Sorption of trichloroethylene under dynamic conditions

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Abstract. The solution to the problem of obtaining water that is safe against organohalogen pollutants, including trichloroethylene, can be the use of adsorption purification methods. For engineering calculations of the treatment plant, adsorption constants, kinetic parameters and dynamic characteristics of the adsorption process are required. It is advisable, at the stage of technology development, to optimize the parameters and modes of the sorption columns using mathematical modeling based on equations of external diffusion dynamics of adsorption.

Currently, humanity is faced with the problem of obtaining water that is safe for health. Adverse water quality of the centralized drinking water supply system is determined, as a rule, by the following main factors:

- quality of water used by water sources;
- applicable technologies, including reagents used for disinfection.

Water sources undergo significant degradation due to both large water intake and pollution as a result of human activities. Anthropotechnical pollution arises in several ways; one of them is the discharge of insufficiently treated wastewater from various industrial enterprises.

Existing methods of preparing drinking water at water intake stations are not effective against various chemical pollutants, and the use of the chlorination process, with a sufficiently high efficiency of the method to improve epidemiological indicators, leads to the formation of a number of volatile organic chlorinated compounds. Among the organohalogen compounds entering the water, trichloroethylene can be distinguished both for the first and second reasons.

Trichloroethylene is widely used in areas such as:

- printing house, printing industry;
- as a solvent in various industrial sectors;
- excellent degreasing, which is especially important for the production of refrigerants, paints and varnishes, several types of acids and others;
- household services, in particular dry cleaning of clothes and fabric processing;
- food industry involves the use of TCE for the preservation of eggs;
- as the basis for the means of extermination of parasites and pests.
Trichloroethylene is an increased danger to all aquatic organisms and is guaranteed to lead to a deterioration of the aquatic ecosystem. Trichloroethylene is detected in surface, rain and drinking waters, in the air, in marine organisms (invertebrates, fish muscles, seabird eggs, seal fat). It is also found in food (in ground coffee, in spice essential oils).

The absorption of trichloroethylene in mammals can occur when it is inhaled, ingested through the mouth and / or skin. It penetrates the bloodstream, and from there it enters the adipose tissues.

Trichloroethylene exhibits acute toxicity, which increases with the presence of ethanol, carbon tetrachloride, carbohydrates, and its carcinogenic effect is found. Accumulated data [1-3] about the risk of developing cancer, most often cancer of the pancreas, bladder, colon and rectum associated with the use of water containing trichloroethylene. TCE affects the central nervous system, irritates the skin and eyes, and has an allergenic, mutagenic effect.

It is obvious that it is necessary to reduce the concentration of trichloroethylene in the water used for drinking needs and in food production, and adsorption recovery for this purpose is a promising direction.

The sorption method of purification is the most effective and environmentally acceptable method to purify water of various categories from organic pollutants. Its advantages are the ability to remove contaminants of an extremely broad nature to almost any residual concentration, regardless of their chemical resistance, the absence of secondary pollution and process control.

Adsorption of dissolved substances is carried out by filtering the liquid through a dense layer of adsorbent grains loaded into the column; such an adsorption column operates until a “leakage” of contaminant is observed in the filtrate.

Optimization and intensification of adsorption processes, increasing their economic efficiency, the selection of adsorbents are issues that constantly attract the interest of sorption researchers.

The choice of sorbent material is determined by the properties of the material, i.e. developed specific surface, high absorption capacity of substances can also serve as a carrier for fixing various compounds on the surface during their modification. One of the materials that have the listed characteristics is activated carbon. At the same time, active carbons have a relatively low cost.

For the design of adsorption equipment, it is necessary to carry out comprehensive studies, including the study of the equilibrium, kinetics and dynamics of the adsorption process.

The adsorption equilibrium and the extraction of trichloroethylene from aqueous solutions under kinetic conditions were previously studied.

According to the equilibrium adsorption of trichloroethylene from aqueous solutions, the adsorption isotherm is constructed on the active carbon of the ABG brand. Analysis of the initial section of the obtained isotherm made it possible to attribute it to the S-type isotherm according to the Hill’s classification [4]. This form of isotherms implies that the interaction between TCE molecules exceeds in strength the interaction of TCE - AC surface. For a more complete characterization of the adsorbent and calculation of the main adsorption parameters, theories were applied that were generalized for the case of adsorption of solutions of limited soluble substances: monomolecular adsorption (Freundlich and Langmuir models), polymolecular adsorption (BET method) and volume filling of micropores - TVFM (Dubinin - Radushkevich model). The trichloroethylene adsorption isotherm is analyzed in the corresponding coordinates. Adsorption parameters are calculated, which suggest that the adsorption of TCE occurs mainly not in micropores, but in mesopores.

