Extraction of Chloroform from Wastewaters of Halogen Organic Synthesis Enterprises by Sorption

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Abstract

The results of studies seeking to create ecologically safe and resource-saving technologies for the production of halogen organic substances are presented. A method of optimization of adsorption filter parameters and adsorption purification regimes is proposed. A technique has been developed for regenerating exhaust sorbents. A technological flowsheet of an adsorption plant for purification of wastewaters from chloroform is presented; its introduction in the known technological schemes of obtaining organochlorine substances will make it possible to avoid environmental pollution.

The ecological aspect of sustainable development formulated by the UNO conference on environment and development provides for environmental protection and rational management of natural resources. One of the ways of realizing these requirements is to develop and put into practice low-waste and no-waste processes with local purification of liquid wastes to ensure extraction of valuable components and to bring wastewaters to technological standards for their utilization and for environmental protection.

At enterprises of organohalogen synthesis using chloroform as a substrate, this compound is the major component of wastewaters [4, 5]. Thus in freon production, wastewater contains from 0.5 to 2.0 g/dm^3 of chloroform [6]. At present, there are no rational techniques for wastewater treatment and in most cases wastewaters are released into ponds.

When released into environment, chloroform destroys the ecosystems, lowers the quality of potable water, and increases the morbidity and mortality of the population. Chloroform possesses toxic properties [1–3]. According the data of the National Institute of Oncology (USA), chloroform may be responsible for 2 % of the total number of liver and kidney cancer cases.

The aim of the present work is liquid waste treatment as a method of solving the problem of creating ecologically safe and resource-saving processes at enterprises producing organohalogen compounds from chloroform. Adsorption seems to be the most promising method of purification for low-concentrated solutions of organic compounds. To create adsorption technology it is necessary to carry out a comprehensive study of the adsorption process including the equilibrium, kinetics and dynamics studies, optimization of adsorption filter parameters and regeneration of exhaust sorbents. The results of the equilibrium, kinetics, and dynamics studies of chloroform adsorption from water solutions using activated carbons are presented in [7–9]. Analysis of the data obtained has demonstrated that the degree of chloroform extraction is as high as 90 % and that activated carbon (AC) SKD-515 is the most efficient sorbent (Fig. 1).

Optimization of adsorption filter parameters and adsorption purification regimes is generally reduced to successive selection of parameters (sorbent, length of immobile layer, flow

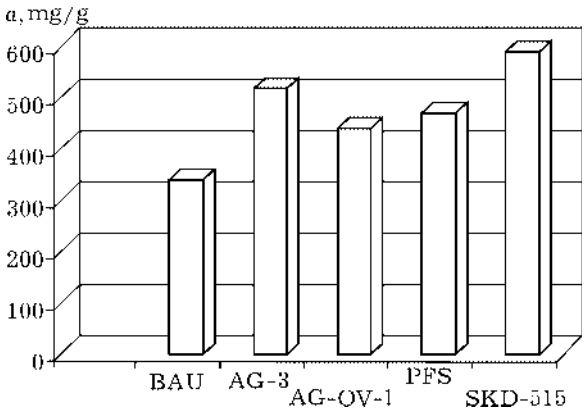

Fig. 1. Dependence of adsorption on the sorbent brand at equal concentrations of chloroform in wastewaters.

rate, *etc.*) to obtain experimental output curves depending on one variable (*e. g.*, solution flow rate) at fixed values of others. Therefore, optimization should be done by mathematical simulation of dynamics based on the material balance equations and experimental data on the equilibrium and kinetics of sorption, which considerably reduces the amount of experimental work to study sorption dynamics.

Mathematical simulation of dynamics was performed by calculating the output curves using the fundamental equation of external diffusion adsorption dynamics:

$$\sqrt{\tau} = \sqrt{L}\sqrt{a_0/(C\upsilon)} - b\sqrt{a_0/(C\beta_n)} \qquad (1)$$

where τ is the working time of a sorbent layer with a length L until overshoot concentration of the sorbed substance C has appeared; a_0 is the content of the substance in the stationary phase equilibrating with C_0, mmol/kg; $b = \Phi^{-1}[1 - C/(0.54C_0)]$; Φ^{-1} is a function reciprocal to the Cramp function; C_0 is the initial concentration of the substance in the flow, mmol/dm^3; υ is the average flow rate, m/h; β_n is the coefficient of external mass transfer.

The applicability criterion for this model is coincidence of the experimental and calculated dynamic curves (for given extraction parameters). Figure 2 presents the experimental output curves and those calculated by model eq. (1) for the stationary filter layer of the sorbent (SKD-515) with a length of 0.3 m and mean flow rate of 8 m/h (chloroform content in the aqueous solution is 0.5 g/dm^3). The curves have the same shape and coincide within the experimental error (15 %) in all instances. Therefore, this approach to simulation is justified and may be used to calculate the output curves of chloroform adsorption from wastewaters.

