



DIFFUSIVE AND KINETICS CONTROL OF THE LIQUID PHASE ADSORPTION OF TOLUENE ON SOME GRAPHITE/CLAY COMPOSITIONS AND PURE GRAPHITE

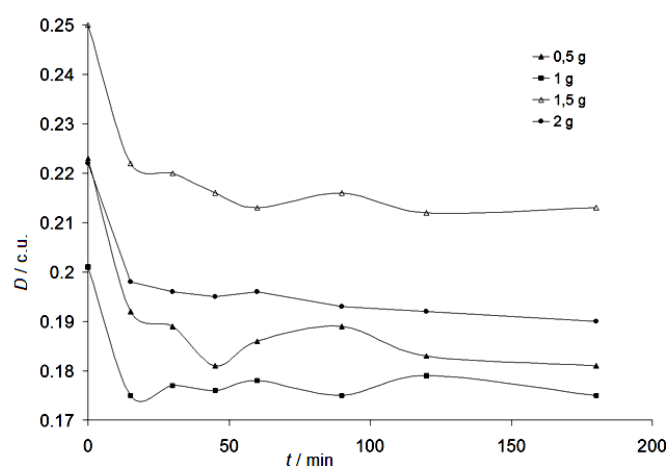
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Received March 21, 2018

A dynamics of toluene adsorption on some porous graphite/clay compositions and pure graphite material has been investigated for various contents of graphite using the UV-photometry determination of residual toluene content in the solution. Temporal changes in concentration of toluene prove that the diffusive transfer of an adsorptive is the limiting stage of adsorption running on all graphite/clay compositions while for the pure graphite adsorbent the process is controlled by the kinetics stage. It is supposed that the toluene transfer across the liquid/solid adsorbent interphase boundary and further, towards the active centres located deeply in graphite pores, not 'transportation' from a bulk towards the interphase is the stage that in fact controls the overall adsorption process rate. As a result, no significant intensification in extraction of toluene from water can be reached by using stirring/mixing of the solution in case of the graphite/clay adsorbents. Final toluene adsorption values are expectedly increasing with rise in graphite content in the adsorbent since adsorption of toluene on its mineral component (clay) is negligibly low.



INTRODUCTION

Numerous theoretical concepts can be employed to describe adsorption of various aromatic compounds on activated carbon or graphite. A constant and significant interest towards this problem is maintained because the results obtained can potentially be applied in a

wide area ranged from water/wastewater cleaning/decontamination technologies or extraction of some toxic compounds to mostly theoretical approaches dealing with background of the adsorption models. Understanding of the mechanism of adsorption facilitates better intensification of the processes since even minor influence on the limiting stage would result in

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substantial changes in the process rate and depth while same influence on the non-limiting stage would remain rather ineffective.

In many cases, the authors confine themselves by consideration the kinetics adsorption models such as Gibbs', Langmuir's, BET or others, which can ensure a satisfactory description of the experimental data.¹⁻³ However, this approach cannot be taken as a universal tool since in many cases kinetics stages of the reactions run much faster than delivery of an adsorptive, especially in case of highly porous materials when transportation of the reagents inside the pores is seriously complicated. As a result, the diffusion models can provide a better agreement between experiments and theoretical simulations when classical adsorption kinetics models seem inapplicable. It should be mentioned that empirical models such as Freundlich's, Elovich's are more flexible and can be utilized successfully in many cases related to description of the liquid phase adsorption of various aromatic compounds on activated carbon substrate.⁴⁻⁶

A more sophisticated approach was used by D. Chatzopoulos *et al.*,⁷ where a combined mass-transfer-homogenous surface diffusion model was applied to take into account the peculiarities of the adsorptive transportation in case of highly porous adsorbent such as activated carbon or graphite. This method has also ensured good agreement between experimental data and the results predicted theoretically.

