Kinetics of organic compound adsorption on carbon sorbents

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Abstract. Adsorption of trichlorethylene from aqueous solutions by activated carbons of various grades was studied previously under static conditions [6]. We carried out a comprehensive study of the trichlorethylene adsorption process in the presence of chloroform by carbon sorbents, including the study of equilibrium, kinetics, and adsorption process dynamics in order to create an adsorption technology for purifying natural waters from organic compounds. The aim of the study was to establish the mass transfer mechanism and obtaining the mass transfer coefficients required for engineering calculations, using various models that describe the kinetics of sorption extraction. The kinetic parameters of sorption process are influenced by various factors, including specific surface area, carbon sorbents’ structure, and conditions for the transfer of adsorbed substance molecules to the grain surface of adsorbent.

So, as a result, calculated coefficients of external mass transfer allow us to expect a high rate of the component extraction from the water to be purified by filtering through a fixed sorbent layer of the AC grades: SCLF-515, AG-WV-1, PPS, Purolat-standard.

1. Introduction

Today, a wide range of organic substances is present in water supply sources [1], which part can be transformed into new, in some cases more dangerous organic compounds during water treatment. Such substances include chloroform, phenol, aniline, formaldehyde and some others. The content of pollutants in water bodies for drinking water can lead to a number of diseases in the population, for example, neoplasm appearance.

The problem of carcinogenic risk for humans is also associated with the use of chlorinated drinking water [2]. The research materials of its effect on malignant neoplasms appearance show the harm caused by halogen-containing compounds, products of water chlorination, which have a blastomogenic hazard for consumers.

The list of the global harmonized system of classification and chemicals labeling (HSC) includes water chlorination products, where chloroform and a group of trihalomethanes are distinguished [2], including trichlorethylene of the 1st hazard class. The maximum permissible concentration (MPC) of trichlorethylene in water bodies of domestic, drinking, and cultural and domestic water use is 0.005 mg / dm³.

The research data [3-4] on the possibility of developing cancer in humans, associated with the use of water containing trichlorethylene. Recent studies suggest that trihalomethanes increase the cancer risk of liver, kidneys, esophagus, cervix, pancreas, children’s leukemia.

Monitoring trichlorethylene and chloroform amount helps lower levels of other unidentified chlorination by-products.
The leading and most promising direction in the technology of extracting organic substances from aqueous solutions is the sorption method using active carbons (AC) and polymer sorbents [5]. It is necessary to carry out a comprehensive study of the trichlorethylene adsorption process in the presence of chloroform by carbon sorbents, including the study of equilibrium, kinetics, and adsorption process dynamics in order to create an adsorption technology for purifying natural waters from organic compounds.

2. Materials and methods
The objects of study were activated carbons (AC) of grades: ABG, Purolate - Standard, SCLF-515, AG-WV-1, LAC, BAC, AG-3, PPS, CsAC. The studied sorbents differ in raw materials, preparation method, chemical state of the surface, and characteristics of its structure. Physico-chemical parameters of the studied sorbents are presented in tables 1-2.

Table 1. Characteristics of activated carbons.

| Grades of(AC) | Raw materials | Total surface area | Total pore volume | Micropore Volume | Mesopore volume |
|---------------|---------------|--------------------|-------------------|------------------|-----------------|
| Granular      |               |                    |                   |                  |                 |
| PPS           | Phenol formaldehyde resin | 1037               | 1.20              | 0.42             | 0.08            |
| SCLF-515      | Mixture of fossil fuels | 791                | 0.62              | 0.36             | 0.20            |
| AG-WV-1       | Mixture of fossil fuels | 682                | 1.03              | 0.22             | 0.24            |
| AG-3          | Mixture of fossil fuels | 540                | 0.86              | 0.27             | 0.06            |
| Crushed       |               |                    |                   |                  |                 |
| LAC           | Apricot kernels | 823                | 1.00              | 0.35             | 0.10            |
| CsAC          | Coconut shell  | 1512               | 0.95              | 0.62             | 0.11            |
| BAC           | Birch wood     | 580                | 0.78              | 0.23             | 0.08            |
| ABG           | Brown coal     | 419                | 0.99              | 0.02             | 0.24            |
| Purolate - Standard | Anthracite | 311                | 0.50              | 0.07             | -               |

