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## Removal of a cationic dye from water by activated pinecones

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**Abstract:** Adsorption of a cationic phenothiazine dye, Methylene Blue onto activated carbon prepared from pinecones was investigated. The parameters contact time, dye concentration and pH were varied. The kinetic data were found to follow closely the pseudo-second-order kinetic model. The equilibrium data were best represented by the Langmuir isotherm with a maximum adsorption capacity of 233.1 mg g<sup>-1</sup>. The adsorption was favored by using a higher solution pH. Textural analysis by nitrogen adsorption was used to determine the specific surface area and pore structure of the obtained carbon. Boehm titrations revealed that carboxylic groups were present in a high degree on the carbon surface. The results indicate that the presented method for activation of pinecones could yield activated carbon with significant porosity, a developed surface reactivity and a considerable adsorption affinity toward the cationic dye Methylene Blue.

**Keywords:** activated carbon; adsorption; kinetics; Methylene Blue.

### INTRODUCTION

Activated carbons are considered one of the most effective adsorbents with a wide range of applications due to their high surface areas, surface reactivity and large adsorption capacities. The structure of activated carbons was shown to be composed of microcrystallites consisting of fused hexagonal rings, the reactive edges of which contain a variety of functional groups.<sup>1</sup> The size of microcrystallites is influenced by the temperature of carbonization and the structure of the precursor.<sup>2</sup> For industrial production of activated carbons, carbonaceous precursors such as coconut shell, coal, wood and peat are used. However, since commercial activated carbons are rather expensive, some alternative precursors are required for the production of cheaper adsorbent with the same, or even better,

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quality. The thermochemical conversion of waste biomass into activated carbon is a method of growing prominence in innovating economical solutions for activated carbon production. For this purpose, there are numerous studies on application of lignocellulosic waste biomass, such as: nutshells,<sup>3</sup> fruit stones of different origin,<sup>4,5</sup> sawdust,<sup>6</sup> cotton stalks,<sup>7</sup> corn stover,<sup>8</sup> corncob,<sup>9</sup> organic peel,<sup>10</sup> *etc.*

The European Black Pine (*Pinus nigra*) is a species of pine occurring across large areas of Europe and northwest Africa. It is a large evergreen tree that is frequently used as an ornament in parks. Its pinecones are 5–10 cm long, have rounded spirally arranged scales that contain a lot of lignin and resins. They usually fall from the tree in October and November. On park footpaths, they can be considered as municipal waste that has to be collected, transported and disposed of.

In this study, the cones of the European Black Pine were used for the preparation of powdered activated carbon, which was further characterized by its pore structure and surface chemistry. In addition, the batch adsorption of Methylene Blue (MB) onto the obtained carbon was investigated. MB (Fig. 1) is a basic cationic phenothiazine dye that is commonly used as an adsorbate for the investigation of the adsorptive properties of novel activated carbons.

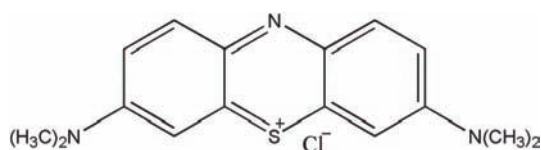


Fig. 1. Structural formula of Methylene Blue.

The goal of this study was to investigate isotherms and kinetics of adsorption of the cationic dye MB onto the powdered activated carbon obtained from pinecones. Pinecones were chosen since they are a low-cost and locally abundant raw material that can frequently emerge as a municipal waste. To the best of our knowledge, this material has not hitherto been used for the synthesis of activated carbon.

## EXPERIMENTAL

### *Preparation of pinecone activated carbon (PCAC)*

The pinecones were collected in Čair Park in Niš, Serbia. First, they were milled and sieved through a sieve of mesh size 0.841 mm. The cone dust was impregnated with 85 mass %  $\text{H}_3\text{PO}_4$  (Merck) in weight ratio of 1:1. The resulting slurry was transferred to several ceramic crucibles and placed in a programmable muffle furnace to undergo a two-stage activation process. The first stage was semi-carbonization with a heating rate of  $6\text{ }^\circ\text{C min}^{-1}$  up to  $170\text{ }^\circ\text{C}$  and 60 min holding at this temperature. Subsequently, the heating was continued at a rate of  $8\text{ }^\circ\text{C min}^{-1}$  up to  $500\text{ }^\circ\text{C}$  with a 60 min soaking time. Both stages were performed under a nitrogen flow of  $100\text{ cm}^3\text{ min}^{-1}$ . The product was cooled to room temperature, washed with  $100\text{ cm}^3$  of warm 0.1 M HCl and then with hot distilled water until the pH of the washings reached 5.3. After drying at  $110\text{ }^\circ\text{C}$  overnight, the material was crushed in a mortar and sieved through a

0.149 mm mesh sieve. The obtained black powder was denoted as PCAC and stored in an airtight bottle for further analysis.