In general, an extended discussion of various adsorption isotherms applicability to different

adsorption equilibriums can be found in the review by R. S. Bansal and M. Goyal.⁸

Therefore, it is obvious that both approaches: kinetics or diffusion models are capable to achieve good agreement with the experimental results in case of the adsorption processes running on activated carbons. However, it is essential to understand the applicability limits for each of these approaches and factors that influence better or worse agreement between experimental data and these theoretical explanations. In this context, our investigation was aimed onto finding possible dependencies in the adsorption behaviour for a process of toluene adsorption on various graphite/clay substrates that can be applied in some water/wastewater treatment technologies.

EXPERIMENTAL

All experimental investigations were performed with the pure graphite material and some graphite/clay compositions, which are used regularly for the pencil rods manufacturing. The latter material is suitable for the purpose of our investigation since the ratio between the graphite and clay components is known exactly from the rod material standard hardness degree. The two samples used in this work were 2B and 2H and their graphite/clay mass percentage ratio values were 72/28 and 60/40 respectively.⁹ A high purity graphite material obtained from unused nuclear reactor neutron moderator module was used as a clay-free graphite sample. All samples were roughly ground without special control of the grinding degree since this parameter influences only the rate of adsorption, not its final value. Since all experiments were carried out during the time needed to achieve the adsorption equilibrium (24 hours),^{6,10} grinding degree was not considered as an influential parameter of the system.

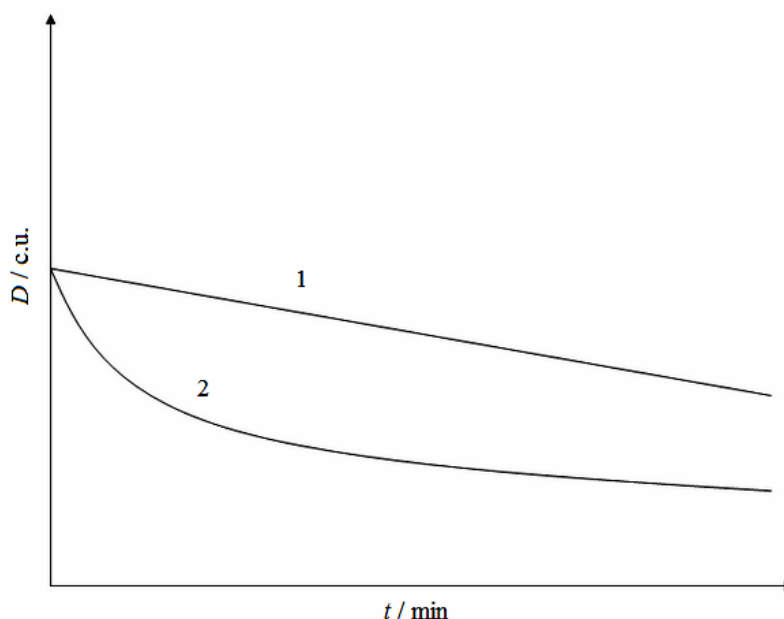


Fig. 1 – A theoretical pattern of temporal changes in absorbance (D) of a solution of the optically active adsorptive in case of the transportation (diffusion) (1) or kinetics control (2) of adsorption.

Toluene adsorption was calculated from the results of the UV-photometry determination of its concentration in water.^{5,6,10-12} This concentration was derived from the optical density measurements at the wave length 258 nm that corresponds to the toluene's characteristic light absorbance peak. A difference between optical densities before and after adding an adsorbent corresponds to the amount of toluene adsorbed on the substrate.

All working solutions were prepared by adding 0.2 mL of toluene to 1 liter of distilled water. Then the mixture was left for 24 h for stabilization and its initial optical density was measured afterwards. Further, an adsorbent sample was added to the stabilized system and then a series of the optical density determination was performed again.

Since optical density is a linear function of molar concentration of the light absorbing component, it can be used directly in further calculations instead of the component's concentration. Therefore, a series of diagrams of temporal changes in the optical density (D) was built in the coordinates D vs time. Any kinetically controlled process assumes nonlinear, mono- or multiexponent pattern of the dependence while the transportation (diffusion) control of the processes assumes the zero order kinetics and linear pattern of the dependence (Fig 1). Of course, the pattern becomes more complex or a combination of the two abovementioned cases when the processes runs under the mixed control or if there is switch between different limiting stages during the process.

