Determination of Trichloroethylene Adsorption Kinetic Parameters for Engineering Calculations of Industrial Adsorption Columns

To cite this article: T A Krasnova et al 2019 IOP Conf. Ser.: Earth Environ. Sci. 224 012035

View the article online for updates and enhancements.
Determination of Trichloroethylene Adsorption Kinetic Parameters for Engineering Calculations of Industrial Adsorption Columns

T A Krasnova, A K Gorelkina, I V Timoshchuk, N V Gora, M P Kirsanov

Kemerovo State University, Russia, 650056, Kemerovo, Stroitelei Blvd., 47

E-mail: ecolog1528@yandex.ru

Abstract. We studied the adsorption of trichloroethylene kinetics from aqueous solutions on sorbent agents of various brands. We studied the mechanism of mass transfer during the trichloroethylene adsorption on activated carbons. The kinetic curves were plotted and analysed in g against t axis, which made it possible to determine the model of the carbon granule structure. It was determined that the limiting stage of the adsorption process in the range of 5-40 minutes, depending on the properties of the activated carbon, is external diffusion. We calculated the coefficients of external mass transfer, their values are rather high, which indicates a high rate of the sorption process limited by external mass transfer. We obtained the findings necessary for engineering calculations of the adsorption column parameters.

1. Introduction

One of the most important current problems of our time is to provide the population with clean drinking water. The water quality in the system of centralized drinking water supply in virtually all regions of Russia causes serious concerns of specialists, doctors and ecologists. The urgency of this problem is due to the pollution of surface and underground water sources by the sewage of various industrial enterprises, among which mining, fuel and energy, metallurgical, coke and chemical industries, as well as the agro-industrial sector and public utilities, have significant anthropogenic pressure. Trichloroethylene is among the pollutants which belong to the group of trihalomethanes and can always be found in the water. It is 1st hazard category substance.

Trichloroethylene is used for the production of herbicides, refrigerants, various acids. It is also widely used for degreasing metal products, as a solvent for resins, dyes, bitumens, phosphorus and other chemicals. Trichloroethylene enters water bodies with wastewater, worsening water quality and destroying ecosystems.

In the process of water treatment at the stage of water disinfection with chlorine or chlorine-containing reagents, the probability of trichloroethylene appearance in water as a by-product is very high. The danger of trichloroethylene is in its toxic, mutagenic and cancer-causing effects on the human body.

In this regard, research aimed at developing technology for purifying water from trichloroethylene is timely.

2. Literature review

In 2012 World Health Organisation recognised trichloroethylene a cancer-causing compound [1], which has a mutagenic effect and changes in the frequency of chromosomal aberrations, gene mutations and an increase in the incidence of cancer are associated with its entry into the body [2 - 4].
There is evidence that trichloroethylene increases the risk of liver, kidney, esophagus, cervix cancers. A link was found between the regular exposure of trichloroethylene to the human body and the subsequent development of Parkinson's disease [4].

Trichloroethylene is dangerous to aquatic life and can cause significant changes in the ecosystem. According to the Hygienic standards HS 2.1.5.2280-07 'Maximum Permissible Concentrations (MPC) of Chemicals in the Water of Water Bodies of Household, Drinking and Cultural and Domestic Water Use' (Amendments and Changes No. 1 to HS 2.1.5.1315-03) MPC of trichloroethylene in the water of household, drinking and cultural and domestic water use is of 0.005 mg / dm$^3$ [5].

One of the successfully used methods for extracting small amounts of organic substances from aqueous solutions can be called adsorption using porous materials. It provides a high degree of component extraction, and makes it possible to use adsorbents repeatedly [6]. Recently the possibility of replacing expensive adsorbents with affordable and cheap mineral materials, both artificial and natural, has been investigated. For example, materials based on inorganic compounds (metal oxides, aluminosilicates), polymers of various classes and carbon sorbents are used. Such materials are characterized by a developed specific surface area, and high absorption capacity for solutes. When extracting organic compounds from aqueous media, carbon sorbents are most effective [7].

3. Materials and research methods

To develop an adsorption technology for treating water from trichloroethylene on activated carbons, it is necessary to carry out comprehensive studies, including those of the equilibrium, kinetics and dynamics of the adsorption process.