Table 2. Physico-chemical parameters of activated carbons.

| Grades of(AC) | Particle size mm | Bulk density, g / cm3 | Strength % | pH of the aqueous extract | Mass fraction of ash,% | Adsorption iodine activity, mg / g | Adsorption activity on methylene blue, mg / g |
|---------------|------------------|-----------------------|------------|----------------------------|------------------------|------------------------------------|--------------------------------------|
| AG-WV-1       | 1.5              | 0.52                  | 70         | 6.80                       | 31                     | 65                                 | -                                    |
| ABG           | 1-5              | 0.49                  | 70         | 7.50                       | 12                     | 60                                 | 160                                  |
| Purolate - Standard | 0.1-3.0   | 0.68                  | 75         | 8.50                       | 6                      | 60                                 | 140                                  |
| SCLF-515      | 0.5-1.5          | 0.526                 | 75         | 7.0                        | 6                      | 60                                 | -                                    |
| BAC           | 0.5-1.5          | 0.38                  | 60         | 7.9                        | 6                      | 60                                 | -                                    |
| AG-3          | 1.5-2.8          | 0.48                  | 75         | 6.5                        | 8                      | 40                                 | -                                    |
| PPS           | 1-1.5            | 0.37                  | 86         | 7.8                        | 0.8                    | 78                                 | -                                    |
| LAC           | 0.5-1.5          | 0.42                  | 90         | 9.6                        | 5.4                    | 60                                 | -                                    |
| CsAC          | 1.5-3            | 0.49                  | 97         | 9.0                        | 5.0                    | -                                  | -                                    |

Kinetic studies were carried out on model aqueous solutions of a trichlorethylene and chloroform mixture in a ratio of 1 to 70, according to the limited-volume method, shaking a portion of the adsorbent with a solution and determining the remaining substance concentration. The adsorption value of the organic compound was calculated by the formula:
where $a_t$ – coal adsorption to the time of the solution contact with sorbent, mmol / g; $C_o$ – initial concentration of the substance in solution, mmol / dm$^3$; $C_t$ – substance concentration in the solution after contact with the sorbent, mmol / dm$^3$; $V$ – sample volume of solution, dm$^3$; $m_n$ – sorbent mass.

The solution’s contact time of the organic components mixture with activated carbon samples ranged from 1 to 42 minutes. Throughout the experiment, the temperature ranged from $25 \pm 2$ °C.

In order to model the kinetics of trichlorethylene adsorption from its mixture with chloroform on AC, pseudo-first order, pseudo-second order models were used. The pseudo-first order equation is widely used to describe the rate of pollutants adsorption from aqueous solutions [7]. In linear form, this equation is as follows:

$$\ln(a_e - a) = ln(a_e - k_1 t)$$

where $k_1$ – pseudo-first order rate constant, min$^{-1}$.

This equation describes the cases of film diffusion, which controls the adsorption rate during the first few minutes in experiments with stirring [8]. The pseudo-second order equation is widely used to describe the kinetic laws of adsorption. In integrated form, this equation can be represented as follows [9]:

$$\frac{t}{a} = \frac{1}{(k_2 a_e^2 + t/a_e)}$$

where $k_2$ – pseudo-second order adsorption rate constant, g mg$^{-1}$ min$^{-1/2}$.

The suitability of using kinetic models was determined by linearizing data in the coordinates of their integral equations with determining the determination coefficients.

It is necessary to take into account the models’ type (quasi-homogeneous or biporous) the sorbent grains belong to, considering the kinetics of organic substances adsorption.

If the adsorbent grain is considered as a system formed by a random interweaving of micro- and mesopores, where it is impossible to distinguish between areas having only or mainly mesopores, or areas containing only micropores, then such a grain can be attributed to a quasi-homogeneous model.

In the case of biporous model, a grain contains two pore systems delimited in space. This system consists of relatively large mesopores and a certain fraction of micropores, united by the general concept of “transport pores”. The solute diffuses along the concentration gradient arising in the fluid filling these pores. A second pore system is formed by micropores in each primary particle of the formed granule. Adsorbed molecules migrate under the influence of the specific adsorption gradient in these pores.