RESULTS AND DISCUSSION

Averaged data of the temporal changes in light absorbance for three experiments with different adsorbent amounts added to the system are shown in Fig. 2 (2H graphite/clay composition), Fig. 3 (2B composition) and Fig. 4 (pure graphite) while initial and final light absorbance values are given in Table 1.

The cross-analysis of the first two cases (2H and 2B samples, see Figs. 2 and 3) shows the following.

It can be seen that the absorbance is decreasing with time in course of the toluene adsorption development throughout all experiments.

There is no dependence of the adsorption rate on the adsorbent mass as seen from the line slopes in Fig. 2, which are very close for all three trends. Same conclusion can be drawn from closeness of the angular coefficients for the trend line equations in Fig. 2. In case of 2B adsorbent the situation is similar (see Fig. 3). This means that the amount (concentration) of the adsorbent does not control the rate of the reaction and, therefore, it can be characterized as the zero order adsorption process, which is controlled by the adsorptive diffusion (transportation).

On the other hand, none of the dependencies in Figs. 2 and 3 correspond to the 'kinetics' type (Fig. 1,

line 2), and this is another proof of the diffusion control over both processes.

An 'adsorption bridge' phenomenon¹¹ is distinct in case of 0.5 and 1 g samples for both series (2H and 2B). It manifests itself through some initial increase in the adsorptive concentration followed by its further reduction. An explanation for this phenomenon is given in details in our previous paper.¹¹

A character of adsorption is different in case of the pure graphite adsorbent (Fig. 4). It is easy to notice that all the lines match typically 'kinetic' pattern (line 1 in Fig 1). The dependencies are clearly exponential, which evidences the kinetic control over the overall process. Therefore, establishing bonds between adsorptive and adsorbent is the rate controlling process in case of adsorption of toluene on the pure graphite adsorbent.

These results can be explained in the following way.

The bulk concentration of toluene is decreasing constantly in course of its adsorption. Zero order kinetics of this process means that it is controlled by diffusion of toluene from the bulk of the system towards the adsorbent surface and/or through the surface. This mass transfer process is not influenced by amount of the adsorbent added and, that is why the rate of adsorption does not depend on the adsorbent amount (all trend lines' angular coefficients are similar for any amount of adsorbent, see Figs. 2 and 3). On the other hand, overall amount of toluene captured by the adsorbent would definitely depend on the adsorbent amount and that is why the residual adsorptive concentration is in the strong dependence on the adsorbent amount. The greater is the adsorbent mass, the lesser would be the final concentration of toluene remaining in the solution (see Table 1).

It is important to understand if there is at least any kind of influence of different contents of the adsorption active graphite in the samples on the adsorption dynamics. A comparison between the angular coefficients for 2B and 2H materials proves that their values are similar notwithstanding the fact that the former material consists of about 72 mass % of graphite while the latter – only 60 %. This evidences that there is no any influence of the adsorbent content of the process rate. That is why its mechanism can be classified as fully diffusion, not mixed (diffusion/kinetics) type.

