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Article

Kinetics of caffeine adsorption from aqueous solutions on active charcoal AC-0-9

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Abstract
The process of the kinetics of caffeine adsorption from aqueous solutions on activated carbon AC-0-9, obtained from apple wood, was studied. Analysis of nitrogen adsorption-desorption isotherms demonstrated that this carbon adsorbent is basically mesoporous. The pseudo-two model describes best the kinetic process, highlighting the role of functional groups on the activated carbon surface. The pseudo-one model only initially describes the kinetic process of caffeine adsorption on this activated carbon. It was found that the kinetics of the adsorption process of caffeine on AC-0-9 activated carbon takes place in two stages. In the first stage, the speed of intraparticle diffusion is high, due to the adsorption of caffeine molecules in macro- and mesopores, and in the second stage, the speed of intraparticle diffusion is low, given the fact that adsorption occurs in micro- and supermicropores.

Keywords: *adsorption kinetics, activated carbon, caffeine*

INTRODUCTION

1,3,7-trimethylxanthine or commonly known as caffeine, is a weak alkaloid from the methylxanthine family. This compound is classified as a drug, is a nervous system stimulant and causes transient changes in blood pressure. Caffeine is used as an adjuvant in many pharmaceutical combinations to increase its analgesic effects. It is present in beverages such as coffee, tea, chocolate drinks, etc. [1].

Caffeine is an emerging compound that is found in surface and wastewaters due to increased use of coffee by the population and its elimination through urine [2, 3]. Emerging pollutants are increasingly present in the environment, because of irresponsible human actions such as poor management of toxic waste, pharmaceuticals and excessive use of pesticides and other chemicals in agriculture. As a rule, the emergent compounds are non-biodegradable, for this reason they must be removed from wastewater at treatment plants. Advanced oxidation and adsorption processes are usual ones to remove emergent pollutants from wastewater. According to Otalvaro et al [4], one of the most efficient technologies of emerging pollutants removal is the adsorption method.

In scientific literature the kinetics of caffeine adsorption on the Verde-Lodo mineral adsorbent, from aqueous solutions, at different temperatures was studied [5]. It aimed to investigate the use of thermally modified Verde-Lodo bentonite for the discontinuous adsorption of caffeine from aqueous solution. The adsorption kinetic study was carried out at 25 °C. The stirring time of the solid and liquid phases was 40 hours. The analysis of the experimental results showed that the pseudo-two model describes the adsorption kinetics process.

The other article shows scientific results for the activated carbon fibres obtaining from pineapple leaves and their application for the adsorption of caffeine from aqueous solutions [6]. Activated carbon was obtained by chemical activation with phosphoric acid. The specific surface area and structure of activated carbon was determined from N_2 adsorption and desorption isotherms, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, Boehm titration and the pHpzc method. The paper highlights the fact that the specific BET surface area of the carbonic

