

Characterization of activated carbon Prepared from sludge paper for methylene blue adsorption

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Abstract

The activated carbon prepared from paper sludge was performed using various activating agents. In this study, the chemical activation of paper sludge was carried out using K_2CO_3 . The effect of preparation condition on the produced activated carbon characteristics as an adsorbent was investigated. The results showed that the surface area at the experimental conditions is achieved to $908 \text{ m}^2\text{g}^{-1}$. In addition to these advantages of preparation, the porous properties of activated carbon are excellent because of the well-developed micro-pore. The adsorption behavior of Methylene Blue dye from aqueous solution onto activated carbon was investigated as a function of equilibrium time, pH and concentration. The adsorption isotherm data were fitted to two adsorption isotherm models and found to closely fit the Freundlich model with R^2 equal 0.99 at pH 8, indicating a multilayer of adsorption. The maximum retention capacity of the produced activated carbon was 280 mg/g adsorbent and was obtained at this pH value. The obtained results show that paper sludge is a promising low cost precursor for the production of activated carbon.

1. Introduction

Paper sludge, which has always been considered as an ecological burden for the society is a byproduct of the process of recycling old paper [1]. A great part of this waste paper is used to produce paper. The paper sludge contains water, fiber, organic compounds, inorganic salt, and mineral fillers [1]. The paper sludge application has many purposes. Moreover, in agriculture, it is used as a compost [2,3]. In chemical industries, it is used for the production of bioethanol [4] and methane [5,6]. The paper sludge is also used as a supplementary cementing material [7].

In addition, one of the most recent applications of activated sludge has been the preparation of activated carbons [8]. These materials are characterized by their extraordinary large specific surface areas, well-developed porosity and tunable surface-containing functional groups [9]. For these reasons, activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water and wastewater [10,11]. In general the activated carbons were prepared by two methods: the wet and the dry oxidation. The low cost method is the wet oxidation which involves the reaction between the carbon surface and solutions of oxidizing agents such as phosphoric acid H_3PO_4 , zinc chloride $ZnCl_2$, potassium hydroxide KOH , potassium carbonate K_2CO_3 .

However, there is little information on the production of activated carbon from sludge paper and its potential use as adsorbent for the removal of Methylene Blue dye from aqueous solutions.

The objective of this work was to give new insights and deepen the study on this subject by elaborating activated carbon from paper sludge. The specific surface areas, pores volumes, of the activated carbons were studied for its potential use as adsorbent for the removal of Methylene Blue dye from aqueous solutions. Results of this study are expected to be useful for future scale up using this material as a low cost adsorbent for the removal for Methylene Blue dye from wastewater.

2. Materials and Methods

2.1. Materials

The sample of sludge paper used in this study was obtained from Tunisie-Ouate a producer of paper tissue in Nfidha- Tunisia. Methylene Blue dye, with the molecular formula $(C_{16}H_{18}N_3SCl)$ and molecular weight of 319.852 g was chosen as adsorbate.

2.2. Preparation of activated carbon from sludge paper

The samples were prepared by chemical activation using K_2CO_3 and by physical activation using steam. The detailed preparation conditions were conducted as was reported in previous works [5]. In the chemical activation process, sludge paper was impregnated with K_2CO_3 solution (sludge paper: K_2CO_3 = 1:1 mass ratio) and the dried sludge fired in flowing dry N_2 at a heating rate of $10^\circ C/min$. After activation, the products were washed sufficiently with deionized water. The activation temperature were 700, 800, and $900^\circ C$ at a heating rate of $10^\circ C/min$ with an introduction of wet N_2 for 2 hours.