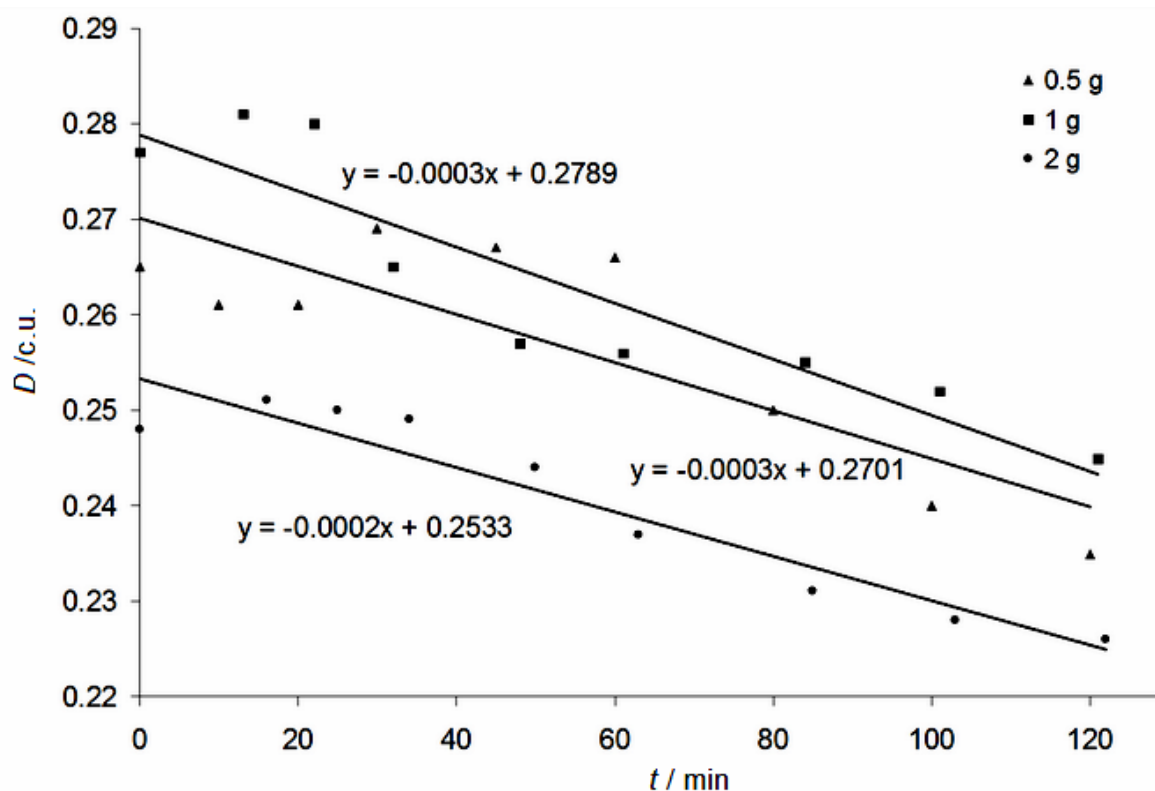


Fig. 2 – Temporal changes in light absorbance ($D /$ conventional units) for the 2H grade adsorbent samples added to the water/toluene mixtures: \blacktriangle – adsorbent content 0.5 g l^{-1} ; \blacksquare – 1 g l^{-1} and \bullet – 2 g l^{-1} . Solid lines represent the approximation linear trends corresponding to the nearby equations.

