t is the amount adsorbed at time t, k_{id} (µmoLg^{-1}min$^{-0.5}$) is the intraparticle diffusion rate constant and C is the intercept.

3. Results & discussion

Cardoon consists of cellulose, hemicellulose and lignin components.

Figure 1: FTIR spectra of activated cardoon with HCL or H_2SO_4 (5M) before and after MB adsorption.

According to the FTIR analysis (Fig.1), the absorption bands at 1244 and 1234 cm^{-1} indicate the presence of MB in adsorbents due to the appearance of C-N streching vibrations. The bands at 1593 cm^{-1} reflect the aromatic ring vibrations plus the carbonyl group stretching while the bands at 1647 cm^{-1} reflect C=O streching vibration. Activated cardoon after MB adsorption presents higher wavenumbers at 1596 cm^{-1} instead of 1593 cm^{-1} and lower values 1633 cm^{-1} instead of 1647 cm^{-1} indicating the creation of amide groups between MB and cardoon. Moreover, the wavenumbers of 1106 and 1054 cm^{-1}, which refer to activated cardoon that adsorbed MB, correspond to -C-O stretching vibrations of alcohols and ethers and present a transportation to higher values than the wavenumbers of activated cardoon before adsorption, i.e. 1103 or 1090 and 1051 or 1047 cm^{-1} for cardoon activated with HCL or H_2SO_4. Functional groups such as –OH and -C-H were also presented at 3330 and 2930, 2890, 1450, 1425 cm^{-1}, respectively. The wavenumbers of 1726, 1159, 1031, 890 cm^{-1} belong to C=O streching vibrations unconjugated, –C-O-C- asymmetrical streching, –C-O streching vibrations and glycosidic linkages, respectively. Bending vibrations of C-H and C-O groups were also appeared at 1360 and 1315 cm^{-1} (Bodîrlău and Teacă, 2009; Fiore *et al.*, 2011).

(a)

(b)

(c)

(d)
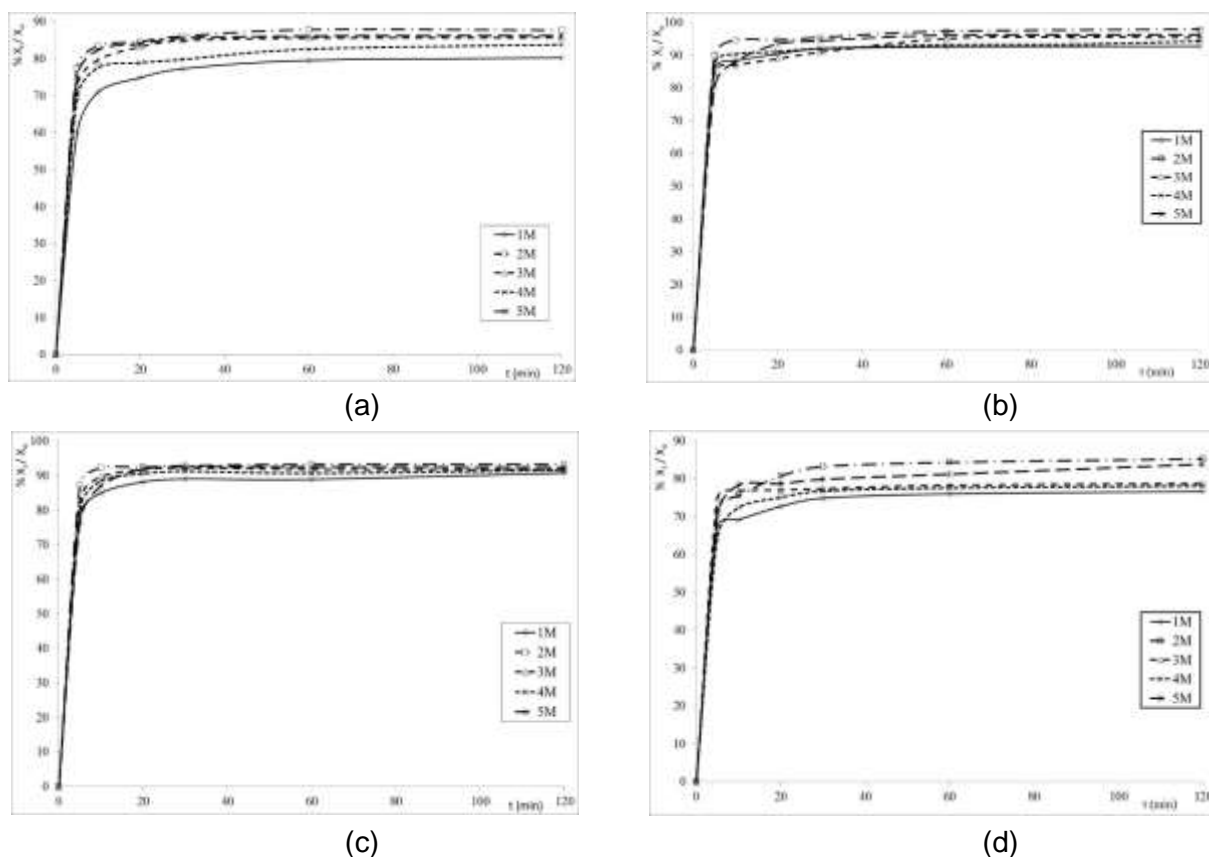
Figure 2: Uptake of MB from aqueous solutions onto chemical activated cardoon either with HCL acid in (a) pellet and (b) powder form or with H_2SO_4 acid in (c) pellet and (d) powder form at different concentrations (1-5 M)