To select rational parameters of purification, we calculated the output curves for different parameters of the filter layer and sorption regime (Fig. 3). The work time of the layer before the overshoot of chloroform to the filtrate increased when the length of the filter layer increased from 1 to 3 m (see Fig. 2, curves *1–8*) but decreased when the flow velocity increased from 2.5 to 8 m/h (see Fig. 2, curves *1, 4, 7*; *2, 5, 8* and *3, 6*). The minimal work time of the filter layer before chloroform overshoot was achieved at L = 1 m and υ = 8 m/h; the maximal time, at L = 3 m and υ = 2.5 m/h.

One of important problems in sorption purification technology is sorbent regeneration. Regeneration of activated carbons traditionally employs thermal and reagent methods. The use of the latter entails the formation of secondary wastes. Therefore, the possibility of using thermal methods of activated carbon regeneration after chloroform adsorption was considered.

We estimated the recovery of adsorption properties of SKD-515 with respect to chloroform after regeneration with steam, hot water (temperature of 70 °C), and air or inert gas (nitrogen) flow heated to 150 °C (Fig. 4). The

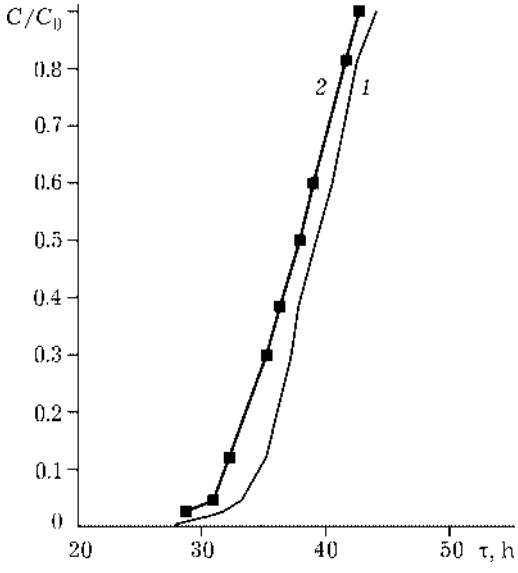

Fig. 2. Outlet curves in the SKD-515 AC – aqueous chloroform system (flow rate 8 m/h, filter layer length 0.3 m); *1, 2* – experimental and calculated curves, respectively.

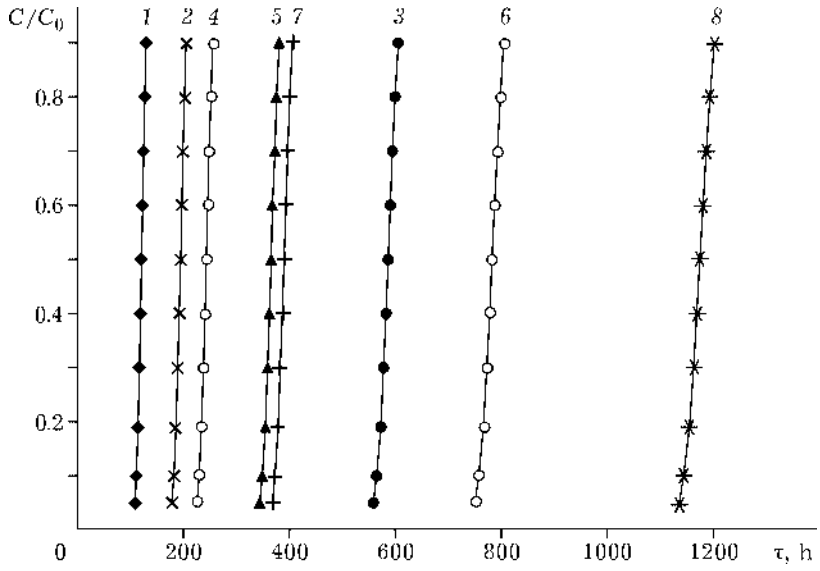

Fig. 3. Theoretical outlet curves of sorption of SKD-515 AC from aqueous chloroform solutions. υ = 8 m/h, *L*, m: 1 (*1*), 2 (*2*), 3 (*3*); υ = 5 m/h, *L*, m: 1 (*4*), 2 (*5*), 3 (*6*); υ = 2.5 m/h, *L*, m: 1 (7), 2 (*8*).

adsorption isotherms show that when steam and heated air flow are used, the adsorption capacity on regenerated carbon decreases by 5–7 %. This is probably associated with the natural loss of activated carbon within the limits of 5–10 % during regeneration. Therefore, these methods may be considered to be rather efficient. At the same time, the results obtained for activated carbon after regeneration with hot water indicate that adsorption capacity decreased to 40 % of the initial value.

For SKD-515 AC, the recovery of adsorption properties after multiple regenerations with an air flow heated to 150 °C (10 sorption – desorption cycles) was estimated in laboratory conditions (Fig. 5). The data presented point to a practically complete recovery of the adsorption properties of carbon after five regeneration procedures.

Based on the results presented here, regeneration with a flow of air or inert gas heated to 150 °C is recommended for recovery of the adsorption capacity of carbons after chloroform adsorption.

Adsorption technology of wastewater treatment is recommended for use in current technological schemes.