Based on the results of studies of the adsorption of trichloroethylene from aqueous solutions under kinetic conditions, data were obtained that suggest that external diffusion mass transfer controls the rate and is a limiting stage of the adsorption process for the active carbon – aqueous solution of trichloroethylene system at the initial moment of sorption extraction [5, 6].

Experimental studies of the process of extraction of trichloroethylene in a continuous mode were performed using activated carbon of the ABG brand (the choice of this brand of coal is due to its high sorption ability and low cost). An experimental output curve is obtained.

The results of a study on the influence of the layer height on the efficiency of TCE adsorption by ABG active charcoal at a constant solution flow rate of 6 cm³/min show that the time of the protective
action and the shape of the output curves depend on the height of the adsorbent layer. At a layer height of 3 cm, adsorption in the layer reaches equilibrium at an infinitely high speed. The area where the first stage of TCE adsorption from the stream ends — the complete saturation of the adsorbent, which is equilibrium with the concentration of the solution entering the layer, is infinitely small, therefore, the output curve comes out almost directly from the beginning coordinates [7].

With increasing layer height, the operating time of the layer to breakthrough increases: at layer heights of 5, 25 cm, it equals, 4 and 30 hours, respectively. Consequently, the dynamic adsorption capacity is also growing. With decreasing layer height, the slope of the output curve becomes sharper (steeper). A change in the slope of the curve with increasing layer height is associated with mass transfer processes. Over time, internal diffusion will have an increasing influence on the rate of the sorption process: the lower the standing height of the charge, the faster the effect.

The effect of the solution flow rate on the adsorption efficiency in a column with a layer height of 5 cm, at a TCE solution flow rate of 6 and 12 ml/min was also studied. The data obtained show that at a speed of 12 ml/min the output curve exits almost from the origin. This is due to the fact that at a small layer height and a higher velocity, the initial section of the layer quickly saturates to equilibrium and does not participate more in the adsorption process [6]. In this case, the layer working in the sorption process will be longer. A decrease in the flow rate of the solution through the filter increases the dynamic adsorption capacity, which indisputably confirms the intra-diffusion inhibition of mass transfer.

The study on the dynamics of sorption involves a consistent selection of the characteristics of the adsorption column and the mode of the continuous cleaning process. A full account of these factors in experimental research leads to significant costs: financial, time and labor. In practice, it is necessary to find a compromise between the cost of production and the level of its effectiveness.

It is indisputable that it is advisable to include in the process of developing a technological scheme and control system the stage of mathematical modeling based on the theory of adsorption processes. The presence of an adequate mathematical model in a wide range of control actions will allow finding new ways to increase the efficiency of adsorption plants.

To solve the optimization problem, the applicability of the following equations of external diffusion dynamics of adsorption was studied:

- in the case of a linear isotherm

\[ \sqrt{\tau} = \frac{a_o}{w \cdot C_o} \cdot \sqrt{H - b} \cdot \frac{a_0}{\beta_n \cdot C_0} \]  \hspace{1cm} (1)

- at low concentrations for a concave isotherm

\[ \tau = \frac{a_o}{wC_o} \left[ H - \frac{w}{\beta_n} \left( \ln \frac{C_o}{C} - 1 \right) \right] \]  \hspace{1cm} (2)

- in the case of the Langmuir isotherm

\[ \tau = \frac{a_o}{wC_o} \cdot \left\{ L - \frac{w}{\beta_n} \left[ \frac{1}{p} \ln \left( \frac{C_o}{C} - 1 \right) + \ln \frac{C_o}{C} - 1 \right] \right\} \]  \hspace{1cm} (3)

where \( \tau \) - adsorption duration, s; \( w \) - flow rate related to the total cross section of the apparatus, m/s; \( H \) - activated carbon layer height, m; \( C_0 \) - initial concentration of adsorbed substance, kg/m\(^3\); \( a_0 \) - the amount of adsorbed substance, equilibrium with the concentration of the stream \( C_0 \), kg/m\(^3\) (taken from the adsorption isotherm in kg/kg and multiplied by the bulk density of coal in kg/m\(^3\)); \( \beta_n \) - external mass transfer coefficient, s\(^{-1}\); \( b = \Phi^{-1} \cdot (1 - C / 0.54C_o) \); \( \Phi^{-1} \) - inverse function of the Kramp function; \( p = C/C_{0.5} \), \( C_{0.5} \) - the content of the absorbed substance in the stream, equilibrium with the amount of substance equal to half.