Earlier a study was conducted of the trichloroethylene equilibrium adsorption from aqueous solutions on activated carbons (Table 1) in the concentration range $2 \times 10^{-4} - 2.00$ mmol / dm$^3$. An approximation of the experimentally obtained adsorption isotherms was carried out using the Freundlich monomolecular adsorption models and the Dubinin-Radushkevich volume filling theory. It was found that the data of the theory with a high degree of correlation describe the process of trichloroethylene adsorption from aqueous solutions on activated carbons. The constants of all these equations are determined and the features and mechanism of adsorption are established, the main adsorption parameters are also obtained [6].

We studied the kinetics of adsorption. The studies were aimed at establishing the mass transfer mechanism and calculating the mass transfer coefficients necessary for performing engineering calculations of the parameters of the industrial adsorption column.

The object of the study was the sorbents of the following brands: SKD-515, PFS, KAU, BAU, AG-OV-1 (OJSC ‘Sorbent’, Perm), ABG (‘Karbonika F’, Krasnoyarsk), KSAU (‘Eurocarb’, UK), Purolat-Standart (OJSC ‘Sintez’, Rostov-on-Don), their main physical and chemical properties are presented in Table 1.

Adsorption, like any real process, occurs in time. The kinetics of adsorption deals with the questions of the rate of mining of the adsorption capacity of adsorbent granules and the issues of adsorptive diffusion in single granules. Therefore, the study of kinetics is one of the most important issues in the study of adsorption.

The kinetics of trichloroethylene adsorption was investigated according to limited volume method. The content of trichloroethylene is determined by the standard method by gas-liquid chromatography [8].

To determine trace amounts of trichloroethylene in water, an equilibrium gas phase analysis method is used. When performing measurements, the following conditions are met: the processes of solution preparation and sample preparation to the analysis are carried out under normal conditions according to National state standard (GOST) 15150-69 air at a temperature of $20 \pm 10$ C, atmospheric pressure 630-800 mm Hg and 80% air humidity.

Before performing the measurements solution preparation, preparation of a chromatographic column, construction of a calibration graph, samplings were carried out.
Table 1. Physical and chemical properties of sorbents.

| Indicator                                      | Brand of sorbent |
|------------------------------------------------|------------------|
|                                                | KAU    | KsAU     | AG-OV -1 | SKD-515 | BAU    | ABG    | PFS    | Purolat-Standart |
| Bulk density, g / dm$^3$                        | 417    | 490      | 531      | 526     | 240    | 490    | 374    | 680               |
| Strength, %                                     | 90     | 97       | 70       | 75      | 60     | 70     | 86     | 70-80             |
| Mass fraction of total ash, %                  | 5.4    | -        | 15       | 31      | 7      | 12     | 1.3    | -                 |
| PH aqueous extract                             | 9.25   | -        | 6.85     | 7.65    | 7.85   | 7.45   | 7.85   | 8-9               |
| Total pore volume, cm$^3$ / g                  | 0.97   | 0.951    | 0.44     | 0.7-1.0 | 0.47   | 0.5-0.57 | 1.1 | 0.5               |
| Pore volume, cm$^3$ / g                        |        |          |          |         |        |        |        |                   |
| Micro-                                         | 0.31   | 0.622    | 0.32     | 0.28    | 0.25   | 0.09   | 0.34   | 0.07              |
| Meso-                                          | 0.66   | 0.110    | 0.14     | 0.11    | 0.1    | 0.38   | 0.76   | 0                 |
| Macro-                                         | -      | 0.219    | 0.44     | 0.33    | -      | 0.12   | -      | 0.43              |
| Adsorption iodine activity, %                  | 78     | 60       | 65       | 56      | 60     | 60     | 226    | -                 |
| Granule form                                   | irregular | irregular | irregular | cylinder | irregular | fragmented | spherical | irregular |

4. Results

The primary information on the adsorption rate obtained during the experiment, i.e. the rate of granule saturation by adsorbate is represented by kinetic curves (Fig. 1), which characterize the change in the value of adsorption with time.

Figure 1. Kinetic curves of the trichloroethylene adsorption by carbon sorbents of the following brands: a) 1 KsAU, 2 AG-OV, 3 Purolat – Standart 4 KAU; (1), c) 5 PPS, 6 SKD-515, 7 BAU, 8
Kinetic curves are analysed in coordinates $\gamma$ from $\tau$ (Fig. 2). The degree of achievement of the adsorption equilibrium was calculated by the formula:

$$\gamma = \frac{a_\tau}{a_p},$$  \hspace{1cm} (1)

where $a_\tau$ is adsorption during $\tau$; and $p$ - the value of the equilibrium adsorption.

