Dynamics of trichloroethylene adsorption on activated carbons

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Abstract. We studied trichloroethylene adsorption from aqueous solutions on activated carbons (SKD-515, ABG, and Purolat-Standard brands), which differ in composition, method of production, structure and surface chemical state. Performance time of the filter layer before the breakthrough decreased in SKD-515 > ABG > Purolat-Standard respectively, which was caused by their porous structure and the nature of functional oxygen-containing groups on carbon surface. The interaction of trichloroethylene with functional groups of carbon surface was also noted. We studied the layer height on efficiency of trichloroethylene adsorption on different activated carbons at a constant flow rate. The reduction of the solution flow rate through the filter contributed to the increase of the dynamic adsorption capacity, which indisputably proved pore diffusion resistance of mass transfer.

The problem of water conservation and sustainable use of water resources is gaining increasing attention due to shortage and deficit of fresh water, while the need in intensive industrial use is only growing.

Industrial pollution of water bodies poses a particular hazard to the sanitary conditions of water use. This is due to the constant increase of industrial wastewater, its multicomponent composition.

Trichloroethylene (TCE) is one of the components constantly found in water as a result of its contamination by industrial sewage. It is of a trihalomethane group and its presence is not permissible by water sources sanitary requirements, since TCE is 1st hazard class [1] and is characterized by a low value of the maximum permissible concentration.

Trichloroethylene is one of the least toxic organochlorine solvents. Due to this quality, as well as its non-combustibility, and high solubility in relation to fats, waxes, resins, rubber, sulfur, phosphorus and many other compounds, trichloroethylene is widely used in industry for the degreasing of tissues, leather, metals, fat, oil and resins extraction, extractive substances, etc. [2] In addition, trichloroethylene is used for the production of herbicides, refrigerants, and various acids. Due to the variety of applications, trichloroethylene is a component of the wastewater of many industries (consumer goods, metallurgy, wood-chemical, etc.).

Trichloroethylene is extremely hazardous to aquatic organisms and can cause significant changes to the ecosystem. According to Hygienic Standards 2.1.5.2280-07 ‘Maximum permissible concentrations (MPC) of chemicals in water objects of drinking and household and cultural and domestic water use’ (Amendments №1 to HS 2.1.5.1315-03) MPC of trichloroethylene in water objects of household and drinking and public amenities water use is 0, 005mg/dm³ [3,7].
To reach MPC level of trichloroethylene in water bodies is only possible after effective wastewater treatment. In this regard, a need to develop adsorption technology for extracting trichloroethylene from water arises. For this purpose, the use of adsorption methods with activated carbons is promising. Dynamic analysis in the adsorption study is important in the development of adsorption technological processes, because in practice continuous cleaning technologies of natural and wastewater are normally used.

Laboratory studies of the dynamics of TCE adsorption on activated carbons that differ in structural characteristics and chemical state of the surface were carried out in columns: 40 cm height, 1.5 cm diameter at 6 and 12 ml/min flow rates. The objects of study were activated carbons SKD-515, ABG and Purolat-Standard. Structural characteristics and active groups on the carbon surface of these adsorbents are given table 1 [4].

| AC brand          | SD-515 | ABG | Purolat-Standard |
|-------------------|--------|-----|------------------|
| Particle size, mm | 0.5 – 1.5 | 1 – 5 | 0.1 – 3          |
| Bulk density, g/cm³ | 0.52 | 0.49 | 0.68             |
| Strength,%        | 75     | 70  | 70 – 80          |
| Specific pore surface (S BET), m²/g | 791 | 419  | 311              |
| Total pore volume on water, cm³/g | 0.62 | 0.990 | 0.500          |
| Pore volume, cm³/g: micro | 0.36 | 0.020 | 0.070          |
| Meso              | 0.20   | 0.240 | 0.000           |
| Macro             | 0.06   | 0.730 | 0.430           |
| pH of water hood  | 7.6    | 7.5  | 8 - 9            |
| acid type general (SOE OH⁻) | 0.190 | 0.238 | 0.238         |
| phenolic -OH      | 0.130  | 0.218 | 0.218           |
| carboxyl -COOH    | 0.020  | -    | -                |
| lactonic -COOH    | 0.040  | 0.020 | 0.020           |
| basic type (SOE H⁴⁺) | 0.920  | 0.120 | 0.120         |

We studied the influence of activated carbons, bulk layer height, and the flow rate of the solution on the efficiency of TCE adsorption.