2.3. Structural and textural characterization methods.

Powder XRD patterns were obtained using a PANalytical X'Pert High Score plus diffractometer in the range $2\theta = 3-60^\circ$, at a scanning rate of 2 deg. min^{-1} and employing $CuK\alpha$ filtered radiation. FTIR absorbance spectra of solid samples were obtained through KBr technique, with the analysis performed on a Nicolet Magua IR 560 in the wave number range of $4000-300 \text{ cm}^{-1}$. The solid samples were mixed with KBr at a ratio of roughly (1/300), and then the mixture was ground in agate mortar to very fine powder. After drying at $100^\circ C$ for 12 h in a vacuum oven, about 300 mg of the fine powder were used to make a pellet. After preparation, the pellet was analyzed immediately and the spectra were recorded by 64 scans with 2 cm^{-1} resolution. The specific surface area and porosity measurements of activated carbons produced from sludge paper have been performed by N_2 adsorption (at 77K), using a surface analyzer (Quantachrom- Autosorb 1).

3. Results and discussion

3.1. Structural and textural characterization

Mineralogically, the paper sludge was formed by a mix of organic matter (microfiber of cellulose) and different inorganic minerals (calcite, clay mineral). Figure 1 confirms the existence of a mineral phase and the amorphous phase which are presented by boss in the range of 2θ (10 to 30).

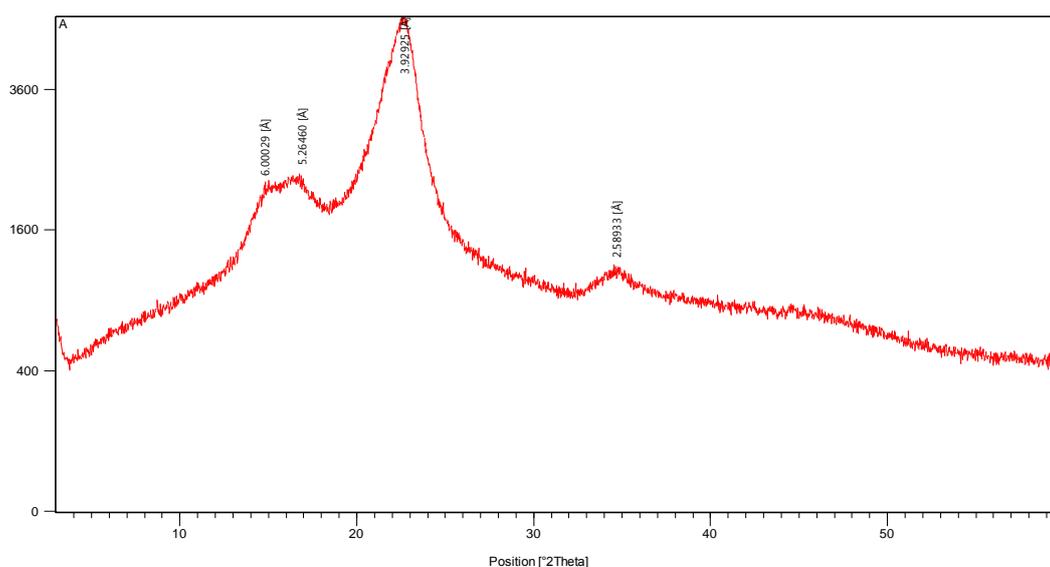


Figure 1: X-ray diffractogram for paper sludge

The results of analysis of the sludge utilized in this study are shown in table 1. These results show that this waste consists of minerals fraction that comprise SiO_2 and Al_2O_3 shown in table 1.

Table 1: Mineralogical composition of paper sludge

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	P_2O_5	I.L.
%	19.69	7.74	0.52	25.20	1.24	0.58	0.50	0.18	44.35

The FTIR spectra of the raw sludge materials and activated carbons showed some different bands (figure 2). The bands at 2923 and 2855 cm^{-1} are ascribed to C-H aliphatic stretching as was explained in previous works [12,13]. Other important absorption bands at 1022 cm^{-1} and $1100-1120 \text{ cm}^{-1}$ represent C-O stretching as was shown in an earlier study [9].