Activated cardoon was used as adsorbent in a batch operation. As it is shown from Fig. 2a,b, the maximum MB adsorption percentage was equal to 87.65% and 97.92% at 60 min for the cardoon activated with HCL (2M) in pellet and in powder form, respectively while the lowest MB adsorption was equal to 80.22% and 92.71% for the cardoon activated with HCL 1M in pellet and in powder form, respectively. Examining cardoon activation with H_2SO_4 (Fig. 2c,d), it seems that the maximum MB adsorption percentage was equal to 93.26% and 85.25% at 60 min for the cardoon activated with H_2SO_4 (2M) in pellet and in powder form, respectively while the lowest MB adsorption was equal to 90.74% and 76.61% for the cardoon activated with H_2SO_4 1M in pellet and in powder form, respectively. All the other activations of the cardoon with HCL or H_2SO_4 acid in concentrations equal to 3, 4 and 5 M presented intermediate MB adsorption percentage values. The percentage of MB adsorption onto the cardoon depends on the HCL or H_2SO_4 acid concentration, which activated cardoon and increases according to the order: 2M>5M>3M>4M>1M. During activation, the acid attacks to hemicellulose and lignin due to their amorphous structure and then to crystalline cellulose. As a result, glycosidic linkages are hydrolyzed in hemicellulose and cellulose and aryl-ether bonds in the lignin are cleaved. The above reactions led to molecular weight reduction especially of hemicellulose, i.e. production of glucose molecules and lignin, i.e. formation of ketones. Other reactions consists of aliphatic chains cleavage such as –C=C- cleavage of lignin (Marsh and Rodríguez-Reinoso, 2006). The lack of –C=C- and the intense presence of –C=O and –C-O- functional groups explained also by the FTIR analysis of activated cardoon. According to Pandey and Nair (1974), the degree of cellulose polymerization decreased increasing acid concentration and temperature. Acid interacts with cellulose producing swelling in crystalline and inter-crysrtalline regions leading to a breakdown of cellulose chains (Marsh and Rodríguez-Reinoso, 2006; Pandey and Nair, 1974).
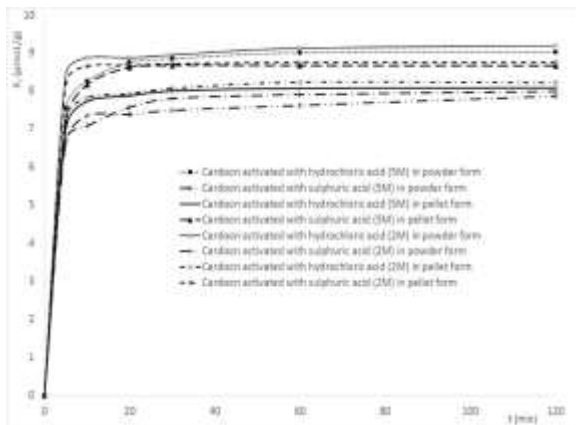
Figure 3: Comparison of MB adsorption between different types of activated cardoon (in pellet or powder form), different acid (HCL or H_2SO_4) for activation and different concentrations (2 or 5 M).
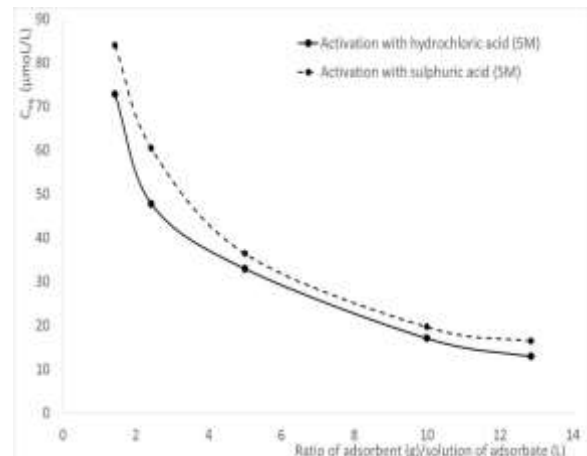
Figure 4: Study of MB solution in equilibrium (C_{eq}) after its adsorption on chemical activated cardoon with HCL or H_2SO_4 (5M) at different ratios of adsorbent to adsorbate, i.e. 1.4, 2.4, 5.0, 10.0, 12.9 g/L.