The value of the coefficient \( b \) is taken from the reference guides (table 1).
Table 1. Coefficient b values.

| C/C₀ | b   | C/C₀ | b   | C/C₀ | b   |
|------|-----|------|-----|------|-----|
| 0.005| 1.84| 0.2  | 0.63| 0.7  | -0.27|
| 0.01 | 1.67| 0.3  | 0.42| 0.8  | -0.46|
| 0.03 | 1.35| 0.4  | 0.23| 0.9  | -0.68|
| 0.05 | 1.19| 0.5  | 0.09| -    | -    |
| 0.1  | 0.94| 0.6  | -0.1| -    | -    |

To confirm the possibility of using equations (1 - 3) in the description of adsorption dynamics, the output curves are calculated and compared with the experimentally obtained curve (figure 1).

Figure 1. The output trichloroethylene adsorption curves for a dense layer of active carbon ABG: 1 - experimental, calculated by the equation: 1 - 3, 2 - 2, 4 - 4.

The model equation includes the experimentally obtained quantities: the substance content a₀, the external mass transfer coefficient b and the variable parameters: average flow velocity u and the length of the fixed layer L. Figure 2 presents calculated output curves on the example of aqueous solution system TCE AC of the ABG brand with various parameters of the filter layer and mode, because it is necessary to select the elution rate to achieve maximum sorption efficiency.

Figure 2. The output curves of the aqueous solution system TCE AC of the ABG brand for various parameters of the filter layer and sorption mode: a) v = 7m/h at L = 1m (1), 2m (2), 3m (3); b) v = 5m/h at L = 1m (1), 2m (2), 3m (3); c) v = 2.5m/h at L = 1m (1), 2m (2), 3m (3).
With an increase in the length of the filter layer from 1 to 3 m, the operating time of the layer until the trichloroethylene penetrates into the filtrate increases (figure 2), and with an increase in the flow velocity (from 2.5 to 7 m/h) it decreases. The minimum operating time of the filter layer before the trichloroethylene breakthrough is achieved with the parameters: \( L = 1 \text{ m}, u = 7 \text{ m/h}, \) maximum \( L = 3 \text{ m}, u = 2.5 \text{ m/h}. \)

The proposed optimization method, using mathematical modeling of adsorption, is aimed at solving a number of practical problems, i.e. makes it possible to select the parameters and modes of continuous adsorption cleaning, applicable in the engineering design of industrial adsorption plants.

The results obtained show that equation (2) satisfactorily describes the experimental output curve, which confirms the validity of the proposed approach to modeling adsorption and the possibility of determining the dynamic characteristics of adsorption without additional experimental studies based on the equation of external diffusion dynamics of adsorption in the low concentration area for a concave isotherm.

The dynamic characteristics of the adsorption of TCE and the equations given in [5] were used to calculate the dynamic characteristics of the sorption process: the length of the column and the amount of water to be purified depending on the filtration rate, the height of the fixed layer and the length of the unused layer, the coefficient of protective action, the operating period of the column and the height of the fixed layer and the size of the column which are given in the table 2.

**Table 2.** The dependence of the column parameters on the initial concentration of TCE in the solution, the filtration rate and the length of the adsorption layer of AC brand ABG.