#### *Physical characterization*

The surface morphology of the PCAC samples was analyzed before and after MB adsorption by scanning electron microscopy using a JEOL JSM 5300 microscope (Japan). The gold sputtered samples were placed in the SEM specimen chamber and observed at an accelerating voltage of 30 kV.

Nitrogen adsorption isotherms were determined at  $-196\text{ }^{\circ}\text{C}$  using a Sorptomatic 1990 instrument (Thermo Fisher Scientific, USA). Before the measurements, the carbon samples were out-gassed for 4 h at room temperature, then for 8 h at  $110\text{ }^{\circ}\text{C}$  and finally 12 h at  $200\text{ }^{\circ}\text{C}$ . The specific surface area of the PCAC was calculated using the BET method.<sup>11</sup> The cumulative pore volume ( $\text{cm}^3\text{ g}^{-1}$ ), the median pore diameter (nm) and the area of the mesopores ( $\text{m}^2\text{ g}^{-1}$ ) were calculated using Barrett–Joyner–Halenda method.<sup>12</sup> The Dubinin–Radushkevich Equation was applied to obtain the micropore volume.<sup>13</sup>

The ash and moisture content analysis of the PCAC followed ASTM D 2866-94<sup>14</sup> and ASTM D 2867-04, respectively.<sup>15</sup>

#### *Surface chemistry characterization*

Oxygen-containing surface functional groups were determined according to the Boehm method.<sup>16</sup> PCAC samples (0.5 g) were placed in PVC bottles of  $100\text{ cm}^3$  capacity with  $40\text{ cm}^3$  of the following 0.1 M solutions: NaOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and HCl. The bottles were sealed and shaken for 24 h and then filtrated using Whatman 44 filter paper. Excess of residual base in  $20\text{ cm}^3$  of filtrates from the NaOH,  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  probes was pH-metrically titrated in open system using 0.1 M HCl standard solution. The excess residual acid in  $20\text{ cm}^3$  filtrate from the HCl probe was titrated using a 0.1 M standard NaOH solution. The reaction between the reagents and the acidic oxygen containing functional groups on the carbon surface is based on the difference in acid/base strength (carboxylic>lactonic>phenolic). It was assumed that NaOH neutralizes carboxylic, lactonic and phenolic groups;  $\text{Na}_2\text{CO}_3$ , carboxylic and lactonic groups;  $\text{NaHCO}_3$ , carboxylic groups only. The phenolic groups were determined from the differences in the neutralization by NaOH and  $\text{Na}_2\text{CO}_3$ . The quantity of surface basic groups was calculated from the titration with 0.1 M HCl. A blank was not used in the analysis.

Carbon particles in an aqueous medium adsorb  $\text{H}^+$  or  $\text{OH}^-$  rendering their surface positively or negatively charged. The pH value when the carbon surface has zero net charge is known as  $\text{pH}_{\text{PZC}}$ . The  $\text{pH}_{\text{p.z.c.}}$  of the PCAC was determined by the modified pH drift method which can be described as follows:  $30\text{ cm}^3$  of 0.1 M  $\text{KNO}_3$  solution was added to a series of PVC bottles and their pH values were adjusted in the range from 2 to 12 using small amounts of 0.01 M HCl and/or NaOH. When the pH values became constant, they were measured using a pH meter SensION3 (Hach, USA) and the values denoted as  $\text{pH}_{\text{initial}}$ . Then, 0.1 g of carbon samples were added to the bottles that were then well-sealed and shaken for 24 h to reach equilibrium. After 24 h, the pH values of the suspensions were measured and denoted as  $\text{pH}_{\text{final}}$ .  $\text{pH}_{\text{p.z.c.}}$  is regarded as the pH value when  $\text{pH}_{\text{initial}}$  is equal to  $\text{pH}_{\text{final}}$ .<sup>17</sup>

#### *Batch adsorption experiments*

MB ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ ,  $\text{CI} = 52015$ ,  $M_r = 319.86\text{ g mol}^{-1}$ ,  $\lambda_{\text{max}} = 662\text{ nm}$ ) supplied by Riedel-de-Haen (Germany) was dried for 2 h at  $90\text{ }^{\circ}\text{C}$  prior to use. A stock solution of  $1000\text{ mg dm}^{-3}$  was prepared using distilled water and afterwards diluted to the required concentrations.

