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Absorption of methylene blue from aqueous solutions on activated coal CAN-9: kinetics and equilibrium studies

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Abstract
The adsorption of methylene blue and kinetics of its adsorption from aqueous solutions on activated carbon CAN-9, obtained from walnut shells by chemical activation with orthophosphoric acid were studied. It has been shown that methylene blue adsorption isotherm from aqueous solutions on CAN-9 in the linear coordinates of the Langmuir model is a straight line (R = 0.99427) and is of Langmuir type. The kinetics of methylene blue adsorption on CAN-9, measured at two initial concentrations, showed an increase in K_{int} and C values with the increase of the initial concentrations. The process of intra-particular diffusion occurs in only one stage and takes place in the mesopores.

Keywords: *methylene blue, activated carbon, adsorption kinetics, adsorption in static conditions*

INTRODUCTION

Methylene blue is an organic dye with various uses. In medicine, it is used as an antiseptic for the treatment of infections of the oral cavity and genitourinary tract [1, 2]. It is used to detoxify the human body in case of poisoning with cyanide, carbon monoxide and hydrogen sulphide. It is applied in the treatment of Alzheimer's disease [3, 4]. Methylene blue is widely used to determine the quality index of activated carbon [5]. This dye is commonly used in dyeing cotton, wool, and silk fabrics. Wastewater from textile factories that use methylene blue as a dye is toxic [6]. This dye when entering the biological wastewater treatment systems endangers the good activity of activated sludge. Therefore, wastewater polluted with methylene blue must be treated at local stations. One of the most effective methods of removing methylene blue from aqueous solutions is the sorption of this dye on carbon adsorbents. The results of scientific research related to the study of the adsorption processes of methylene blue on native carbon adsorbents may serve as a scientific base for development of wastewater treatment technologies.

There are several publications on the adsorption study of methylene blue from aqueous solutions on carbon adsorbents, obtained from various raw materials [7-12]. In these works, the efficiency of removing cationic dye - methylene blue - from aqueous solutions has been demonstrated.

Hatem et al. [7] studied the process of removing methylene blue from aqueous solutions on activated carbon obtained from cotton waste. The Langmuir model well describes the adsorption process. The pseudo-two model best describes the kinetics of the process. The mechanism of adsorption of methylene blue was spontaneous and endothermic in nature.

Two viscose carbon fibre samples (VACFF-1300 and VACFF-1600) with different specific surfaces and different porous structures were used as adsorbents for the removal of methylene blue from aqueous solutions [8]. The results showed that the Langmuir model well describes the experimental data. The kinetics of the adsorption process on both fibre samples correspond to the pseudo-two model and the intra-particle diffusion, for both VACFF-1300 and VACFF-1600, the external diffusion is a stage of control of the process speed.