The findings (figure 1-3) showed that the diagrams and the performance time of the layer till the breakthrough (protective power time) depends significantly on the structural and surface characteristics of the activated carbons. The performance time of the filter layer before the breakthrough decreases in SKD-515 > ABG > Purolat-Standard respectively, which is caused by the porous structure and the nature of functional oxygen-containing groups on carbon surface. In the case of Purolat-Standard, even when a layer height is 25 cm (figure 1), TCE breakthrough is observed in the first minutes of the column work (it contains mostly macropores). With higher mesopore content (ABG), the layer's working time before the breakthrough increases and the breakthrough of the TCE is recorded in 5.8 hours. SKD-515 contains mainly micro-, as well as meso- and macropores: the protective power time is significantly increased and the breakthrough is observed in 30.5 hours. The findings were also related to the adsorption mechanism. Meso- and macropores are known to provide transport of substance to micropores, where interaction occurs between molecules and the surface of the sorbent. At the same time, it should be taken
into account, that the surface of carbon in meso- and macropores is rough: it has elevations, edges, angles, chips. Local active centers, existing on them, can also interact with trichloroethylene. In the case of SKD-515 the adsorbate is able to fill micro-, meso- and macropores. The size of the supermicropore of 0.7-0.8 nm allows the penetration of 0.7 nm trichloroethylene molecules, where the interaction of the TCE molecules with the active centers of the surface of the carbons due to Van der Waals’ forces. The interaction between local active centers on the surface of the activated carbons and the TCE molecules is also carried out in meso- and, to a lesser extent, macropores, as the distance between molecules and active centers the energy of their interattraction decreases. As a result, in the case of SKD-515, the highest adsorption takes place and the performance time of the column increases before the breakthrough. With the reduction of active centers and the increase of the distance between the interacting particles, semicokes naturally reduce the performance time of the column before the breakthrough. Functional groups on the carbon surface also influence the TCE adsorption. The TCE molecule has negative groups (Cl⁻). In this regard, adsorption occurs repelling of adsorbate molecules from active groups of the activated carbons surface bearing partially negative charge, for example, carboxyl and carbonyl, in this case adsorption decreases, and attraction to structures bearing partially positive charge, for example, pyronic and carbon atoms in alpha position to negative groups, resulting in increased adsorption [5]. As follows from [4], SKD-515 and Purolat-Standart have no carboxyl groups. It provides an increase in the amount of adsorbed substances in SKD-515 and a slight increase in the case of Purolat-Standart. The findings also showed that the diagrams of the carbons at the same height of the adsorbent layer and the flow rate of the solution had different inclination angle [6].

With a reduction in the time of protective power, they become steeper. This must be due to the peculiarities of mass transfer during adsorption. When the layer height changed, the general patterns of adsorption on different types of activated carbons were preserved (figure 1 – 3).

**Figure 1.** Diagrams of TCE adsorption from aqueous solutions by: 1 – Purolat-Standart, 2 – ABG, 3 – SKD-515. The adsorbent layer height is 25 cm.

**Figure 2.** Diagrams of TCE adsorption from aqueous solutions by: 1 – ABG, 2 – SKD-515. The adsorbent layer height is 15 cm.
Figure 3. Diagrams of TCE adsorption from aqueous solutions by: 1 – Purolat-Standart, 2 – ABG, 3 – SKD-515. The adsorbent layer height is 5 cm.

Figure 4. Diagrams of TCE adsorption from aqueous solutions by SKD-515 at the length of the filter layer: 1 – 3 cm, 2 – 5 cm, 3 – 15 cm, 4 – 25 cm.

Figure 5. Diagrams of TCE adsorption from aqueous solutions by Purolat-Standart at the length of the filter layer: 1 – 2 cm, 2 – 5 cm, 3 – 25 cm.
Figure 6. Diagrams of TCE adsorption from aqueous solutions by ABG at the length of the filter layer: 1 – 5 cm, 2 – 25 cm.

For small sorbent layer heights, the adsorption zone includes fewer ‘working layers’ moving down loading, resulting in a faster increase in the concentration of TCE in the filtrate. [5] When increasing the length of the layer takes much longer than the adsorption zone reaches the lower layers, resulting in the filtrate containing lower concentrations of TCE. When comparing the data obtained for different sorbents (figure 4 — 6), the general dependencies do not change: with increasing the height of the layer increases the time of the column to break, and the patterns in changing the output curves are preserved. At the same time, these dependencies are less pronounced, which is due to the lower adsorption capacity of semicokes due to structural and surface characteristics.

The study of the effect of the solution flow rate on the adsorption efficiency was carried out in a column with a layer height of 5 cm, at the flow rates of the TCE solution 6 and 12 ml/min. The findings showed that at a speed of 12 ml/min the breakthrough curve was almost out of the origin of coordinates. This was due to the fact that at a small layer height and higher speed the initial part of the layer quickly saturates to equilibrium and no longer participates in the adsorption process [11,12]. At the same time, the layer working in the sorption process will be longer. Its large volume remains unsaturated TCE therefore it is less effectively used. Therefore, when the molecules of the TCE appear in the filtrate, the lower part of the filter load will be saturated only partially. With such layer performance, the concentration of TCE in the filtrate will increase rapidly. The reduction of the solution flow rate through the filter contributes to the increase of the dynamic adsorption capacity, which indisputably confirms the intra-diffusion braking of mass transfer.

We presented dynamic studies of adsorption of trichloroethylene on activated carbons that differ in structural characteristics and surface chemistry

It was established that the adsorption capacity of the studied carbons decreases in SKD-515 > ABG > Purolat-Standart respectively.

We studied the influence of the activated carbons nature, the height of the bulk layer, the flow rate of the solution on the efficiency of trichloroethylene adsorption.

The findings can be used in technological schemes of wastewater treatment from trichloroethylene.

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