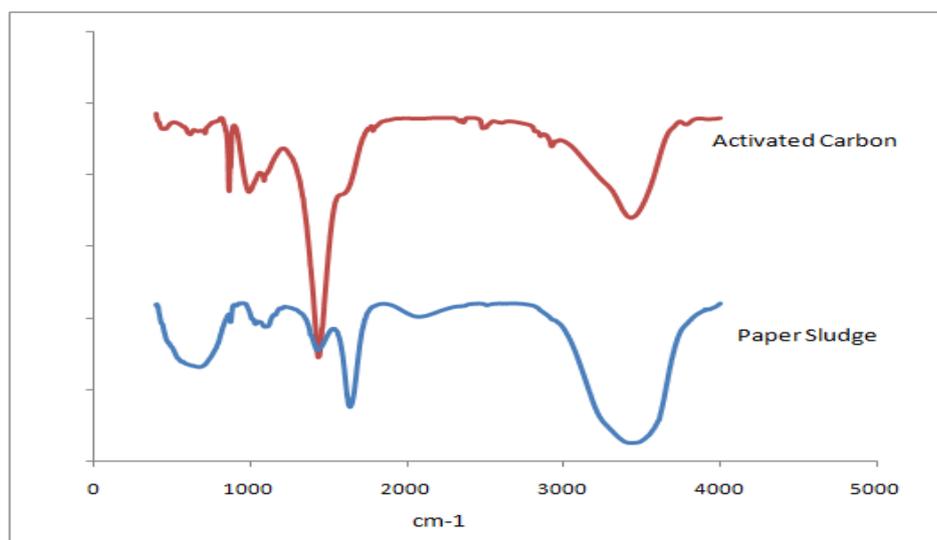


Figure 2: IR-spectra of paper sludge and activated carbon

Strong and broad band at $3300\text{-}3500\text{cm}^{-1}$ correspond to O-H stretching as was revealed by a preceding report [14]. The bands of symmetrical stretching of C=C were also observed at $1600\text{-}1700\text{cm}^{-1}$. There was another band at 1385cm^{-1} due to the presence of -CH_3 stretching. It can be concluded that the activation process increased the CH_3 chain in the activated carbon, so the intensity of bands at 1400cm^{-1} was increased.

The BET surface areas and pore volumes of activated carbons produced at different final activation temperatures using an impregnation ratio of 1 are presented in table 3. BET surface area increased with activation temperature, reaching a maximum at about 900°C . The activated carbons showed a high specific surface area compared to raw paper sludge. Table 2 shows that the highest surface area was $907.9\text{ m}^2/\text{g}$ developed at an activation temperature of 900°C . It can be observed that at all carbonization temperatures from 600°C to 900°C , the specific surface area increased. This increase would be due to the improvement the porosity and the microporosity in the activated carbon.

Table 2: Effect of activation temperature on specific surface.

Activation temperature ($^\circ\text{C}$)	Specific surface (m^2/g)
Sludge paper	16
700	77.26
800	859.90
900	907.90

3.2. Adsorption of MB by activated carbon

3.2.1. Effect of pH on MB Adsorption

The pH of aqueous solution is an important variable that influences the adsorption of anions and cations at the solid – liquid interfaces. Fig. 3 shows the variation of amount MB adsorbed per mass unit on activated carbon as a function of equilibrium pH, for a concentration of 10 mg/l of MB. The maximum adsorption was obtained at basic pH. In this pH range the surface of activated carbon was negatively charged and MB was positively charged (-S^+). The deprotonated groups of activated carbon were mainly carboxylic group (-CO-O^-), phenolic (-O^-). At solution $\text{pH} \geq 4$, the removal capacity of MB was expected to increase as the adsorbent was negatively charged and dye molecules were positively charged. The constant adsorption capacity of activated carbon for dyes over the $\text{pH} \geq 9$ was an indication that the electrostatic mechanism was not the only mechanism for dye adsorption in this system. Activated carbon can also interact with dye molecules via hydrogen bonding and hydrophobic-hydrophobic mechanisms as was explained by Newcombe and Drikas [15].

3.2.2 Effect of agitation time on adsorption of MB

The effect of contact time on the amount of the adsorbed MB was investigated at the optimum pH concentration of MB, and the results are presented in fig.4.