In the work [9] for the removal of methylene blue from solutions, activated carbons obtained from date kernels by chemical activation with zinc chloride were used.
Graphene-carbon nanotubes (G-CNT) were used for the removal of organic dyes from solutions, which were prepared directly, using the simple method by the hydrothermal process, in one-step. These nanotubes have demonstrated a good ability to adsorb methylene blue from aqueous solutions. The adsorption kinetics of methylene blue is best described using the pseudo-two model, and the adsorption process of methylene blue is best described by applying the Freundlich model. This study suggests that graphene-carbon nanotubes can be successfully used to remove organic pollutants from water [10].
Vetiver roots were used to obtain activated carbon by chemical activation, after impregnation with orthophosphoric acid. The adsorption process of methylene blue on this adsorbent is a complex one [11]. Rafatuiiaha et al. [12] describe the use of activated carbon obtained from agricultural waste for the removal of methylene blue from wastewater. Imam and Abdullahi [13] presented the scientific results on studying the processes and mechanisms of adsorption of methylene blue from aqueous solutions on carbon adsorbents. The activated carbons used were obtained from peanut shells by chemical activation impregnated with Fe_3O_4.
Qun [14] studied the adsorption process and the adsorption kinetics of methylene blue from aqueous solutions on the molecular sieve MCM-41. It has been shown that the adsorption of methylene blue on MCM-41 could be described using the Freundlich model and the pseudo-two order kinetic model and that the adsorption value of methylene blue can reach 24.5 mg/g in 30 min.
The adsorption of methylene blue from aqueous solutions on activated charcoal obtained from pea husks increases with the increase of temperature and contact time [15]. The Langmuir model best describes the adsorption isotherm of methylene blue.
Gao et al. [16] studied the adsorption process of methylene blue on activated carbon obtained from tea seed husks, by chemical activation with $ZnCl_2$. The Langmuir model best describes the adsorption process. The kinetics of the adsorption process indicate that the pseudo-two model best describes the kinetic data. Thermodynamic studies have shown the exothermic nature of the adsorption process.
Activated carbon obtained from flaming pods showed a particularly good adsorption capacity of methylene blue dye, better than several carbon adsorbents described in the literature. The mechanism of adsorption of methylene blue is complex and includes electrostatic interaction, hydrogen bonding, and electron donor-acceptor and π-π interaction [17].
From the data presented in the literature it can be concluded that carbon adsorbents, obtained from food industry waste, can be successfully used for removal of organic pollutants from water, and in particular for methylene blue. The mechanism and kinetics of the adsorption process depend on structural parameters of the adsorbent and homogeneity of its surface.
The aim of the present research is to study the kinetics and static adsorption of methylene blue from aqueous solutions on activated charcoal CAN-9, obtained in the laboratory from walnut shells, by chemical activation with orthophosphoric acid.

MATERIALS AND METHODS

CAN-9 activated carbon was obtained from walnut shells, which are representing a food industry waste. Activated charcoal technology includes impregnating walnut shells with orthophosphoric acid with subsequent heating up to 70 °C for 4 hours followed by chemical activation at 400 °C for 2 hours. Methylene blue (Standard Fluka) was used as adsorbate. The structural parameters of CAN-9 activated carbon were determined from nitrogen adsorption-desorption isotherm, measured on Autosorb-1 [18]. The adsorption isotherms were measured under static conditions, at various initial concentrations of methylene blue solutions using the same mass of activated carbon, at a temperature of 18°C [19].

RESULTS AND DISCUSSION

The chemical structure of methylene blue is shown in Figure 1.

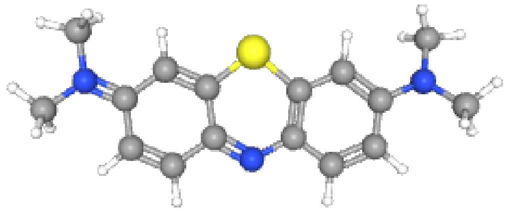


Fig. 1. Chemical structure of methylene blue [20]

Figure 1 shows that the chemical structure of methylene blue is planar.
As for Figure 2, the nitrogen adsorption isotherm on CAN-9 activated carbon on the Autosorb 1 apparatus is shown.

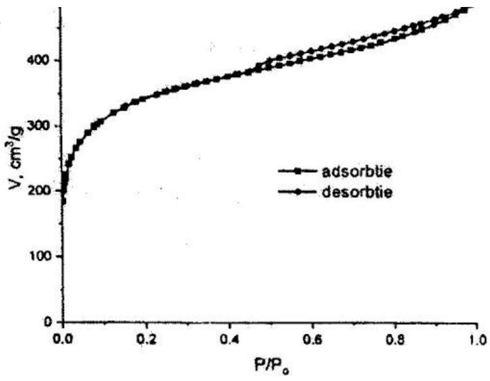


Fig. 2. Nitrogen adsorption isotherm on activated carbon CAN-9

The presence of hysteresis can be observed in Figure 2, which denotes the existence of mesopores on the surface of the studied activated carbon.
Table 1 shows the structural parameters of CAN-9 activated carbon.