The adsorption equilibrium studies were performed by contacting 0.1 g of PCAC with 50 cm<sup>3</sup> of MB solutions, the initial concentrations of which were 300, 350, 400, 450 and 500 mg dm<sup>-3</sup>. The suspensions were stirred using a mechanical magnetic stirrer at 120 rpm in a set of stoppered Erlenmeyer flasks. After 60 min, the suspensions were filtered using filter paper Whatman 44 and the residual MB concentrations were determined by microprocessor-controlled photometer MultiDirect (Lovibond, Germany) at 660 nm. For kinetic studies, MB solutions of 400 mg dm<sup>-3</sup> were stirred in the same manner for 5 to 80 min. An interval of 60 min was established to be enough to reach equilibrium. The effect of solution pH was examined in the range from 3 to 10 by contacting 0.1 g of PCAC with 50 cm<sup>3</sup> of 400 mg dm<sup>-3</sup> MB solutions for 60 min. In all the cases, the adsorption capacity,  $q$  (mg g<sup>-1</sup>), was calculated as:

$$q = \frac{(c_0 - c) V}{W} \quad (1)$$

where  $c_0$  (mg dm<sup>-3</sup>) is the initial MB concentration,  $V$  (dm<sup>3</sup>) is the volume of the solution,  $W$  (g) is the mass of PCAC and  $c$  (mg dm<sup>-3</sup>) is the residual MB concentration at equilibrium or at any time  $\tau$  (min), which then defines  $q_e$  or  $q_\tau$  (mg g<sup>-1</sup>), respectively. The experimental data were fitted to kinetic and isotherm theoretical models.

All adsorption experiments were performed in triplicate at ambient temperature (25 °C) and the average value was used. The chemicals used in the whole study were reagent grade.

## RESULTS AND DISCUSSION

### *Physical characteristics*

Micrographs of the PCAC samples before and after adsorption of MB are shown in Fig. 2. The micrographs show that the adsorption process did not significantly change the morphology of the surface matrix of the carbon samples. However, slight differences in the number and shape of cracks and attached fine particles over the carbon surface are evident.

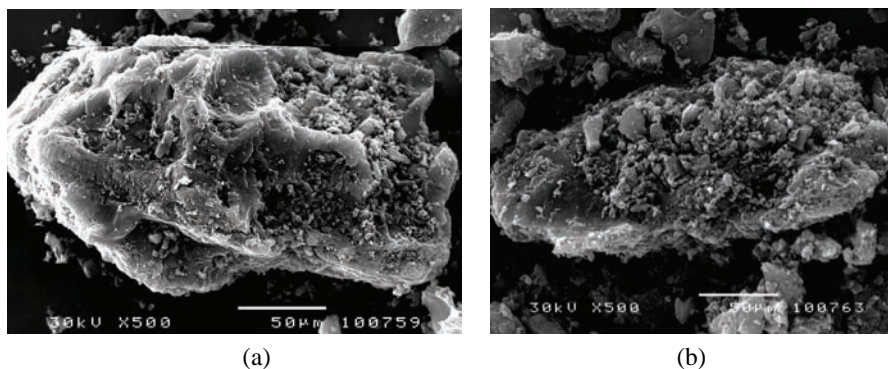


Fig. 2. SEM Micrographs of the carbon particles a) before and b) after MB adsorption.

A textural study revealed that the PCAC had a relatively high specific surface area, measured by nitrogen adsorption. The porosity characteristics and the determined MB adsorption capacities for the PCAC are given in Table I, together

with the corresponding values for other activated carbons obtained from various precursors.

TABLE I. Comparison of maximum MB adsorption capacities of carbons derived from various lignocellulosic precursors

Adsorbent	BET Specific surface area $\text{m}^2 \text{g}^{-1}$	Mesopore volume $\text{cm}^3 \text{g}^{-1}$	Micropore volume $\text{cm}^3 \text{g}^{-1}$	Adsorption conditions	Adsorption capacity for MB $\text{mg g}^{-1}$
Activated sunflower oil cake <sup>25</sup>	240	0.0063	0.111	$c_{i(\text{MB})} = 0\text{--}250 \text{ mg dm}^{-3}$ adsorbent dose $2 \text{ g dm}^{-3}$ , $T = 25 \text{ }^\circ\text{C}$	16
Pinecone activated carbon (this work)	1094	0.70	0.395	$c_{i(\text{MB})} = 300\text{--}500 \text{ mg dm}^{-3}$ adsorbent dose $2 \text{ g dm}^{-3}$ $T = 25 \text{ }^\circ\text{C}$ , pH 6	233
Vetiver roots activated carbon <sup>21</sup>	1272	0.80	0.390	$c_{i(\text{MB})} = 50\text{--}300 \text{ mg dm}^{-3}$ adsorbent dose $400 \text{ mg dm}^{-3}$ , $T = 25 \text{ }^\circ\text{C}$ , pH 4–5	394
Bamboo-based activated carbon <sup>26</sup>	1355	0.14	0.485	$c_{i(\text{MB})} = 0\text{--}250 \text{ mg dm}^{-3}$ adsorbent dose $1 \text{ g dm}^{-3}$ $T = 25 \text{ }^\circ\text{C}$	183
Bituminous coal-based activated carbon <sup>27</sup>	875	/	0.390	$c_{i(\text{MB})} = 100\text{--}1000 \text{ mg dm}^{-3}$ , adsorbent dose $1 \text{ g dm}^{-3}$ , pH 4	298