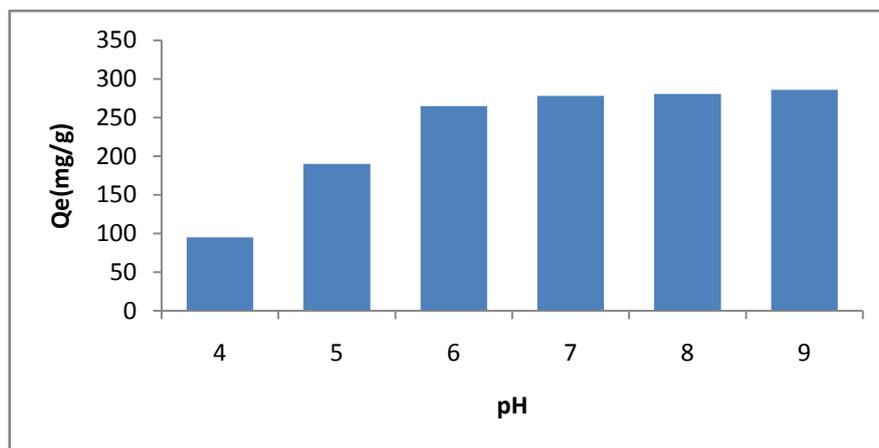


Figure 3: Effect of pH on the adsorption of Methylene Blue on activated carbon.

It can be seen that most of MB adsorption on the adsorbents was completed in 1 hour. The time required to attain the state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption (260 mg/g) capacity of adsorbent under those operating conditions. It seems obvious that the activated carbon. That activated carbon prepared from sludge paper was an efficient agent to absorb MB dye from aqueous solutions. This can be explained by the fact that this activated carbon is composed of a large structure with a large internal surface area of 907 m²/g.

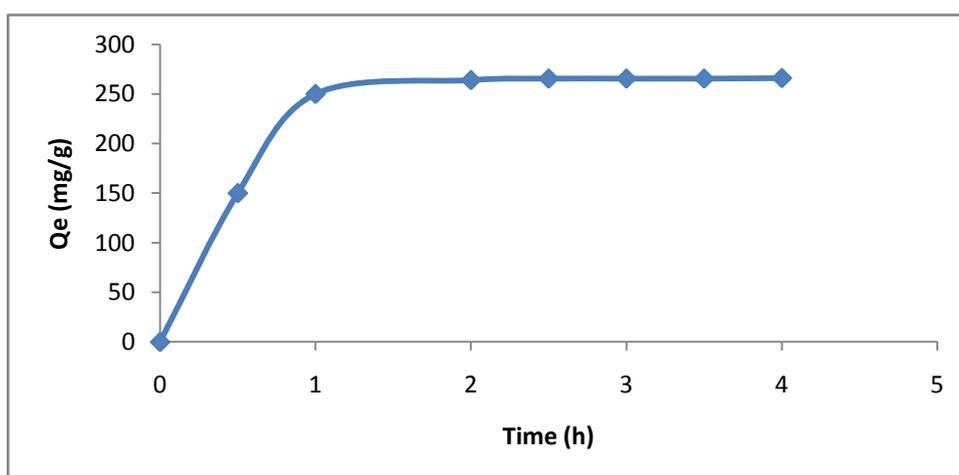


Figure 4: Effect of contact time on the adsorption of Methylene Blue.

In batch type adsorption systems, a monolayer of adsorbate is normally formed on the surface of adsorbent [16] and the rate of removal of adsorbate species from aqueous solution is controlled primarily by the rate of transport of the adsorbate species from the exterior/outer sites to the interior sites of the adsorbent particles [16,17].