adsorbent is 1031 m^2/g, the mesoporous volume is equal to 1.27 cm^3/g, the average pore diameter is equal to 5.87 nm. Acidic functional groups are present on the surface of activated carbon. Studies of the adsorption processes indicated that the adsorption isotherm is of the Langmuir type and the adsorption kinetics is described by the pseudo-two model.
In paper [7] the adsorption of caffeine on multi-walled carbon nanotubes (MWCNTs) as an adsorbent was studied, under distinct experimental conditions. Using the pseudo-two model, the authors described the kinetics of the caffeine adsorption process on the nanotubes under study (R^2 = 0.993). The adsorption process obeys the Langmuir-Freundlich model. The model assumes the heterogeneity of the adsorbent and consists of energetically different sectors, distributed over its entire surface.
The work [8] focuses on the problem of the various substances' low speed of sorption and desorption, on the causes of these phenomena occurrence inside the solid phase particles, and on the link of these phenomena to the intraparticle transfer of pollutants.
The carbonic adsorbent (PNCO), which was used to remove caffeine from aqueous solutions, was obtained from pine needles. This adsorbent was also used in the study of caffeine adsorption kinetics. The analysis of the obtained results demonstrates that the pseudo-two model perfectly describes the process of caffeine adsorption kinetics on PNCO [9].
The kinetics of caffeine absorption in the human organism was studied in the paper [10]. In this work it is specified that, in the human organism, caffeine is metabolized due to oxidation reactions, up to paraxanthine, theobromine and theophylline.
The study of caffeine adsorption on oxidized carbon obtained from Luffa Cylindrica (OLC) demonstrated that the kinetic experimental data follow the pseudo-two model, and the caffeine adsorption isotherms from aqueous solutions are well described, based on the Langmuir and Freundlich equations [11]. Adsorption of caffeine at pH values between 4.0 and 10.4 is due to electrostatic interactions between the negative OLC surface and the cationic form of caffeine.
The results of scientific research regarding the impact of pH, temperature, adsorbent dose on the efficiency of caffeine adsorption from aqueous solutions are presented in the paper [12]. It was highlighted that the caffeine adsorption value varied between 10 and 1000 mg/g depending on the nature and properties of the adsorbent. The experimental results highlighted the pseudo-second order of the adsorption kinetics and the Langmuir model of the adsorption isotherms.
In other paper, the kinetics of the adsorption processes of caffeine and diclofenac on granulated activated carbon were studied [13]. Diffusion (PSDM) model has been used to predict the fixed-bed breakthrough curves for caffeine aqueous solutions. Biot (Bi) number values, ranging from 1 to 100, were obtained, indicating that the surface diffusion inside the micropores represents the rate-controlling step in the process for the experimental conditions used in the study.
The analysis of bibliography related to the kinetics of caffeine adsorption on carbon sorbents highlights that these processes on activated carbons obtained from the wood of fruit trees are understudied. Based on the above-mentioned, the aim of the current work is to study the kinetics of caffeine adsorption from aqueous solutions on activated charcoal CA-0-9 obtained from apple wood in fluidized bed.

MATERIALS AND METHODS

AC-0-9 activated carbon was obtained from apple wood in fluidized bed. The technology of active charcoal production includes charring of apple wood in the first phase, at a temperature of 450°C, in the absence of oxygen. In the second phase, the process of charcoal activation is carried out at a temperature of 1000°C, with water vapour, for 30 minutes.
Caffeine was purchased from Sigma Aldrich, Merck.
The structural parameters of AC-0-9 activated carbon were determined from the nitrogen adsorption-desorption isotherm, measured on Autosorb-1, MP, Quantachrome Instruments, USA [14]. The kinetics of the adsorption processes was established by measuring the adsorption value as a function of the stirring time until the equilibrium of the process was established at a temperature

of 25 ℃ [15]. The adsorption isotherms were measured under static conditions, at different initial concentrations of caffeine solutions at the same mass of activated carbon, at a temperature of 25℃.

RESULTS AND DISCUSSIONS

The chemical structure of caffeine is shown in Figure 1.

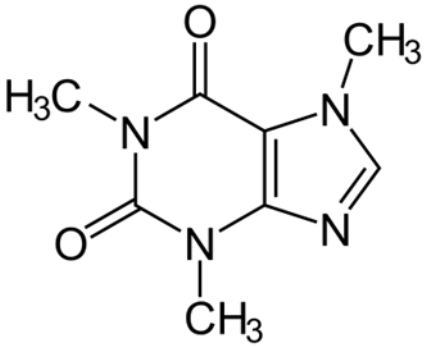

Fig. 1. The chemical structure of caffeine.

The kinetics of caffeine adsorption from aqueous solutions on AC-0-9 activated carbon at t= 25 ℃ is shown in Figure 2.

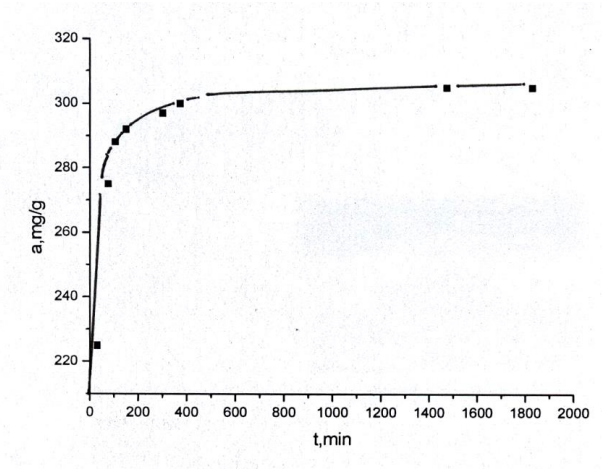

Fig. 2. The kinetics of caffeine adsorption from aqueous solutions on activated carbon AC-0-9, t=25℃

The specific BET surface area and structural parameters of AC-0-9 activated carbon are presented in Table 1.