### Surface chemistry

The characteristics of the pinecone activated carbon and the results of the Boehm titration are given in Table II. Functional groups are important since they determine the acid–base character of activated carbons. Their electrical charge may also influence the adsorption of target molecules. Carboxylic groups were the major oxygen-containing surface functional groups on the PCAC surface. Only a small number of phenolic groups were found. The neutralization with HCl revealed the total amount of basic groups and showed that the number of acidic groups present was more than double the number of basic groups, probably due to the production method that involved phosphoric acid as the activating agent. In comparison to other activated carbons, the PCAC possessed a high number of functional groups (Table III).

The result of the  $\text{pH}_{\text{p.z.c.}}$  determination is presented in Table II. The low  $\text{pH}_{\text{p.z.c.}}$  value is consistent with the results of the Boehm titrations, which showed a dominance of acidic groups at the surface of the PCAC. At native (unadjusted) pH of MB solution, the PCAC surface was most probably negatively charged, which leads to an electrostatic attraction between the carbons surface and the MB cation.

TABLE II. Characteristics of the studied pinecone activated carbon

Parameter	Value
Yield, %	55.7
pH <sub>p.z.c.</sub>	3.06
Contact pH	3.51
Ash, %	6.35
Moisture, %	2.87
Density, g cm <sup>-3</sup>	1.58
Textural properties	
S <sub>BET</sub> / m <sup>2</sup> g <sup>-1</sup>	1094.1
Mesopore volume, cm <sup>3</sup> g <sup>-1</sup>	0.701
Mesopore area, m <sup>2</sup> g <sup>-1</sup>	481.65
Micropore volume, cm <sup>3</sup> g <sup>-1</sup>	0.395
Median pore diameter, nm	7.68
Surface functional groups, meq g <sup>-1</sup>	
Acidic groups	2.958
Carboxylic	1.742
Lactonic	0.723
Phenolic	0.493
Basic groups	1.357

TABLE III. Results of the Boehm titrations for activated carbons from various sources

Adsorbent	Synthesis parameters	Phenolic meq g <sup>-1</sup>	Lactonic meq g <sup>-1</sup>	Carboxylic meq g <sup>-1</sup>	Total acidic meq g <sup>-1</sup>	Total basic meq g <sup>-1</sup>
Jute fiber carbon <sup>28</sup>	Precursor: 15 % H <sub>3</sub> PO <sub>4</sub> 1:3, hot air oven, 12 h	0.045	0.01	0.025	0.08	–
Activated jackfruit peel waste <sup>29</sup>	Precursor: 85 % H <sub>3</sub> PO <sub>4</sub> 1:3, 550 °C, 45 min, N <sub>2</sub> , washing with warm distilled water	0.261	0.391	0.737	1.389	1.025
Pinecone activated carbon (this work)	Precursor: 85 % H <sub>3</sub> PO <sub>4</sub> 1:3, 500 °C, 60 min, N <sub>2</sub> , washing with warm HCl and distilled water	0.493	0.723	1.742	2.958	1.357
Activated sunflower oil cake <sup>25</sup>	Precursor: H <sub>2</sub> SO <sub>4</sub> 1:1.9, 600 °C, 120 min, N <sub>2</sub> , washing with hot and cold distilled water	0.362	0.125	0.325	0.812	–
Bamboo-based activated carbon <sup>26</sup>	Precursor: H <sub>3</sub> PO <sub>4</sub> 1:3, 600 °C, 90 min, N <sub>2</sub> , washing with distilled water	0.12	0.16	0.74	1.02	0.025

### Adsorption kinetics

The experiments of adsorption kinetics were performed to establish the effect of time on the adsorption process (Fig. 3). Four theoretical kinetic models were applied.