Figure 3 compares the different cardoons that were activated at two acid concentrations, i.e. 2 and 5 M, for their adsorption ability. According to the previous results (Fig.2), cardoons activated with either HCL or H_2SO_4 acid at 2 and 5 M presented the best MB adsorption percentages. It seems that the increase of MB adsorption follows the order: cardoon activated with HCL (2M) in powder form > cardoon activated with HCL (5M) in powder form > cardoon activated with H_2SO_4 (2M) in pellet form > cardoon activated with H_2SO_4 (5M) in pellet form > cardoon activated with HCL (2M) in pellet form > cardoon activated with HCL (5M) in pellet form > cardoon activated with H_2SO_4 (2M) in powder form > cardoon activated with H_2SO_4 (5M) in powder form. The highest MB adsorption per g of adsorbent was equal to 9.19 $\mu molLg^{-1}$ at 120 min and was presented for the cardoon activated with HCL (2M) in powder form while the lowest MB adsorption per g of adsorbent (8.00 $\mu molLg^{-1}$) was presented for the cardoon activated with H_2SO_4 (5M) in powder form. All the other activations and shapes of the cardoon with HCL or H_2SO_4 presented intermediate MB adsorption values.

Equilibrium studies of MB adsorption onto chemical activated cardoon in a concentration of 5M at different ratios of adsorbent to adsorbate were also investigated (Fig. 4). According to Fig.4, the gradual increase of the ratio of adsorbent to adsorbate from 1.4 to 12.9 g/L led to gradual decrease of MB molecules in the solution from 72.69 to 12.79 $\mu moL/L$ for cardoon activated with HCL and from 83.93 to 16.38 $\mu moL/L$ for cardoon activated with H_2SO_4. The increase of the ratio of adsorbent to adsorbate solution increases the adsorption sites of adsorbent leading to an increase in MB adsorbed molecules and a decrease to MB molecules in the solution. Corncob activated with phosphoric acid (El-Sayed *et al.*, 2014), which was used for methylene blue removal, has shown that the percentage removal of the dye increased with the increase in dose of adsorbent due to the increase in availability of surface active sites.