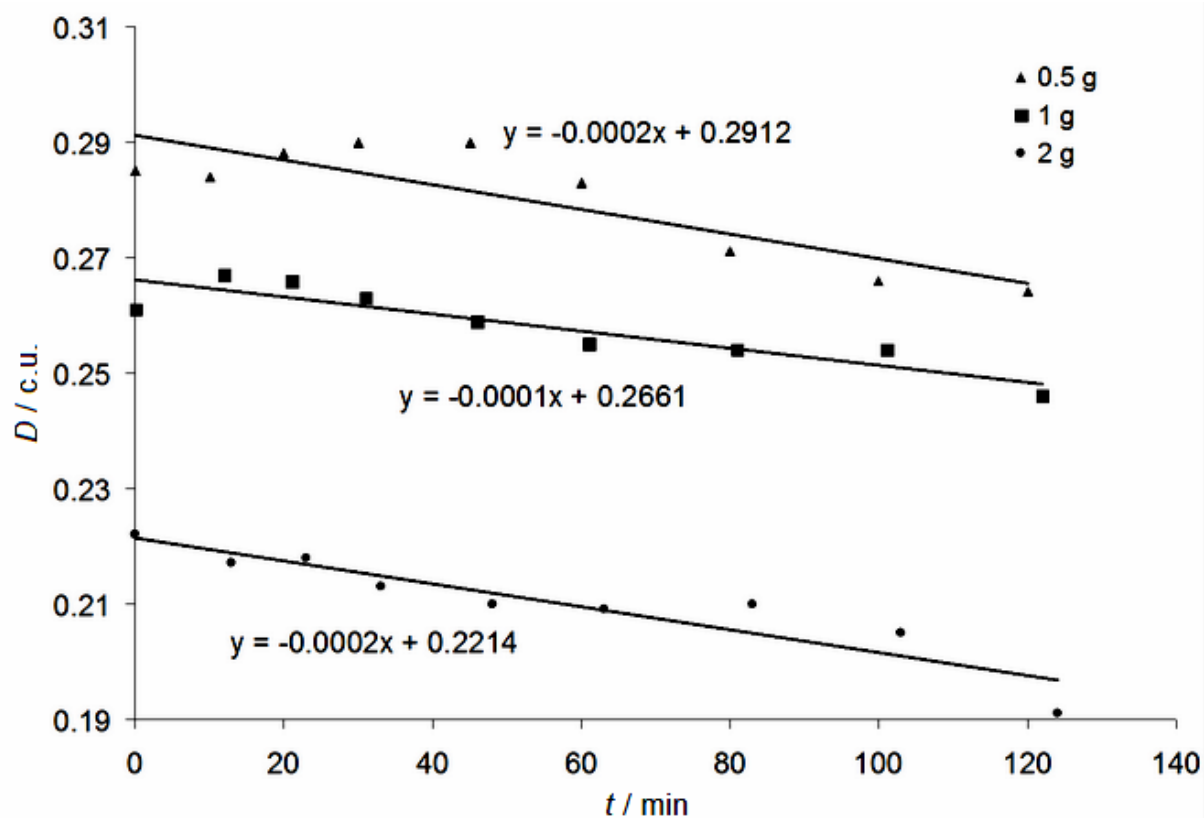


Fig. 3 – Same as in Fig.2 but for the 2B grade adsorbent added to the water/toluene mixtures: \blacktriangle – adsorbent content 0.5 g l^{-1} ; \blacksquare – 1 g l^{-1} and \bullet – 2 g l^{-1} .

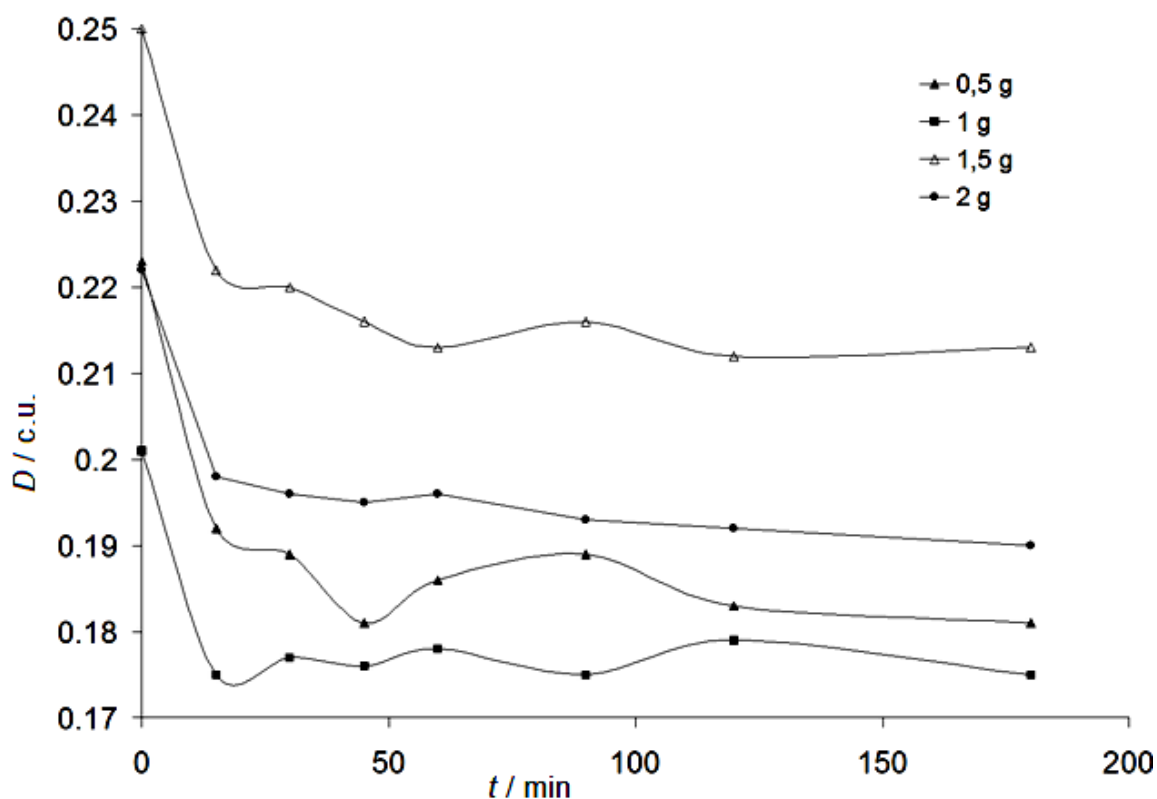
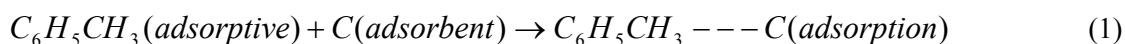