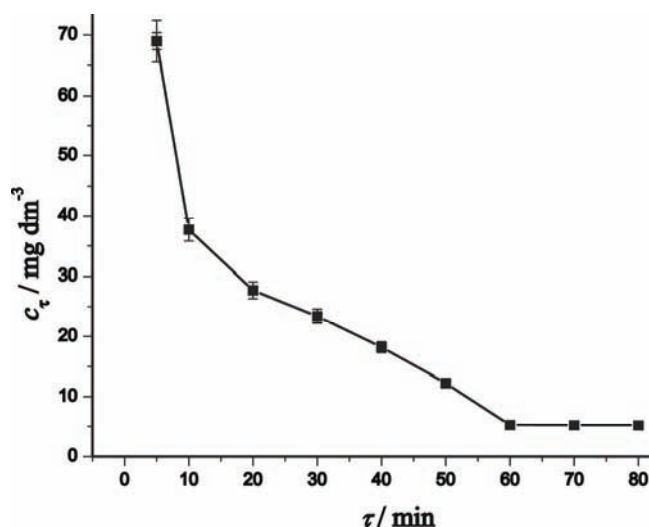


Fig. 3. Effect of contact time on MB adsorption by PCAC.

The pseudo-first-order kinetic model defined by Lagergren is one of the most used adsorption models defining the adsorption of an adsorbate from a solution.<sup>18</sup> It can be written as:

$$\ln(q_e - q_\tau) = \ln q_e - k_1 \tau \quad (2)$$

where  $k_1$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of pseudo-first-order adsorption. The values of  $k_1$  were obtained from the slopes of the linear plots of  $\ln(q_e - q_\tau)$  vs.  $\tau$  (Fig. 4a).

The pseudo-second-order kinetic model may be expressed as:

$$\frac{\tau}{q_\tau} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tau \quad (3)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the equilibrium rate constant for a pseudo-second-order adsorption and was calculated from the plot of  $\tau/q_\tau$  against  $\tau$  (Fig. 4b).<sup>19</sup>

The Elovich model is represented as:

$$q_\tau = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln \tau \quad (4)$$

where  $\alpha$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $\beta$  ( $\text{g mg}^{-1}$ ) are constants of the adsorption and were determined from a plot  $q_\tau$  vs.  $\ln \tau$  (Fig. 4c).<sup>20</sup>

A Weber and Morris plot is used to examine the intraparticle diffusion model.<sup>21</sup> This model is defined by the following equation:

$$q_{\tau} = k_i \tau^{1/2} \quad (5)$$

where  $k_i$  is the constant of adsorption and was determined from a plot  $q_{\tau}$  vs.  $\tau^{1/2}$  (Fig. 4d).