The method developed by R.M. Marutovsky in order to describe the kinetics of trichlorethylene adsorption [10]. The method is based on solving a system of equations, describing the external diffusion kinetics of substance adsorption from a constant closed volume (i.e., under conditions of the solution, which concentration gradually decreases as it approaches equilibrium). It allows one to obtain theoretical kinetic equations in the form of the relative approximation dependence to the equilibrium $\gamma$ ($a_i/a_p=\gamma$) on the dimensionless quantity $T$ proportional to the time of the process, calculated by the equation

$$T=A\beta t, \quad A=(V_p/V_p+k_1);$$

where $V_p$ - external mass transfer coefficient;
$V_p$ – total adsorbent mass volume, sm$^3$;
$V_p$ – volume of solution in contact with the adsorbent;
$k_1$ – content $k_1=1/ k_h$ (k$_h$ – Henry coefficient $k_h=a_p/C_p$).

The quantity $T$ dependence on $t$ is expressed by a straight line emerging from the origin.

Therefore, the graph of the dependence of $T$ (calculated theoretically) on the value of $\tau$ (experimental time of the process) for $\gamma$ same values should be a straight line if the kinetics of
adsorption is limited by external mass transfer. As we approach equilibrium, the experimental points begin to deviate from the straight line, characterizing the external diffusion, which indicates a gradual decrease in the coefficient of external mass transfer, since the internal mass transfer begins to control the kinetics. This is explained by the fact that, the gradient of specific adsorption decreases, getting to equilibrium and the rate of internal mass transfer proportional to the gradient also decreases consequently.

3. Results
The study’s results of the kinetics of trichlorethylene and chloroform mixture adsorption from aqueous solutions on carbon sorbents are presented in Figure 12.

**Figure 1.** Kinetic curves of trichlorethylene adsorption with chloroform from aqueous solutions with activated carbons AG-WV-1, PPS (2), SCLF-515 (3), AG-3 (4).

**Figure 2.** Kinetic curves of trichlorethylene adsorption in the presence of chloroform from aqueous solutions with active carbons of the grades: Purolat-standard (1), ABG (2), LAC (3), BAC (4), CsAC (5).

Analysis of the obtained kinetic curves shows that trichlorethylene adsorption in the presence of chloroform on AC: CsAC, Purolate - standard, ABG, LAC, PPS, AG-3, and SCLF-515 proceeds quickly at the initial stage and slows down, approaching the equilibrium state. Adsorption equilibrium is reached after 300 minutes (AG-3), 120 minutes (SCLF-515), 90 minutes (PPS), 30 minutes
(CsAC), and 60 minutes (ABG and LAC). The nature of the dependence for active carbons AG-WV-1 and BAC (Figure 3) indicates that diffusion in the sorbent grain controls the overall process rate [8]. The obtained values of the determination coefficients (table 3) allow the use of pseudo-first order and pseudo-second order models to describe the kinetics process.

**Table 3.** Determination factors ($R^2$).

| Sorbent     | Model of Pseudo first-order | Model of Pseudo second order | Sorbent     | Model of Pseudo first-order | Model of Pseudo second order |
|-------------|-----------------------------|-----------------------------|-------------|-----------------------------|-----------------------------|
| PPS         | 0.92                        | 0.99                        | CsAC        | 0.44                        | 0.99                        |
| SCLF-515    | 0.38                        | 0.99                        | BAC         | 0.98                        | 0.99                        |
| AG-WV-1     | 0.76                        | 0.99                        | ABG         | 0.85                        | 0.99                        |
| AG-3        | 0.98                        | 0.98                        | Purolate - standard | 0.95 | 0.99                        |
| LAC         | 0.95                        | 0.99                        |              |                             |                             |

Kinetic curves were also analyzed in the coordinates $\gamma$ from $\tau$ (Figure 3, 4) and the dimensionless coefficient $T$ from $\tau$ (Figure 5) used in the R.M. method Marutovsky.

**Figure 3.** Dependence of the degree of the adsorption equilibrium achievement $\gamma$ on the adsorption time $\tau$: 1 AG-3, 2 PPS, 3 AG-WV-1, 4 SCLF-515.