Table 1. CAN-9 activated carbon structure parameters

Parameter	S_{BET}, M^2/g	Vs, cm^3/g	V_{mi}, cm^3/g	V_{me}, cm^3/g
CAN-9	1246	0.753	0.408	0.345

According to the data presented in Table 1, there is a significant share of the volume of the mesopores, slightly smaller than the micropores. The specific surface area of charcoal is quite large.
Figure 3 shows the pore distribution curve, by size, on CAN-9 activated carbon, determined based on nitrogen adsorption-desorption isotherm on the sample under study.
From the data presented in Figure 3 it can be found that, on this coal, the effective radius of the large pores is 27Å, so it presents small mesopores. There are also larger mesopores with an effective pore radius of around 45 Å. As can be seen from the pore distribution curve by size, activated carbon presents many ultra-micropores with an effective radius of up to 7 Å. These pores will probably not be accessible to the relatively large molecules of methylene blue in the adsorption process.

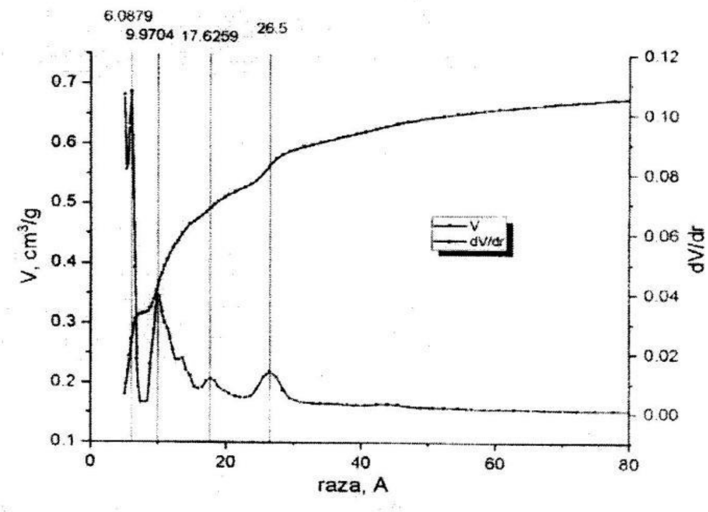
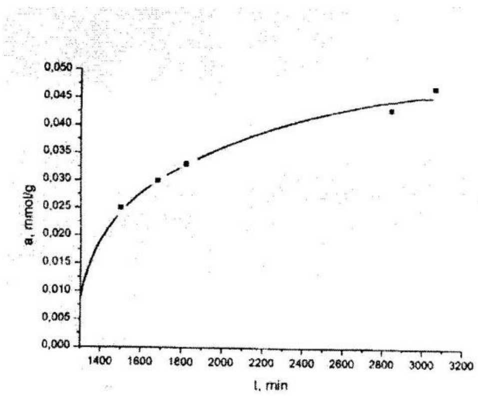


Fig. 3. Pore distribution curve by size on CAN-9 activated carbon

Figure 4 shows the adsorption kinetics curve of methylene blue from aqueous solutions on CAN-9 at the initial concentration of methylene blue $C_o = 0.125$ mmol/L, t = 18 °C.



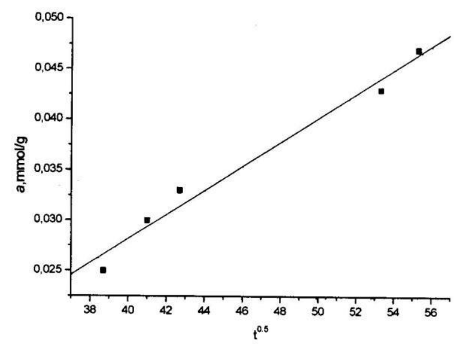


Fig. 4. Kinetics of methylene blue adsorption from aqueous solutions on activated carbon CAN-9, ($C_0 = 0.125$ mmol/L), t = 18 °C