Fig. 4 – Same as in Fig.2 but for the pure graphite adsorbent added to the water/toluene mixtures: adsorbent content \blacktriangle – 0.5 g l⁻¹; \blacksquare – 1 g l⁻¹, \triangle – 1.5 g l⁻¹ and \bullet – 2 g l⁻¹.

This result may seem paradoxical because increasing adsorbent contents for series 2H–2B–pure graphite would have resulted in a switch from

the kinetics to diffusion mechanism, while our results were opposite.

Indeed, considering adsorption process as



one can understand that increase in concentration of C would switch competition between transportation of toluene and its adsorption in favor of the latter process making the diffusion delivery of $C_6H_5CH_3$

insufficient in case of high adsorbent contents. Therefore, higher content of C would have switched the adsorption control from kinetics to diffusion. Our experimental results were opposite.

Table 1

Initial and final absorbance values and their relative decrease for different adsorbents

Adsorbent mass, g	Initial absorbance, conventional units	Final absorbance, conventional units	Relative decrease of absorbance, % from the initial value
2H			
0.5	0.285	0.264	7.3
1	0.261	0.239	8.4
2g	0.222	0.181	18.4
2B			
0.5	0.264	0.235	10.1
1	0.285	0.243	14.4
2	0.248	0.196	20.9

Table 1 (continued)

Pure graphite			
0.5	0.223	0.169	24.2
1	0.201	0.148	26.4
1.5	0.25	0.181	28
2	0.222	0.155	30.2

This contradiction can be resolved by consideration the transportation of toluene towards active adsorption centers as the genuine limiting stage. These centers are usually located far from the interphase, often deeply in the pores. In this case, we can subdivide the transportation process into two separate stages: (a) the diffusion transfer of the adsorptive component from the bulk towards the adsorbent surface and (b) penetration of the adsorptive down to the pores towards active centers of adsorption. The more inactive mineral component is present in the adsorbent composition, the more complicated would be the latter stage. That is why the switch from the 'diffusion' towards 'kinetics' mechanism has been registered in our experiments between 2H/2B and pure graphite adsorption substrates: mineral components present in 2H and 2B substrates put obstacles for transportation of toluene towards active centers of adsorption while this problem is not actual in case of pure graphite material.

CONCLUSION

Adsorption of toluene on the graphite/clay compositions 2H and 2B is controlled by the toluene transfer stage. This genuine limiting stage involves exactly interphase transportation of adsorptive towards active centers of adsorption often located deeply in its pores. Transportation of toluene from the system bulk towards surface of adsorbent is not influential. An adsorption mechanism switches to the 'kinetics' control in case of the pure graphite substrate. Final

adsorption values depend on graphite content in the adsorbent. Therefore, no significant intensification of the toluene adsorption on all substrates investigated can be achieved by application of the solution mixing/stirring. This can result in some increase in the adsorption rate while the final value would remain unchanged.

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