Application of adsorption technology for the extraction of chlorine-containing pollutants

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Abstract. The paper conducts a comparative analysis of the adsorption capacity of a number of sorbents of different nature, production method and structure, used to extract chlorine-containing water pollutants. The main regularities, features and mechanism of trichlorethylene adsorption by sorbents were established to compare the adsorption characteristics. It was found that for trichlorethylene (TCE) weak sorbent, i.e., sorbate interaction can be a consequence of electrostatic repulsion of an organic substance molecule from polar groups on the carbon surface and adsorbed water molecules at the initial moment of adsorption. The main parameters of adsorption are calculated using the Dubinin-Radushkevich equation. The paper states that the adsorption capacity of adsorbents with respect to TCE decreases in the series PPS > AG-3 ≥ Purolat. It gives the substantiation of the choice of the sorbent for the extraction of trichlorethylene from aqueous solutions.

In surface and underground sources of water supply, organohalogen compounds are often found. They are accumulating due to their widespread use by various industries in the technological cycle (in the production of refrigerants, herbicides, dyes, solvents, acids). Also, unauthorized landfills can act as a source of pollution of the hydrosphere with organohalogen compounds. Their filtrate penetrating can contaminate ground water through the soil layers. Moreover, organochlorine contaminants are a secondary pollutant of drinking water when chlorine-containing reagents are used for disinfection; chlorine interacts with natural organic substances, forming organohalogen compounds, including TCE.

The problem of pollution of water objects and drinking water with organohalogen compounds requires a solution. It is due to the extreme danger of these compounds, since trichlorethylene can cause significant long-term changes in ecosystems, such as disturbances in the genetic apparatus of aquatic organisms. According to Sanitary Regulations and Norms 1.2.3685-21 "Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors to humans," the maximum permissible concentration of trichlorethylene in water bodies of domestic drinking and cultural and domestic water use is 0.005mg/dm³[1]. The use of water containing TCE (hazard class 1) threatens human health, since this contaminant is a strong narcotic drug that leads to respiratory failure, disorders of the cardiovascular system, and the central nervous system. TCE has a general toxic, mutagenic and carcinogenic effect on the human body being present in water in concentrations exceeding the maximum permissible [2,3].

It may be promising to change the disinfectant reagent to a milder oxidizing agent during water treatment to solve the problem of contamination of drinking water with organohalogen compounds. But it does not solve a problem of reducing a contamination level of water taken from sources. The
adsorption method using activated carbons (AC) and polymer sorbents is the most rational and environmentally acceptable. A wide range of sorbents on the market helps to correlate cost and quality indicators to select the most effective sorbent for use in adsorption plants.

Sorbents used for the absorption of compounds from aqueous solutions in a wide range of concentrations can be categorized according to various criteria, including the nature of the raw material. In turn, the initial material for production affects not only the price category, but also the ability of the sorbent to extract various compounds of their aqueous solutions. It is a key indicator when choosing a filler for adsorbers, taking into account industrial application. The application of various sorbents for the purification of natural waters also depends on their ability to extract compounds of various sizes and properties. The study of the adsorption properties of sorbent materials in relation to various pollutants is decisive when recommending one or another sorbent for the application.

It is necessary to conduct a comprehensive study of the process of TCE adsorption by carbon and polymer sorbents to create an adsorption technology for purifying natural waters from organic compounds [4].

Table 1. Characteristics of carbon sorbents.

| grade of AC | AG-3 | PFCs | Purolat |
|-------------|------|------|--------|
| particle size, mm | 0.5 – 1.5 | 1.0–1.5 | 0.1 – 3 |
| bulk density, g/cm³ | 0.46 | 0.37 | 0.68 |
| strength, % | 88 | 86 | 70 – 80 |
| specific pore surface (S_BET), m²/g | - | 1037 | 311 |
| pore space by water, cm³/g | 0.88 | 1.20 | 0.500 |
| pore volume, cm³/g: | | | |
| micro- | 0.26 | 0.42 | 0.070 |
| meso- | 0.09 | 0.08 | 0.000 |
| macro- | 0.53 | 0.70 | 0.430 |
| pH of the water extract | 6.45 | 7.8 | 8 - 9 |
| active oxygen content, mmol/g | | | |
| acid type total (COE OH-) | 0.322 | 0.252 | 0.238 |
| phenolic – OH | 0.213 | 0.192 | 0.218 |
| carboxyl-COOH | 0.032 | 0.060 | - |
| basic type (COE H⁺) | 0.480 | - | 0.120 |

The objects of study are industrial activated carbon based on coal of the AG-3 grade, semi-coke of the Purolat grade (JSC Sintez, Rostov-on-Don) and a sorbent based on polymeric phenol-formaldehyde resin, PFCs (manufactured by JSC Sorbent, Perm). The choice of these grades makes it possible to evaluate the adsorption capacity of sorbents with different raw materials, production method, porous structure and specific surface area (table 1) [5]. Model solutions of trichlorethylene in a wide range of concentrations, some physicochemical properties of trichlorethylene are presented in table 2. The ultra-purified water was applied for its preparation.
Table 2. Physical and chemical properties of trichlorethylene (TCE).

| Adsorbate | Formula | Molar mass, g/mol | Density, g/cm³ | Solubility at 25°C, g/dm³ | Size, nm |
|-----------|---------|------------------|----------------|--------------------------|---------|
| TCE       | Cl-CHCl | 131.39           | 1.46           | 1.12                     | 0.66 x 0.62 x 0.36 |

The main method for the determination of trichlorethylene in model solutions was gas chromatography with an electron capture detector according to the method described in GOST R31951-2012 [6]. The extraction of TCE under equilibrium conditions with carbon adsorbents was studied in the concentration range $2.00 \cdot 10^{-4} - 2.00$ mmol/dm³.