Kinetic modeling not only allows estimation of sorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. In this respect, two kinetics, the pseudo-first-order (Eq. (1)) and pseudo-second equation (Eq.(2)) [18], were tested. The pseudo first-order equation is given by Lagergren and Svenska [19]

$$\ln (q_e - q_t) = \ln (q_e) - k_1 t \quad (1)$$

Where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and time t (min), respectively, and k_1 the rate constant adsorption (h^{-1}). The value of k_1 was calculated from the plots of $\ln (q_e - q_t)$ versus t (fig.5). Although the correlation coefficient values are higher than 0.51 for activated carbon, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots. This shows that the adsorption of MB on to activated carbon was not a first-order kinetic.

On the other hand, a pseudo second-order equation based on equilibrium adsorption [18] is expressed as:

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

Where k_2 ($\text{g}/\text{mg}\cdot\text{h}^{-1}$) is the rate constant of second-order adsorption. If second-order kinetics was applicable, the plot of t/q versus t should show a linear relationship. There is no need to know any parameter beforehand and q_e and k_2 can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behavior over the whole range of adsorption. The linear plots of t/q versus t (fig.6) showed a good agreement between experimental and calculated adsorption capacity values. The correlation coefficients for the second-order kinetic model were greater than 0.99, indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of MB on activated carbon.

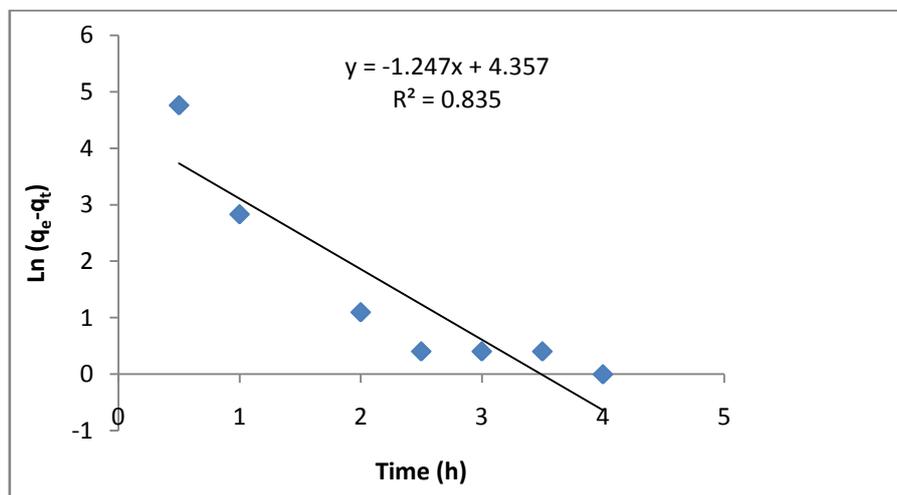


Figure 5: Pseudo first- order kinetic plot for the adsorption of methylene blue on activated carbon.

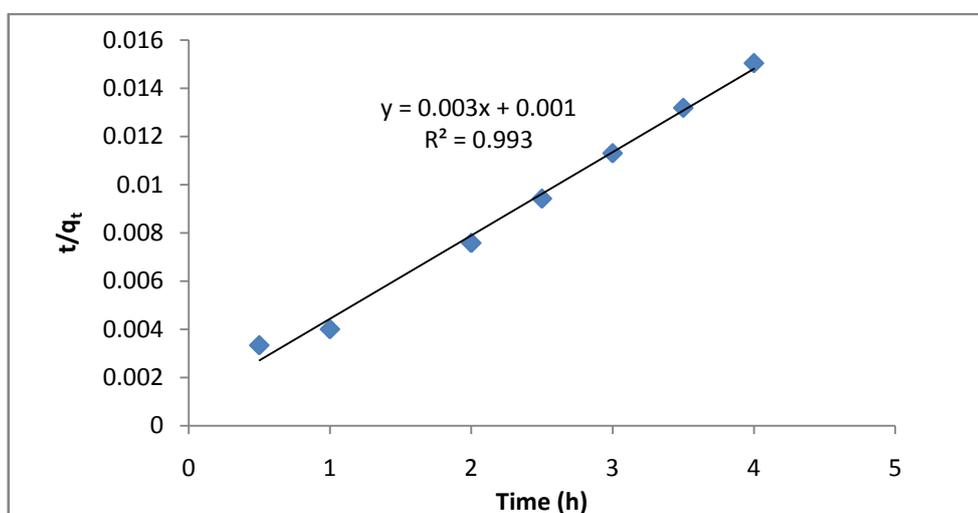


Figure 6: Pseudo second -order kinetic plot for adsorption of methylene blue on activated carbon.