Table 1. Structural parameters of AC-0-9 activated carbon

Parameter	S_{BET}, m^2/g	V_S, _ cm^3/g	V_{mi}, cm^3/g	V_{me}, cm^3/g
AC-0-9	1537	1.359	0.350	1.009

According to data presented in Table 1, AC-0-9 activated carbon is a mesoporous adsorbent, but also with an important content of micropores, that contributes to a larger specific surface of the adsorbent. This can also be seen from the integral and differential pore size distribution curve, shown in Figure 3.

Figure 4 shows the caffeine adsorption isotherm from aqueous solutions on AC-0-9 activated carbon, measured at 25 ℃. Data presented in figure 4 show that the caffeine adsorption isotherm on AC-0-9 is of type 1 according to the Brunuer S. et al. classification [16].

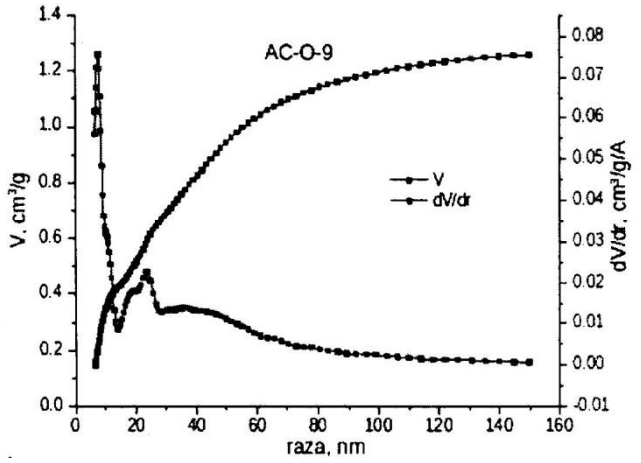

Fig. 3. Pore size distribution curve of activated carbon AC-0-9

In scientific literature [17] it is stipulated that in any molecules ratio of dissolved substance and solvent (water), the entire surface of the adsorbent will be completely covered with molecules of the dissolved substance (adsorbate). The adsorption of one of the solution components (the dissolved substance) is always accompanied by the displacement of an equivalent amount, according to the projection surface of the molecules number of the second component of the solution. Paper [18] presents the types of adsorption isotherms from solutions (C. H. Giles classification), which separates the adsorption isotherms into 4 classes (S, L, H, C, according to the shape of the curve). According to this classification, isotherm shown in figure 4 corresponds to the "L" shape. Paper [18] specifies that the heat of adsorption does not depend on the degree of coverage of the adsorbent surface and the lack of competition from the solvent. The lack of competition from the solvent (in this case, water) justifies the applicability of the gas adsorption isotherm classification (UPAC classification), which states that this type of isotherm describes the adsorption process in micropores.

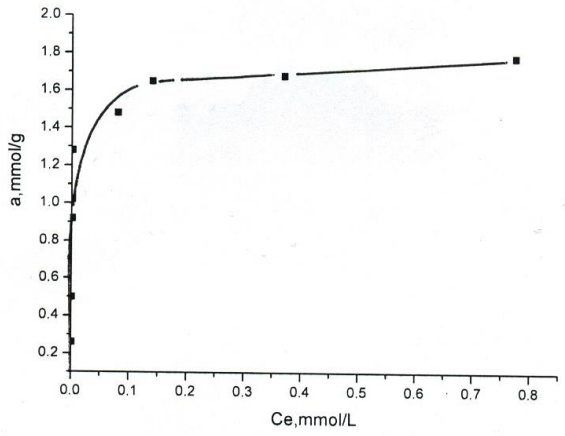

Fig. 4. Adsorption isotherm of caffeine from aqueous solutions on activated carbon AC-0-9, t=25°C

Based on the kinetic curve of caffeine adsorption from aqueous solutions on AC-0-9 activated carbon, the dependence of t/a_t on t_{min} (pseudo-second reaction order, represented in figure 5), was constructed.