One of the objectives of this study is to find a controlling type of mass transfer, which can be solved using the method developed by R. M. Marutovsky [9]. For this purpose dimensionless kinetic parameters $T$ were calculated and graphs of $T$ (calculated theoretically) versus $\tau$ (experimental process time) were plotted for the same $\gamma$ values (Fig. 3).

The speed of approaching the process of adsorption from solutions to equilibrium depends on how far the system is from the equilibrium at the moment, and how much it is proportional to the surface area of the contact of the liquid with the adsorbent $-dS$ [9, 10]

$$\frac{da}{dSd\tau} = \beta_a (a_p - a_\tau),$$  \hspace{1cm} (2)

$$\frac{dC}{dSd\tau} = \beta_c (C_p - C_\tau),$$  \hspace{1cm} (3)

The difference between the concentrations at a given moment $C_\tau$ and the onset of equilibrium $C_p$ or the difference between the equilibrium specific adsorption $a_p$ and the values of specific adsorption $a_\tau$ by the time of measurement $\tau$ is called the driving force of the process; $\beta_a$ and $\beta_c$ in these equations are called mass transfer coefficients.

For activated carbon - aqueous solution of trichloroethylene systems, as studies indicate, the limiting step of the adsorption process is diffusion of external, external mass transfer coefficient ($\beta_a$) can be found from the slope of the line depending on a dimensionless coefficient $T$ $\tau$. The coefficients of external mass transfer are presented in Table 2.
Table 2. External trichloroethylene mass transfer coefficients in activated carbon – water – trichloroethylene systems.

| Brand of sorbent | Purolat-Standard | SKD-515 | KsAU | PFS | AG-OV | KAU | ABG | BAU |
|------------------|------------------|---------|------|-----|-------|-----|-----|-----|
| β_p, sec^-1      | 0.2517           | 0.0293  | 0.0308 | 0.2607 | 0.0282 | 0.0411 | 0.0366 | 0.0137 |

Figure 2. Dependencies on the degree of achievement of the adsorption equilibrium γ from the adsorption time τ: 1 AG-OV, 2 KAU, 3 Purolat-Standard, 4 KsAU, 5 ABG, 6 SKD-515, 7 PFS, 8 BAU.
Figure 3. Theoretical kinetic curves of adsorption in activated carbon - an aqueous solution of trichloroethylene systems: 1 AG-OV, 2 KAU, 3 Purolat-Standart, 4 KsAU, 5 ABG, 6 SKD-515, 7PFS, 8 BAU.
5. Discussion

The study shows that adsorption process in the kinetic conditions for the system under study showed that for all activated carbon samples (SKD-515, PFS, KsAU, Purolat-Standard, AG-OV, ABG, KAU, BAU) equilibrium in the adsorption system is reached within 50 - 200 min depending on the carbon brands.

The dependence of the equilibrium degree on time (Fig. 2) allows us to determine the model of the structure of active carbon granules, since to study the kinetics of adsorption, it is necessary to consider which of the models (quasi-homogeneous or biporous) sorbent grains are. The initial part of the curve of the degree of achievement of the adsorption equilibrium time is of straightforward nature until $\gamma = 0.4-0.9$ high values $\gamma$ a straight section suggest matching granules used sorbents quasi-homogeneous model, grain adsorbent therefore considered as a system formed by random entanglement of micro- and mesopores, in which it is impossible to distinguish between areas that have only or predominantly mesopores, and areas that contain only micropores.

The dependences of $T$ values on $\tau$ (Fig. 3) are direct passing through the origin, indicating that at this stage the adsorption process is limited by external mass transfer for 5-40 min depending on the properties of the activated carbon. For a short time, the degree of achievement of the adsorption equilibrium $\gamma$ was 0.4-0.9. Therefore, up to these values of $\gamma$, $\tau$ is adsorption of trichloroethylene proceeds inside the grain so quickly that it does not affect the overall rate of mass-transfer [10]. As the experimental points approach the equilibrium, they begin to deviate from the straight line, this is because in this case, as the equilibrium approaches, the specific adsorption gradient decreases and, consequently, the rate of external mass transfer proportional to the gradient decreases.

The findings suggest that the external diffusion and mass transfer control the rate and it is a limiting step of the adsorption process for activated carbon - trichloroethylene aqueous solution systems at the initial time of sorption [9, 10].