The fitting of the kinetic study showed that the second- order model was the best because R^2 was of 0.993.

3.3. Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [20]. fig.7 typically shows the adsorption isotherms of MB dye at 25 °C on the activated carbon. Adsorption isotherm is basically important to describe how dye interacts with adsorbents, and is critical in optimizing the use of adsorbents.

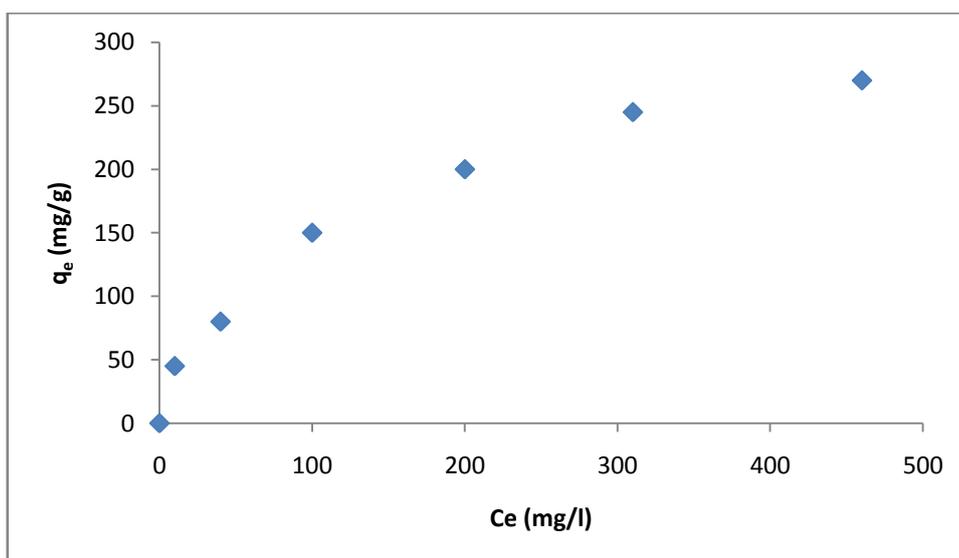


Figure 7: Equilibrium isotherms of methylene Blue on activated carbon.

Adsorption isotherm study is carried out on two well-known isotherms, Langmuir and Freundlich. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites [16]. However, the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [16]. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2 .

The linear form of Langmuir's isotherm model is given in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{1}{q_0} C_0 \quad (3)$$

Where C_e is the equilibrium concentration of the adsorbent MB (mg/l), q_e the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), and b (K_L) and q_0 are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When C_e/q_e was plotted against C_e , straight line with slope $1/q_0$ was obtained, indicating that the adsorption of MB on activated carbon followed the Langmuir isotherm. The Langmuir constants 'b' and 'q₀' which were calculated from this isotherm are given in fig.8.

The experimental data were consistent with the Langmuir isotherm model proving the homogeneous nature of activated carbon surfaces, i.e., each dye molecule/adsorbent adsorption had an equal adsorption energy. In addition, in line with previous works [21, 22, 23], these results confirm the formation of mono layer coverage of dye molecule at the outer surface of activated carbon.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [23], which is defined by:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

Where b is the Langmuir constant and C_0 the highest dye concentration (mg/l). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of R_L ranged between 0.002 and 0.01. These values confirmed the fact that the activated carbon was favorable for adsorption of MB dye under the conditions used in this study.