**Figure 4.** Dependence of the degree of the adsorption equilibrium achievement $\gamma$ on the adsorption time $\tau$: 1 BAC, 2 ABG, 3 LAC, 4 Purolate - standard, 5 CsAC.
Figure 5. Theoretical kinetic curves for the adsorption of trichlorethylene in the system of activated carbon - an aqueous solution of a trichlorethylene and chloroform mixture: 1- CsAC, 2- SCLF -515, 3-PPS, 4-ABG, 5- AG-WV-1, 6- BAC, 7- Purolate - Standard, 8-LAC, 9-AG 3.

The pseudo-first order equation satisfactorily \((R^2=0.85-0.98)\) describes the adsorption patterns at the initial of the adsorption process’ stages for sorbents of such grades as PPS, AG-3, LAC, BAC, ABG, Purolat-standard (table 3), when the phenomenon of external diffusion has a significant effect on the process. The dissolved substance diffuses under the influence of a concentration gradient arising in the liquid, filling the adsorption space. The high values of the pseudo-first order determination coefficients allow us to make an assumption about the great thermodynamic benefit of the adsorbate interaction with the functional groups of carbon sorbent [9].

The pseudo-second order experimental data are described with high accuracy \((R^2=0.98 – 0.99)\) for all studied active carbons. It is assumed that the process is influenced by both the adsorbed substance diffusion and the adsorbate – adsorbate interaction.

The values of the determination coefficients are quite high, which indicates the applicability of the kinetic models, used to describe the kinetics of the trichlorethylene adsorption from its mixture with chloroform by the studied AC grades.

The kinetic dependences, presented in Figures 3-4, allow us to find out a model of the activated carbon granules’ structure. The curve initial portion of the dependence in the achievement degree of adsorption equilibrium on time is straightforward in nature up to \(\gamma =0.4-0.9\). High values \(\gamma\) in a straight section suggest a correspondence between the used sorbents’ granules of the quasi-homogeneous model, i.e., the sorbent is considered as a system, formed by random interweaving of micro and mesopores, where it is impossible to distinguish between areas having only or mainly mesopores and areas containing only micropores.

The presence of a linear section on the curve \(T=f(\tau)\) (Figure 5), constructed using R.M. Marutovsky method, allows us to fairly reliably judge that the adsorption process of trichlorethylene from its mixture with chloroform is limited by external mass transfer for 5-20 minutes, depending on the activated carbon properties, however, during this time the achievement degree of adsorption equilibrium \(\gamma\) was 0.4 - 0.9. Therefore, up to these values \(\gamma\) of trichlorethylene adsorption proceeds inside the grain so quickly that it does not affect the overall mass transfer rate [11]. The data obtained suggest the external diffusion mass transfer controls the rate and is a limiting stage of the adsorption
process for the systems under study. Deviation from the straightforward relationship shows that, internal diffusion has an increasing influence on the rate of the sorption process over time.

External mass transfer coefficients ($\beta_p$), calculated by the direct dependence slope of the dimensionless coefficient $T$ from $\tau$ equal for coal grades CsAC $\beta_p=0.0048$ min$^{-1}$, AG-WV-1 $\beta_p=0.0232$ min$^{-1}$, LAC $\beta_p=0.014$ min$^{-1}$, Purolate - Standard $\beta_p=0.0197$ min$^{-1}$, SCLF -515 $\beta_p=0.0325$ min$^{-1}$, PPS $\beta_p=0.022$ min$^{-1}$, BAC $\beta_p=0.0043$ min$^{-1}$, ABG $\beta_p=0.0026$ min$^{-1}$, AG-3 $\beta_p=0.0022$ min$^{-1}$.

External mass transfer coefficients for activated carbons SCLF -515, AG-WV-1, PPS, Purolate - are close and have fairly high values. The data obtained allow us expecting a high rate of the component extraction from purified water, filtering through a fixed sorbent layer.

4. Conclusion

Otherwise, it can be assumed that the adsorption mechanism has a mixed-diffusion nature, based on the kinetic models analyses. Diffusion models describe the adsorption kinetics’ portion ($\gamma = 0.4 – 0.9$) of trichloroethylene with chloroform by active carbons. Therefore, external diffusion mass transfer controls the rate and is a limiting stage of the adsorption process for the studied system.

The calculated coefficients of external mass transfer allow us to expect a high rate of the component extraction from the water to be purified by filtering through a a fixed sorbent layer of the AC grades: SCLF -515, AG-WV-1, PPS, Purolat-standard.

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