The evaluation of the criterion indicators of the process of absorption of organic substances by various sorbents is based on the analysis of adsorption isotherms, which makes it possible to determine the dependence of the activity of the adsorbent (adsorption capacity in terms of g or m² of the sorbent) on the concentration of the adsorptive under equilibrium conditions [7, 8]. The data of experimental studies of adsorptive extraction under equilibrium conditions are presented in the form of isotherms in figure 1.

![Figure 1](image1.png)

Figure 1. Isotherms of TCE adsorption by crushed AC: 1 - AG-3; 2 - PFCs; 3 - Purolat: A is in a wide range of concentrations, B is in the region of low concentrations.
The choice of the studied grades makes it possible to analyze the possibility of sorbents produced on the basis of various raw materials, and according to the experimental data, the following series was established, PFCs > AG-3 ≥ Purolat. In its accordance, the adsorption capacity of the studied sorbent grades in relation to TCE. The nature of the interaction of the extracted components and the sorbent makes it possible to evaluate the classification of Gielis isotherms [7]. According to them, the experimentally obtained isotherms refer to S-type isotherms. Figure 1 (B) presents the adsorption in the region of low concentrations. This form of isotherms implies that the interaction between TCE molecules exceeds in strength the interaction between TCE and the AC surface. Moreover, in the studied concentration range (up to the value of the limiting solubility of trichlorethylene) for AC PFCs grades, the saturation of the monolayer with the component is not achieved (S1 isotherms). For AC grades AG-3, in the region of high equilibrium concentrations, either the reorientation of adsorbate molecules on the AC surface begins, or the formation of the second layer of the component (S3 isotherm).

The theories generalized for the case of adsorption from solutions of sparingly soluble substances were applied for a more complete characterization of the studied adsorbents and the calculation of the main adsorption parameters. These substances are monomolecular adsorption (Freundlich and Langmuir models), polymolecular adsorption (BET model), and volumetric filling of micropores-TMVF (Dubinin–Radushkevich model) [9]. All isotherms of trichlorethylene adsorption are analyzed in the corresponding coordinates. The calculated adsorption parameters and correlation coefficients of the models ($R^2$) are given in tables 3 and 4.

According to calculations, with a high degree of correlation ($R^2$>90%), the adsorption behavior of trichlorethylene is described by the Freundlich and TCE models for all the AC studied. The rest of the models cannot be used to describe the adsorption of TCE.

**Table 3. Parameters of TCE adsorption by activated carbons, calculated by the equation of polymolecular adsorption.**

| Grade of AC | $a_{\text{max}}$, mmol/g | K | -ΔQ, kJ/mol | S, m$^2$/g | $R^2$ |
|-------------|--------------------------|---|-------------|------------|-------|
| AG-3        | 2.96                     | 1.79 | 2.50       | 1124 (320$^*$) | 24.88 |
| TCE         | -1.38                    | -1.41 | -         | -         | 44.92 |
| Purolat     | 1.16                     | 0.64 | 1.20       | 441       | 9.20  |

* - when a molecule is oriented perpendicular to the AC surface

**Table 4. Parameters of TCE adsorption by activated carbons, calculated according to the TMVF equation.**

| Grade of AC | $a_0$, mmol/g | $a_0$, µmol/m$^2$ | $w_0$, cm$^3$/g | E, kJ/mol | $\chi$, nm | $R^2$ |
|-------------|---------------|------------------|-----------------|-----------|------------|-------|
| AG-3        | 2.27          | 4.20             | 0.20            | 5.10      | 2.40       | 95.17 |
| TCE         | 20.26         | 19.54            | 1.81            | 4.15      | 2.95       | 98.79 |
| Purolat     | 1.57          | 5.05             | 0.14            | 2.21      | 5.43       | 90.13 |

The representation of adsorption isotherms in the coordinates of the TMVF equation also revealed the presence of several linear sections for some AC. This behavior is typical for the adsorption of components in pores of different sizes. The comparison of the calculated value of the limiting adsorption volume occupied by the component ($w_0$) with the characteristics of the porous structure of adsorbents (table 3) suggests adsorption in micro- and mesopores available in size for AG-3 grade AC. The abnormally high value of $w_0$ for PFCs is associated with the swelling of this adsorbent (the degree of swelling is up to 60%). In the case of Purolat, one can talk about filling the available meso- and macropores (the proportion of micropores in these sorbents does not exceed 2 and 12%, respectively).

The calculated values of the characteristic adsorption energy (E) and, accordingly, the half-width of...
the pores filled with the component (χ) (table 2) suggest that the adsorption of TCE proceeds mainly not in micropores, but in mesopores and is the result of a combination of several factors: nonspecific interaction with available a graphene layer and repulsion between chlorine atoms of TCE and polar CFCs of the carbon surface. This manifests itself both in the form of adsorption isotherms and in the chaotic orientation of the adsorbate molecules.

The water purification from trichlorethylene will proceed with the use of a PFCs grade sorbent produced on the basis of phenol-formaldehyde resin more effectively. However, this sorbent is characterized by high hydrophobicity and low wettability, these properties limit its use in adsorption columns with a fixed bed. The similar adsorption characteristics were shown by Purolat and AG-3, but taking into account the lower cost of the studied coal granular AC, it is this (AG-3) that is expedient to use when removing trichlorethylene from aqueous media.

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