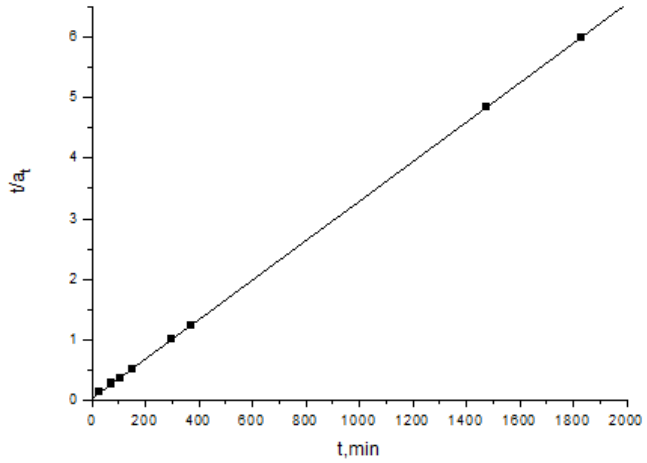

Fig. 5. Kinetics of caffeine adsorption on AC-0-9 activated carbon. The pseudo-two order model

In figure 5, the experimental points lie practically ideally on a straight line, which indicates that the kinetic process of caffeine adsorption from aqueous solutions on AC-0-9 activated carbon corresponds to the pseudo-two model [19], and this indicates that caffeine binds to the surface (pores) of activated carbon via the functional groups on its surface (pores). It should be noted that, on the surface of the activated carbon obtained from woody raw material (fruit tree wood, fruit pits, and walnut shells), functional groups with acidic and basic properties are present, such as: carboxylic, phenolic, chrome groups, ketonic and pyronic [20-22].

Next, the pseudo-one model [23] was used to describe the mechanism of caffeine adsorption from aqueous solutions on active carbon AC-0-9. It was also used to establish whether it can describe the kinetic process of caffeine adsorption on this carbon adsorbent. The dependence of $lg(a_e - a_t)$ on t, min (a_e - caffeine amount on the adsorbent at equilibrium; a_t - caffeine amount on the adsorbent at time "t" in the caffeine adsorption kinetics curve) , which is characteristic for the pseudo-one model is shown in figure 6.

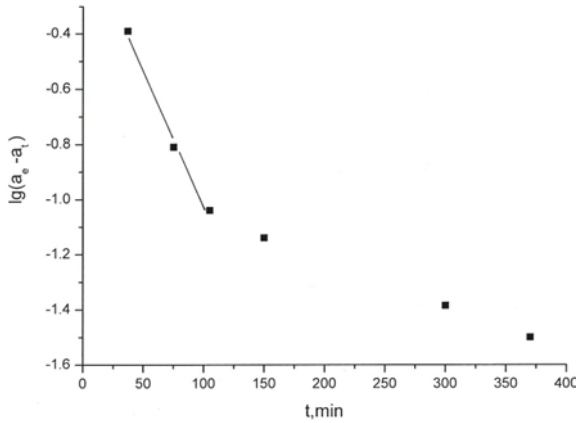

Fig. 6. Kinetics of caffeine adsorption on AC-0-9 activated carbon. The pseudo-one order model

Figure 6 shows that the linear dependence according to the pseudo-one kinetic model is observed only in the 0 to 100 min (R = 0.9212) time interval of the kinetic process of caffeine adsorption on AC-0-9 activated carbon. This phenomenon is explained by the fact that there are various types of functional groups on the surface of AC-0-9 active coal, which interact with caffeine molecules. The caffeine adsorption process on AC-0-9 activated carbon is described by the Langmuir model (figure 7). This is supported by the above-mentioned

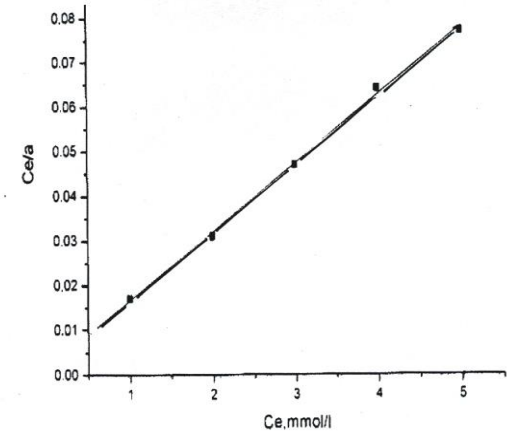

Fig. 7. Caffeine adsorption isotherm on AC-0-9 activated carbon from aqueous solutions, in the linear coordinates of the Langmuir model, t= 25 °C

The Langmuir model predicts adsorption on the centres, and they will obviously play a very important role throughout the time interval of the kinetic process of caffeine adsorption on the activated carbon under study.