The well-known logarithmic form of the Freundlich model is given by the following equation:

$$\log q_e = \log k_f + (1/n) \log C_e \quad (5)$$

Where q_e is the amount adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate ; K_f and n are Freundlich constants, n giving an indication of how favorable the adsorption process and K_f is the adsorption capacity of the adsorbent. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon adsorbent for a unit equilibrium concentration. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [24]. A value for $1/n$ below unity is indicative of cooperative adsorption [25]. The plot of $\log q_e$ versus $\log C_e$ (fig.9.) yielded straight lines with slope '1/n'. The Freundlich constants (K_f and n) were calculated.

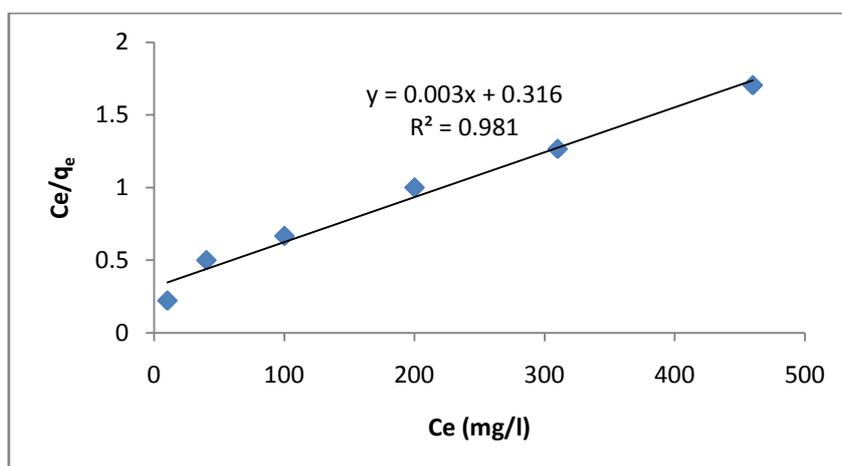


Figure 8: Isotherms obtained by Langmuir models for removal of MB by activated carbon.

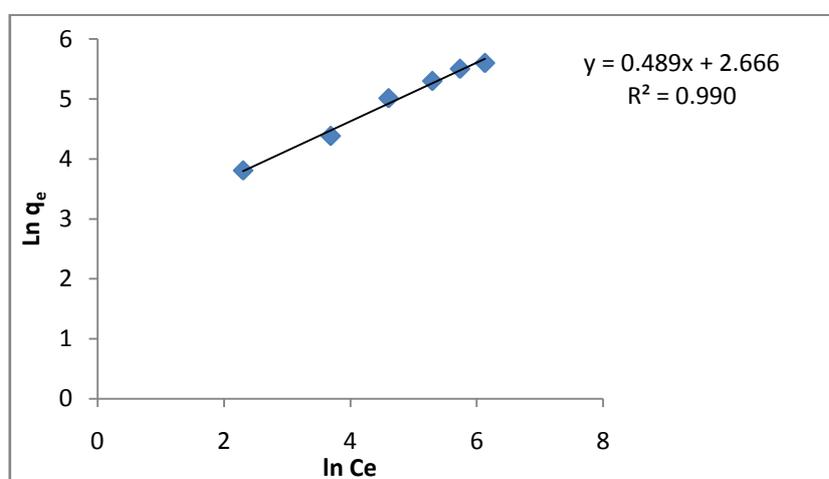


Figure 9: Isotherms obtained by Freundlich models for removal of MB by activated carbon.

Based on the R^2 parameter, the Freundlich model would be the best for fitting the experimental points and would give an idea on the multilayer adsorption.

Conclusion

The present study revealed the feasibility of paper sludge as an efficient raw precursor for the preparation of activated carbon. Chemical K_2CO_3 activation showed good development of pore structures with the surface area of $908 \text{ m}^2/\text{g}$. The activated carbon prepared from paper sludge exhibited amphoteric behavior, indicating its suitability for removal of cationic dyes. Kinetic data followed a pseudo second-order kinetic model. Adsorption behavior was described by a Freundlich type isotherm. The maximum adsorption capacity was 260 mg/g for MB which is comparable with the values for commercial activated carbon.

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