According to MB adsorption in equilibrium either experimental ($X_{e,exp.}$) or theoretical ($X_{e,theor.}$) and correlation coefficient factor (r^2) values applied to kinetic models (Table 1), the pseudo-second order kinetic model fitted very well the experimental MB adsorption data onto activated cardoon either in pellet or in powder form. Since pseudo-second-order mechanism is predominant, the overall rate of dye adsorption would be controlled by the chemisorption process (McKay *et al.*, 1999). Pseudo-first order, intraparticle diffusion and Elovich equations presented relatively low r^2 values showing their inappropriateness for analyzing the experimental data of the entire adsorption process. Similar studies concerning the adsorptive removal of methylene blue from tea waste (Uddin *et al.*, 2009) and seasame hull (Feng *et al.*, 2011) has shown that pseudo second order model fitted well to the experimental MB adsorption data.

Table 1: Pseudo-second order kinetic model parameters of methylene blue adsorption from aqueous solutions on cardoon activated with different acids (HCL, H_2SO_4) and different concentrations (1-5M)

Type of adsorbent	Acid Conc.	$X_{e,exp.}$ ($\mu moLg^{-1}$)	k_2 ($\mu moLg^{-1}min^{-1}$)	$X_{e,theor.}$ ($\mu moLg^{-1}$)	R^2
Activated cardoon with HCL, Pellet form	1M	7.53	0.08	7.64	1.00
	2M	8.22	0.18	8.28	1.00
	3M	8.04	0.17	8.10	1.00
	4M	7.86	0.10	7.93	1.00
	5M	8.08	0.21	8.13	1.00
Activated cardoon with HCL, Powder form	1M	8.70	0.23	8.74	1.00
	2M	9.19	0.17	9.23	1.00
	3M	8.95	0.09	9.05	1.00
	4M	8.84	0.18	8.86	1.00
	5M	9.02	0.13	9.10	1.00
Activated cardoon with H_2SO_4, Pellet form	1M	8.51	0.14	8.55	1.00
	2M	8.75	0.53	8.77	1.00
	3M	8.61	0.48	8.67	1.00
	4M	8.59	0.23	8.60	1.00
	5M	8.66	0.15	8.81	1.00
Activated cardoon with H_2SO_4, Powder form	1M	7.19	0.13	7.25	1.00
	2M	8.00	0.10	8.08	1.00
	3M	7.38	0.33	7.40	1.00
	4M	7.30	0.15	7.39	1.00
	5M	7.87	0.10	7.92	1.00

4. Conclusions

The following conclusions can be mentioned from the present study: a) FTIR analysis of the activated cardoons has shown the presence of functional groups such as –C=O, -C-O, -C-H and –OH. After MB adsorption, new functional groups such as –C-N were presented due to the creation of amides, b) MB adsorption ability on activated cardoon depends on the shape of cardoon and the type of acid used for activation and increases according to the order: HCL, Powder > H_2SO_4, Pellet > HCL, Pellet > H_2SO_4, Powder, c) MB adsorption percentage from aqueous solutions onto the cardoon depends on the acid concentration, which activated cardoon and increases according to the order: 2M>5M>3M>4M>1M for both acids, d) the cardoon in powder form with HCL at a concentration of 2M presented the highest MB adsorption ability from the first 60 min, e)different kinetic models were applied to MB adsorption data indicating that the adsorption process follows pseudo-second order kinetic model and its overall rate is controlled by chemisorption, f) equilibrium studies of MB adsorption on cardoon has shown that dye solution concentration in equilibrium decreased with the increase in the dose of adsorbent due to the increase in availability of surface active sites.

Consequently, *Cynara cardunculus* either in pellet or powder form, is a very promising material in water purification as filter, so it is useful to be investigated thoroughly in the future.

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