Fig. 5. Intra-particular diffusion model for adsorption of methylene blue on CAN-9 activated carbon ($C_0 = 0.125$ mmol/L)

In the evaluation of intra-particle diffusion process, the model described by Liu et al. [8] was used, namely:

$$q_t = k_{int} t^{0.5} + C \quad (1)$$

where q_t is the adsorption value of methylene blue, k_{int} is the value of the intra-particular diffusion constant, numerically being equal to the tangent of the right angle in the q_t - $t^{0.5}$ coordinates, C is the value of the segment on the axis of the ordinate that intersects the line in the coordinate's q_t - $t^{0.5}$.
Figure 5 shows the dependence q_t of $t^{0.5}$ ($q_t = a$, mmol/g), obtained based on the kinetic curve of the adsorption of methylene blue from aqueous solutions on CAN-9 activated carbon.
The data in Figure 5 are placed quite well on a straight line (R = 0.98948), from which were determined the values of k_{int} and C. They are equal to 0.0011 mg/g min and 0.0245 respectively.
Figure 6 shows the adsorption kinetics of methylene blue from aqueous solutions on CAN-9 activated carbon ($C_0 = 0.3125$ mmol/L).

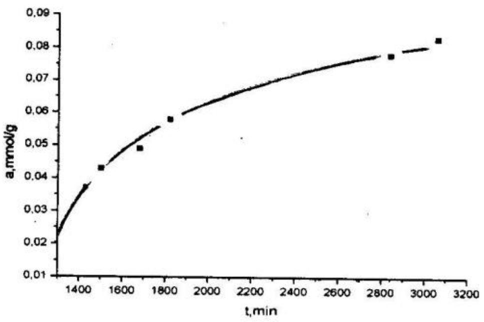


Fig. 6. Kinetics of adsorption of methylene blue from aqueous solutions on CAN-9 activated carbon (C_0 = 0.3125 mmol/L)

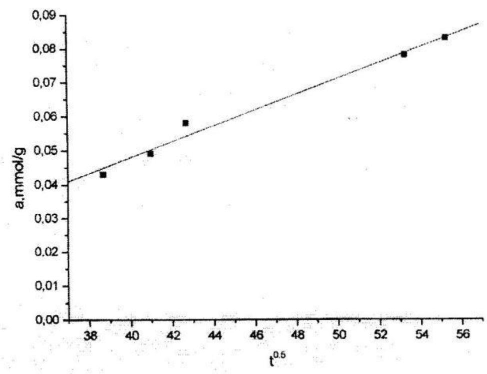


Fig. 7. Intra-particular diffusion model for adsorption of methylene blue on CAN-9 activated carbon (C_0 = 0.3125 mmol/L)

The dependence q_t of $t^{0.5}$ (q_t = a, mmol/g), obtained based on the kinetic curve of methylene blue adsorption from aqueous solutions on CAN-9 activated carbon (C_0 = 0.3125 mmol/g), is shown in Figure 7.

From Figure 7 results that, k_{int} is equal to 0.0021, and C is equal to 0.041. Based on the data shown in Figure 7 the process of intraparticle diffusion occurs only in one stage, probably in mesopores, due to the inaccessibility of methylene blue molecules in the relatively small pores of the studied activated carbon. Comparison of k_{int} and C values calculated from the kinetic curves shown in Figure 4 and 6 measured at different initial concentrations of methylene blue, it can be observed an almost double increase in them. With the increase of the methylene blue initial concentration in the solutions, the speed of inter-particular diffusion increases, but also the thickness of the layer at the interface.

Figure 8 shows the adsorption isotherm of methylene blue from aqueous solutions on CAN-9 activated carbon at a temperature of 18 °C, and Figure 5 shows adsorption isotherm in the linear coordinates of the Langmuir model.