The values of the external mass transfer coefficients $\beta_p$ presented in Table 2 for all the studied grades of carbon sorbents are quite high, which allows us to expect a high rate of extraction of the component from the purified water during filtration through a fixed bed of sorbent. Values of $\beta_p$ for sorbents of the grades PFS and Purolat-Standard, in comparison with other studied brands of sorbents, differ, which is probably due to the developed system of transport pores (macro- and mesopores) for the activated carbons of these grades, the number of oxygen-containing surface functional groups and raw materials [7] used to produce a sorbent; since the migration of a substance from a solution volume can be significantly influenced both by the conditions of transfer of molecules of the adsorbed substance to the surface of the adsorbent grain, and the size and character of the porosity of the adsorbent particles, determining the migration path of molecules from the outer boundary through the pore system to the center of the grain raw materials and method for producing sorbent [8,10].

The external diffusion mechanism and the calculated mass transfer coefficients allow expecting a high rate of extraction of the component from the purified water when filtering through a fixed sorbent layer [10].

6. Conclusion

The study allowed us to find out the model of the granule structure of the sorbents under study. To establish the mechanism of mass transfer in activated carbon - an aqueous solution of trichloroethylene systems and show the effect of coal structure on transfer conditions. The mass transfer coefficient necessary for engineering calculations of industrial adsorption columns is determined.

The study was performed in the framework of the State task 'Initiative scientific projects' 19.4713.2017 / BH.

References

[1] Egorova N. Ah. Bukshuk A., Krasovsky G. N. Hygienic assessment of chlorination products of
drinking water, taking into account the plurality of intake // Hygiene and sanitation, 2013. - № 2. - p. 18-23

[2] Nieuwenhuijsen M.J., Grellier J., Smith R., Iszatt N., Bennett J., Best N. et al. The epidemiology and possible mechanisms of disinfection by-products in drinking water. Philosophical Transaction of The Royal Society A: Physical, Mathematical and Engineering Sciences. – 2009. - vol. 367 (1904), - p. 4043-4076.

[3] Wright J.M., Schwartz J., Dockery D.W. The effect of disinfection by-products and mutagenic activity on birth weight and gestation duration. Environmental Health Perspectives, 2004, vol.112, no. 8, pp. 920-925

[4] Baytak D., Sofuoglu A., Inal F., Sofuoglu S.C. Seasonal variation in drinking water concentrations of disinfection by-products in IZMIR and associated human health risks. Science of The Total Environment. - 2008/. - vol. 407 (1), - p. 286-296.

[5] Sato T., Yamamori H., Matsuda H. An estimation of safety of ozonation and chlorination of a water purification plant // Water Sci. Technol. – 1992. - no. 9-11. - p. 2385-2388.

[6] Krasnova, T. A., Timoshchuk, I. V., gorelkina, A. K., Shulzenko, Yu. S., Water preparation for the production of fruit and whey drinks for the prevention of cance. Mteriály XIV miedzynárodowej naukowi -praktycznej konferencji " Kluczowe aspekty naukowej działalności - 2018". - Poland, Przemyśl, Nauka i studia. -Voume 2. - 2018. - 77-79 str.

[7] Semenova S. A., Gulyaeva T. I., Leontiev N. N., Manina V. S., Drozdov T. S., Fedorova N. I., Ismagilov Z. R. Porous structure of carbon materials based on naturally oxidized coals of Kuzbass // Solid Fuel Chemistry. – 2013. - № 5. -p. 40-45

[8] Corwin, C. J. Adsorption and desorption of trace organic contaminants from granular activated carbon adsorbers after intermittent loading and throughout backwash cycles / Christopher J. Corwin, R. Scott Summers // Water research. – 2011. – Т. 45. – № 2. – p. 417–426.

[9] Krasnova T.A. Effect of Priority Drinking Water Contaminants on the Quality Indicators of Beverages during their Production and Storage/ T.A. Krasnova, I.V. Timoshchuk, A.K. Gorelkina, and O.V. Belyaeva // Foods and Raw materials. - 2018. - №1. -p.230-242.

[10] Fedotkin I. M., Kaganovsky A. M., Roda I. G., Muratovski R. M. On determination of the coefficient of external mass transfer and adsorption from solutions. // Russian Journal of Physical Chemistry/ - 1994. - T. 48. - № 2. -p. 473-475.