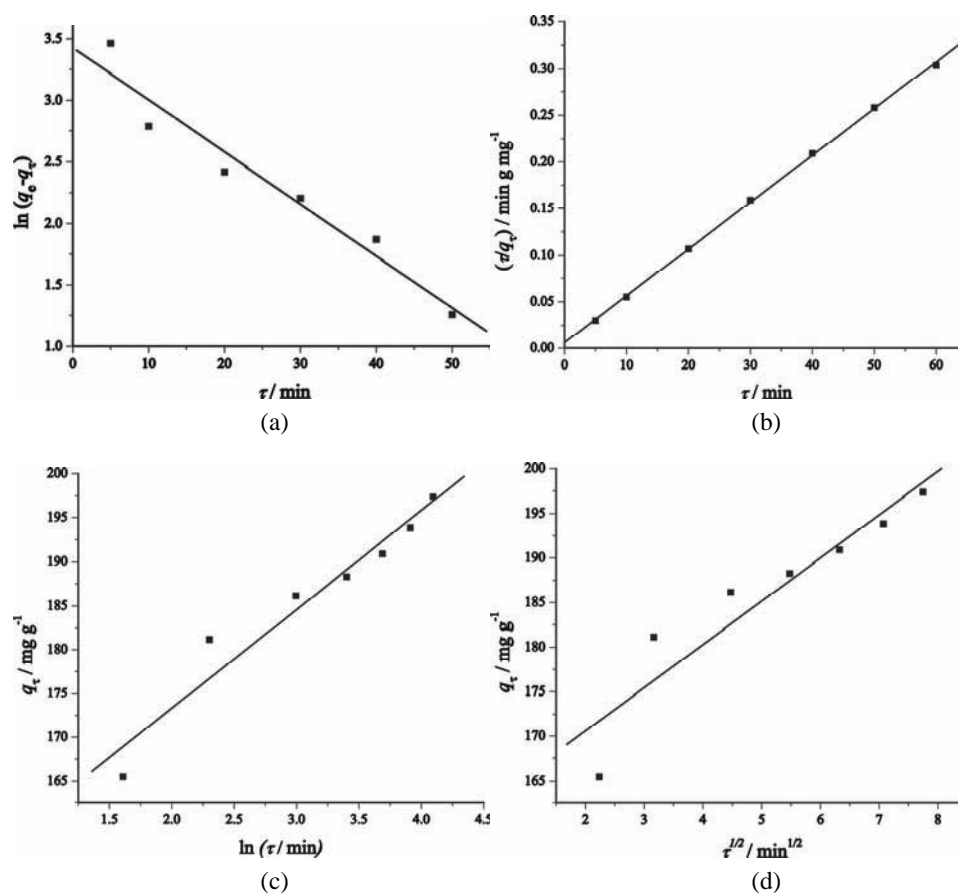


Fig. 4. Kinetic models for the adsorption of MB onto pinecone activated carbon: a) pseudo-first-order, b) pseudo-second-order, c) Elovich model and d) intraparticle diffusion model.

The validity of the exploited models is verified by the correlation coefficient,  $r^2$  (Table IV). The comparison of the  $r^2$  values for the different models implies that the pseudo-second-order kinetic model represents the data in the best way. Hence, it could be concluded that the overall rate of MB adsorption onto the PCAC was controlled by chemisorption processes. The establishment of chemical bonds



and the overlapping of orbitals is, thus, a very probable mechanism of binding of MB to the carbon surface.

TABLE IV. Kinetic parameters for the adsorption of MB onto pinecone activated carbon

Kinetic model	Value
Pseudo-first-order	
$k_1 / \text{g mg}^{-1} \text{ min}^{-1}$	-0.04229
$r^2$	0.97221
Pseudo-second-order	
$k_2 / \text{g mg}^{-1} \text{ min}^{-1}$	0.004
$q_e / \text{mg g}^{-1}$	199.2
$r^2$	0.999
Elovich Equation model	
$\alpha / \text{mg g}^{-1} \text{ min}^{-1}$	7368133
$B / \text{g mg}^{-1}$	0.088
$r^2$	0.971
Intraparticle diffusion model	
$k_i / \text{g mg}^{-1} \text{ min}^{-1}$	4.853
$r^2$	0.937

#### Adsorption isotherms

Adsorption isotherms are used as a function of adsorbate concentration on the adsorbent surface at a constant temperature (Fig. 5). In this study, the equilibrium data were analyzed by considering the linearized Langmuir, Freundlich and Temkin isotherm model equations.

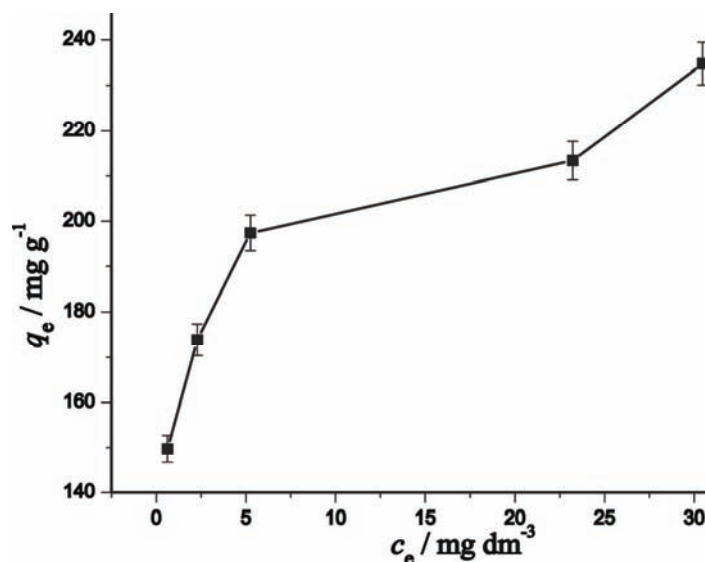


Fig. 5. Adsorption isotherm of MB by PCAC at 25 °C.

The Langmuir isotherm model is given below:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} c_e \quad (6)$$

where  $K_L$  is the Langmuir equilibrium constant ( $\text{dm}^3 \text{mg}^{-1}$ ) and  $q_{\max}$  ( $\text{mg g}^{-1}$ ) is the maximum adsorption capacity (Fig. 6a).<sup>22</sup> The most important feature of Langmuir isotherm is called the Separation Factor,  $R_L$ , which is defined as:

$$R_L = \frac{1}{1 + K_L c_0} \quad (7)$$

The value of the Separation Factor defines the types of isotherms: unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), irreversible ( $R_L = 0$ ), and favorable  $0 < R_L < 1$ .