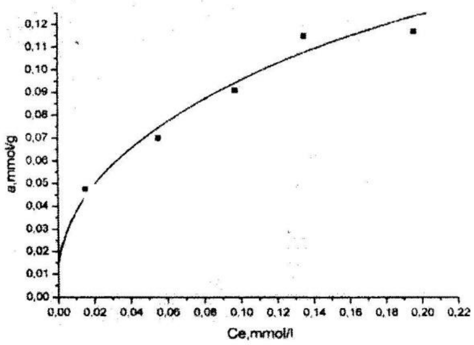


Fig. 8. Adsorption isotherm of methylene blue from aqueous solutions on activated carbon CAN-9, t = 18 °C

From the presented data it can be found that the isotherm of methylene blue adsorption from aqueous solutions on activated carbon CAN-9 is of Langmuir type. This suggests that adsorption of methylene blue takes place on the adsorption centres, and that these adsorption centres are identical. Probably, there will be a collateral interaction between the molecules adsorbed on the centres, but anyway, the experimental points fit quite well on a straight line in Figure 9. The value of the maximum adsorption of methylene blue on CAN-9 activated carbon, based on the data presented in Figure 9 is equal to 0.173 mmol/g (a_m = ctg of the right angle in the coordinates c_e/a of c_e).

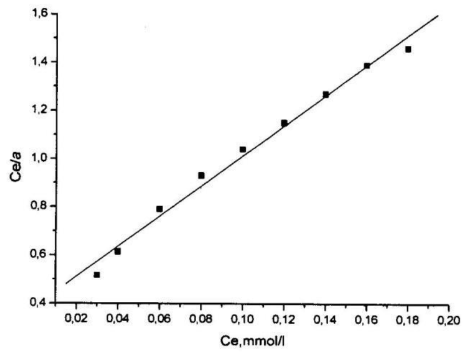


Fig. 9. Adsorption isotherm of methylene blue from aqueous solutions on CAN-9 activated carbon, in the linear coordinates of the Langmuir model

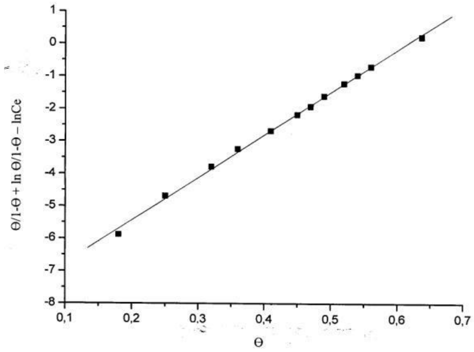


Fig. 10. Adsorption isotherm of methylene blue in the linear coordinates of the Hill-de-Boer model

Figure 10 shows the isotherm of methylene blue adsorption in the linear coordinates of the Hill-de-Boer model [21]:

$$\frac{\Theta}{1-\Theta} + ln\frac{\Theta}{1-\Theta} - lnC_e = lnK_1 + K_2\Theta \qquad (2)$$

$$\Theta = \frac{a}{a_m} \qquad (3)$$

where a_m was determined from the linear shape of the Langmuir model.

The experimental points fit very well to a straight line (R = 0.9990). The tangent of the right angle is numerically equal to K_2 (adsorbent-adsorbent interaction constant in the adsorption layer). Being very small, it justifies the applicability of the Langmuir model to the system under study. K_1 is the adsorbate-adsorbent interaction constant.

Thus, the process of adsorption of methylene blue from aqueous solutions on CAN-9 activated carbon is well described using the Langmuir model in its linear coordinates and the kinetics of the adsorption process of methylene blue is best described by the applicability of the pseudo-two model.

CONCLUSIONS

The process of intra-particle diffusion of methylene blue, calculated based on the kinetic curves of methylene blue adsorption, at various initial concentrations, demonstrates that the adsorption process occurs mainly in mesopores.

As the concentration of methylene blue in the solution increases, the speed of the adsorption process (K_{int}) of the dye on CAN-9 activated carbon increases. The value of the layer thickness at the interface also increases (C).

The study of the methylene blue adsorption from aqueous solutions on CAN-9 activated carbon demonstrates the applicability of the Langmuir model in this system.

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