| \( L_m \) | \( v, \text{m/h} \) | \( U, \text{m/h} \) | \( k \) | \( L_p, \text{m} \) | \( h, \text{m} \) | \( \tau, \text{h} \) | \( \theta, \text{h} \) |
|----------|----------------|------|------|----------------|------|--------|--------|
| 1        | 1              | 1    | 0.001445 | 691.8333 | 0.21014 | 0.10507 | 72.69  | 546.4481 |
| 2        | 1              | 0.000645 | 1550.333 | 0.29763 | 0.14882 | 230.72  | 2639.234 |
| 2.5      | 1              | 0.000527 | 1896.25  | 0.33192 | 0.16596 | 314.70  | 4111.216 |
| 3        | 1              | 0.000446 | 2242.167 | 0.36354 | 0.18177 | 407.56  | 5911.382 |
| 1        | 2.5            | 0.0037 | 270.2762 | 0.33292 | 0.16646 | 44.99   | 180.2958 |
| 2        | 2.5            | 0.001651 | 605.6636 | 0.46923 | 0.23462 | 142.10  | 927.1302 |
| 2.5      | 2.5            | 0.00135 | 740.8017 | 0.52464 | 0.26232 | 194.33  | 1463.348 |
| 3        | 2.5            | 0.001142 | 875.9398 | 0.57534 | 0.28767 | 251.98  | 2123.854 |
| 1        | 3              | 0.00444 | 225.2302 | 0.35830 | 0.17915 | 40.35   | 144.531 |
| 2        | 3              | 0.001981 | 504.7196 | 0.51701 | 0.25850 | 130.47  | 748.4958 |
| 2.5      | 3              | 0.00162 | 617.3347 | 0.57492 | 0.28746 | 177.46  | 1188.42 |
| 3        | 3              | 0.00137 | 729.9498 | 0.62863 | 0.31432 | 229.44  | 1730.978 |
| 1        | 5              | 0.0074 | 135.1381 | 0.46787 | 0.23394 | 31.61   | 71.9104 |
| 2        | 5              | 0.003302 | 302.8318 | 0.66461 | 0.33231 | 100.63  | 404.3977 |
| 2.5      | 5              | 0.0027 | 370.4008 | 0.73761 | 0.36880 | 136.16  | 652.7917 |
| 3        | 5              | 0.002283 | 437.9699 | 0.81665 | 0.40833 | 178.83  | 956.2412 |
| 1        | 8              | 0.01184 | 84.46132 | 0.59073 | 0.29536 | 24.95   | 34.56761 |
| 2        | 8              | 0.005283 | 189.2699 | 0.84559 | 0.42280 | 80.02   | 218.4944 |
| 2.5      | 8              | 0.00432 | 231.5005 | 0.93130 | 0.46565 | 107.80  | 363.155 |
| 3        | 8              | 0.003653 | 273.7312 | 1.02353 | 0.51176 | 140.09  | 541.0216 |

The proposed optimization method, using mathematical modeling of adsorption, is aimed at solving a number of practical problems, i.e. makes it possible to select the parameters and modes of continuous adsorption cleaning, applicable in the engineering design of industrial adsorption plants.

Based on experimental and theoretical studies, it is possible to recommend a method for optimizing the operation of an industrial installation using mathematical modeling based on the equation of external diffusion dynamics of adsorption in the low concentration area for a concave isotherm, which...
enables to establish optimal operating conditions for the adsorption filter, namely, operating modes and parameters.

It is advisable to use the above solution to develop a technology for adsorption water purification of a centralized water supply system with its subsequent application in the production of various drinks, both carbonated and based on milk and whey.

References
[1] Nieuwenhuijsen M J, Grellier J, Smith R, Iszatt N, Bennett J, Best N et al. 2009 The epidemiology and possible mechanisms of disinfection by-products in drinking water Philosophical Transaction of The Royal Society A: Physical, Mathematical and Engineering Sciences 367(1904) 4043-76
[2] Wright J M, Schwartz J and Dockery D W 2004 The effect of disinfection by-products and mutagenic activity on birth weight and gestation duration Environmental Health Perspectives 112(8) 920-5
[3] Hwang B F, Jaakkola J J and Guo H R 2008 Water disinfection byproducts and the risk of specific birth defects: a population-based cross-sectional study in Taiwan Environmental Health 7(1) 19-29
[4] Krossovskiy G N and Egorov N A 2002 Hazard criteria for halogen-containing substances resulting from water chlorination Toxicological Bull. 3(5-6) 12-7
[5] Koganovskiy A M 1990 Adsorption of Organic Matter from Water (L:Khimiya) p 256
[6] Krasnova T A, Timoshchuk A K, Gorelkina A K and Belyaeva O V 2018 Effect of priority drinking water contaminants on the quality indicators of beverages during their production and storage Foods and Raw Materials 1 230-42
[7] Gorelkina A K, Krasnova T A, Timoshchuk N V, Gora N V and Golubeva N S 2019 Dynamics of trichloroethylene adsorption on activated carbon IOP Conf. Series: Earth and Environmental Science 315 052026
[8] Slavinskaya G V 1991 The effect of chlorination on drinking water quality Chemistry and Water Technology 12(11) 1013-22
[9] Krasnova T A, Timoshchuk I V, Gorelkina A K and Dugarjav J 2017 The choice of sorbent for adsorption extraction of chloroform from drinking Foods and Raw Materials 2 189-96