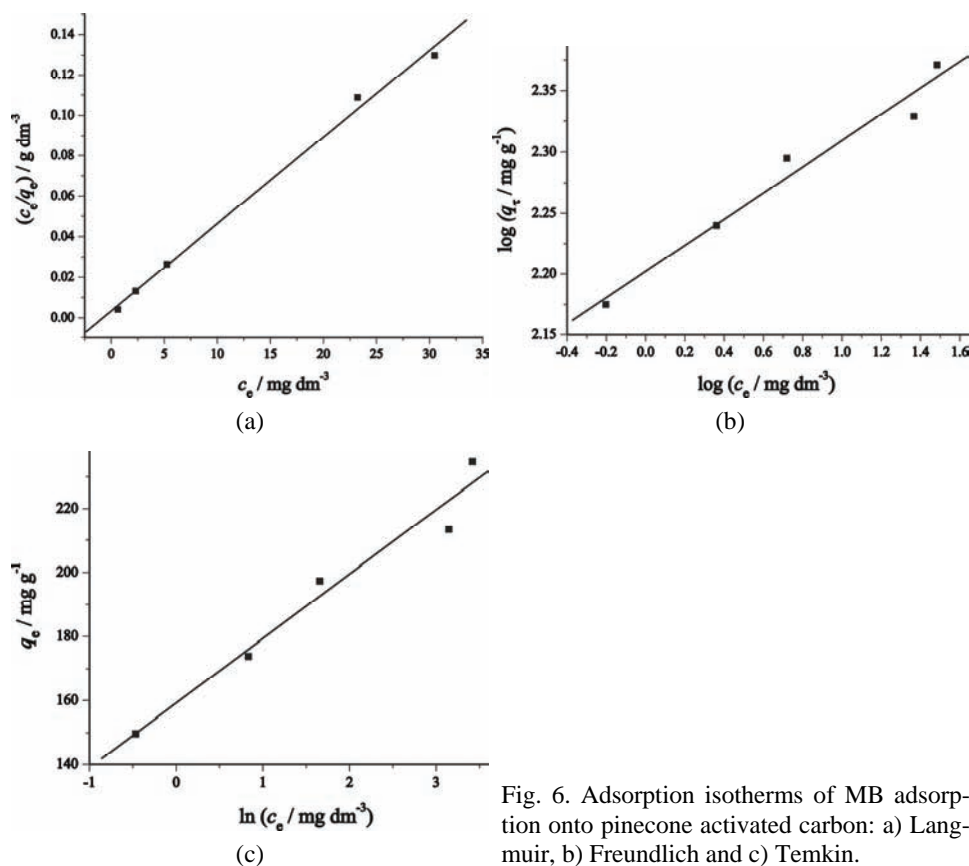


Fig. 6. Adsorption isotherms of MB adsorption onto pinecone activated carbon: a) Langmuir, b) Freundlich and c) Temkin.

The Freundlich adsorption isotherm is based on the adsorption onto heterogeneous surfaces.<sup>27</sup> The equation of the Freundlich adsorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \tag{8}$$

where  $K_F$  ( $(\text{mg g}^{-1}) (\text{dm}^3 \text{mg}^{-1})^{1/n}$ ) is the Freundlich constant and  $n$  is Freundlich exponent, which were determined from the plot shown in Fig. 6b.

The Temkin isotherm is represented by the following equation:

$$q_e = A + B \ln c_e \tag{9}$$

where  $A$  and  $B$  ( $\text{dm}^3 \text{g}^{-1}$ ) are constants easily determined from a plot of  $q_e$  vs.  $c_e$  (Fig. 6c).<sup>24</sup>

The Langmuir isotherm fits quite well with the experimental data quite well ( $r^2 = 0.997$ ) whereas the lower correlation coefficients ( $r^2 = 0.984$  and  $r^2 = 0.852$ ) show that the agreement of the Freundlich and Temkin isotherms with the experimental data was worse (Table V). The Langmuir isotherm assumes a monolayer adsorption onto the carbon surface containing a finite number of adsorption sites. The adsorption process is supposed to be uniform with no transmigration of the adsorbate in the plane of the surface.

TABLE V. The equilibrium model parameters for the adsorption of MB onto pinecone activated carbon

Equilibrium model	Value
Langmuir isotherm	
$K_L / \text{dm}^3 \text{g}^{-1}$	1.262
$q_{\text{max}} / \text{mg g}^{-1}$	233.1
$R_L$	0.0016
$r^2$	0.997
Freundlich model	
$K_F / (\text{mg g}^{-1}) (\text{dm}^3 \text{mg}^{-1})^{1/n}$	159.24
$n$	9.3248
$r^2$	0.984
Temkin isotherm	
$A$	159.21
$B / \text{dm}^3 \text{g}^{-1}$	20.156
$r^2$	0.852

Table III indicates that the activated carbon studied in this work showed a considerably large adsorption capacity for MB along with a high specific surface area and mesopore volume.