Thus, if in the adsorption process, in the structure of the adsorbent, chromene, ketone and pyronic functional groups (AC-0-9) or carboxylic and phenolic groups (peat) are present, which determines the adsorption process, then the applicability of the pseudo-one model over the entire range time of the kinetic process of adsorption is impossible.

Figure 8 shows the dependence of a_t on $t^{0.5}$ in which the experimental points lie very well on two straight lines, marking the intraparticle diffusion of caffeine on AC-0-9 active carbon. Based on the known equation of:

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

where a_t - caffeine amount on the adsorbent at time "t" in the caffeine adsorption kinetics curve,

$t^{0.5}$ - time in the kinetic curve to the 0.5 power,

k^1_{int} - intraparticle diffusion constant 1,

k^2_{int} -intraparticle diffusion constant 2,

k^1_{int} and k^2_{int} can be determined.

Those values are equal to 45.4 and 4.5. C_1 and C_2 being equal to 175 and 271 respectively.

The higher value of k_{int} means a higher rate of intraparticle diffusion at the first stage. The physical meaning of the "C" value is the layer thickness at the interface. Thus, the kinetics of the adsorption process occurs in two steps. In the first step, although the external surface of the AC-0-9 adsorbent is more accessible, the speed of intraparticle diffusion being high (k_{int} = 45.4), adsorption presumably takes place in macropores and mesopores, and in the second step, the speed of intraparticle diffusion being lower (k_{int} =4.5), adsorption presumably takes place in micro- and supermicropores. Figure 8 shows very clearly the break in the line at $t^{0.5}$ =10.25, which corresponds to the caffeine adsorption value of 288 mg/g on the kinetic curve at t=105 min. In the paper [24] it is specified that the outer surface of a porous adsorbent is several orders of magnitude smaller than its inner surface, and the general surface of porous bodies is predominantly equal to its inner surface.

The thickness of the layer at the interface in the second steps greater than in the first presumably due to the decrease in the intraparticle diffusion rate.

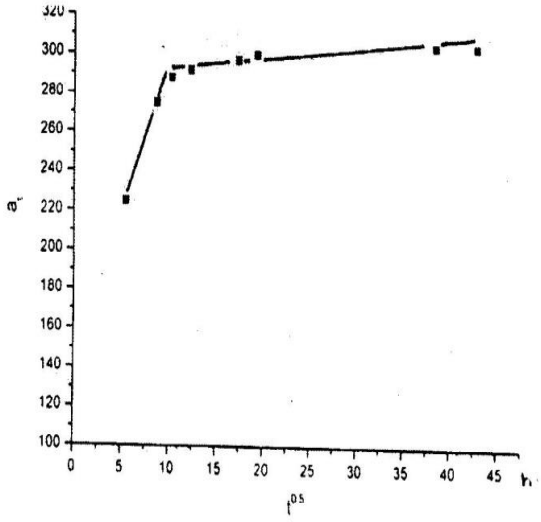

Fig. 8. Intraparticle diffusion model for caffeine adsorption from aqueous solutions on AC-0-9 activated carbon

The diffusion model of caffeine adsorption on AC-0-9 is of type 1. In the sorbent, the size of some pores is so small that no more than one layer of molecules can form on the walls of the adsorbent. The plateau on the isotherm in such an interpretation corresponds to the completion of the monolayer formation.

CONCLUSIONS

The kinetic process of caffeine adsorption from aqueous solutions on AC-0-9 activated carbon corresponds to the pseudo-two model. This result indicates that caffeine binds to the surface (pores) of activated carbon through the functional groups on the surface (its pores).

The kinetics of the adsorption process of caffeine on activated carbon AC-0-9 occurs in two steps. In the first step, the speed of intraparticle diffusion being high (k_{int} = 45.4), adsorption presumably occurs in macro and mesopores, and in the second step, the speed of intraparticle diffusion being lower (k_{int} = 4.5), adsorption presumably occurs in micro- and supermicropores.

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