*Influence of pH on adsorption*

The pH of the solution was reported to be a significant factor that influences the adsorption of MB as it controls the electrostatic interactions between the carbon surface and adsorbate.<sup>25</sup> The pH of the suspension in all kinetic and equilibrium experiments was 6.3. In the case of different pH values, it was esta-



blished that the adsorption of MB increased with the increasing pH (Fig. 7). Lower adsorption of MB at acidic pH is due to the presence of excess  $H^+$  that compete with the MB cations for the adsorption sites. As the surface becomes less positive with increasing suspension pH, the electrostatic repulsion of the MB cations is lower, which results in a higher adsorption. At pH values higher than the  $pH_{p.z.c.}$ , the surface is considered to be negatively charged with predominantly strong electrostatic attraction towards the MB cations.

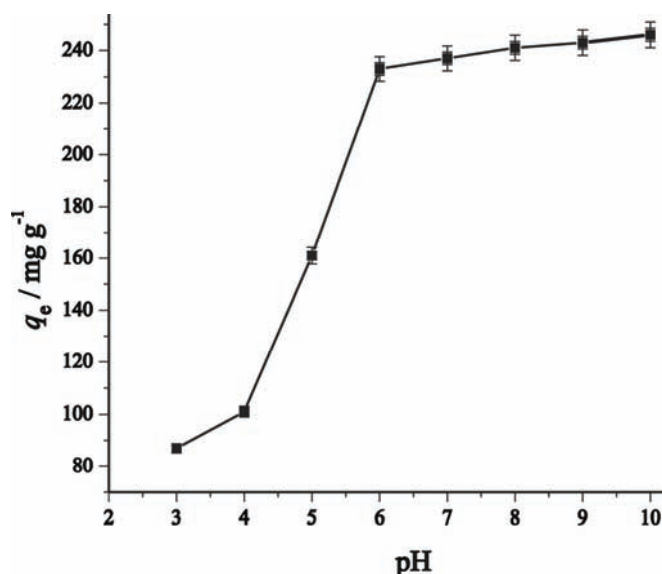


Fig. 7. Effect of pH on the adsorption of MB onto pinecone activated carbon.

#### CONCLUSIONS

In this work, pinecones were efficiently utilized as the raw material for the production of activated carbon with a high specific surface area. The adsorption experiments showed a significant adsorption affinity of the PCAC towards MB with maximum adsorption capacity of  $233.1 \text{ mg g}^{-1}$ . The adsorption of MB onto the carbon particles was found to be a fast process that reaches equilibrium in 60 min. The results of the kinetic study were best fitted by the pseudo-second-order model, which suggests the establishment of chemical bonds between MB and the carbon surface (chemisorption). The equilibrium data agreed well with the Langmuir isotherm model, implying a monolayer adsorption. The obtained  $R_L$  value for the adsorption of MB onto the PCAC was less than 1 and greater than zero, indicating favorable adsorption. Increasing the suspension pH led to a higher uptake of MB because protons compete with the MB cations for the adsorption sites under acidic conditions. The Boehm titration revealed that most of the acidic groups on the carbon surface were carboxyl groups followed by lactonic and

phenolic groups. SEM images showed that the adsorption of MB did not change the carbon surface significantly.

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## ИЗВОД

## УКЛАЊАЊЕ КАТЈОНСКЕ БОЈЕ ИЗ ВОДЕ ПОМОЋУ АКТИВИРАНИХ БОРОВИХ ШИШАРКИ

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Адсорпција катјонске фенотиазинске боје метилен плаво на активном угљу добијеном из шишарке црног бора је испитана уз промену времена контакта, концентрације боје и рН вредности. Утврђено је да се подаци кинетичких испитивања најбоље слажу са моделом псеудо-другог реда. Подаци равнотежних испитивања се најбоље поклапају са Ленгмировим моделом уз максимални адсорпциони капацитет од 233,1 mg g<sup>-1</sup>. Адсорпција је фаворизирана на вишим рН вредностима. Текстурална анализа извршена проучавањем адсорпције азота је искоришћена да се одреди специфична површина и структура пора добијеног материјала. Бомове титрације су доказале да су карбоксилне групе присутне у највећој мери од свих киселих кисеоничних група на површини активног угља. Резултати ове студије указују да се описаном методом за активацију борових шишарки може добити активни угаљ који има значајну порозност, развијену површинску реактивност и висок адсорпциони капацитет према катјонској боји метилен плаво.

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