An adsorption plant consists of adsorption columns (diameter 1 m, filter layer height 3 m) filled with SKD-515 activated carbon, and also of wastewater feeding pumps, purified water outlet, condensers, air pump, and heat exchanger.

It is recommended to use adsorbers with which regeneration of exhaust sorbent is possible without removing the adsorbent from the apparatus. This makes it possible to avoid carbon losses during adsorbent loading and unloading and to reduce plant maintenance costs. To increase the adsorption capacity of activated carbon, circuits of three adsorbers con-

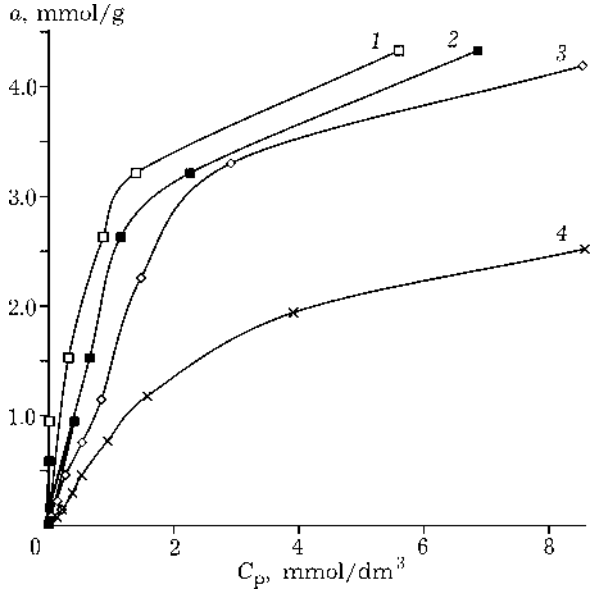

Fig. 4. Adsorption isotherms in the SKD-515 AC – aqueous chloroform system: *1* – initial technical carbon; *2* – carbon after thermal regeneration; *3* – after steam regeneration; *4* – after hot water regeneration (70 °C).

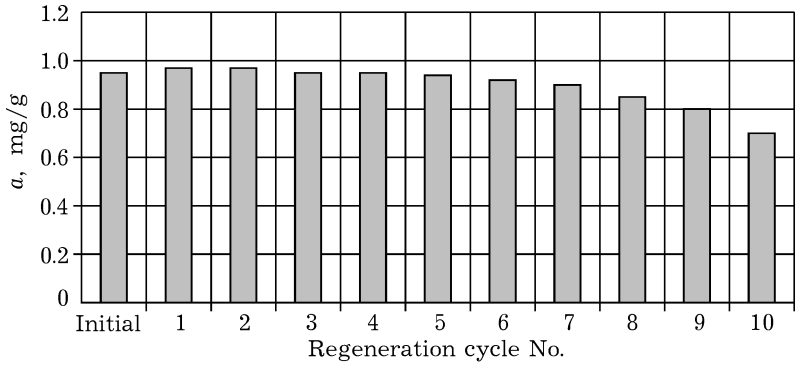

Fig. 5. Recovery of the adsorption properties of SKD-515 AC after repeated regenerations.

nected in series (Fig. 6) are recommended instead of separate parallel columns.

In this case, wastewaters pass through two columns in succession. The first column (in the direction of wastewater movement), which contains activated carbon completely saturated to equilibrium, is the only column that needs to be disconnected for regeneration. The column with regenerated carbon is connected to the second column of the circuit when the first column is disconnected for regeneration by switching over the gates on the strapping pipelines.

At the first stage, wastewater purification takes place in columns A and B, while regeneration of AC is performed in column C (see Fig. 6, *a*). By the moment when chloroform overshoot concentration appears after the layer of column B, activated carbon in column A is completely saturated, and column A is disconnected for regeneration. Instead of column A, column C is connected (see Fig. 6, *b*), and the plant continues to work until chloroform appears in the filtrate fixed after column C. Then column B is switched off for regeneration, and column A is connected after column C (see Fig. 6, *c*).

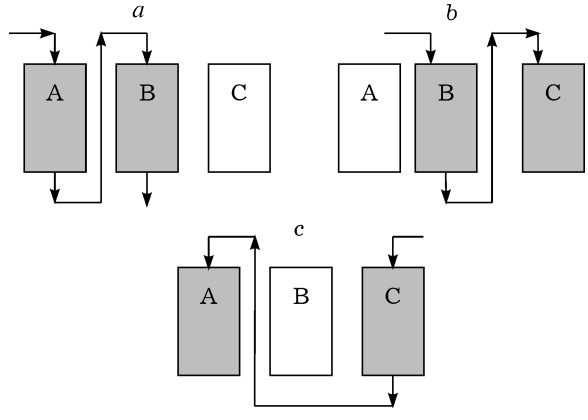

Fig. 6. Flowsheet of one-shot operation of the adsorption line of three apparatuses.

According to the proposed technological scheme, the water to be purified is pumped to the adsorber where chloroform goes from the liquid phase to the sorbent pores:

$$[CHCl_3 - H_2O] + \text{SKD-515 AC} \rightarrow [CHCl_3 - \text{SKD-515 AC}] + H_2O$$

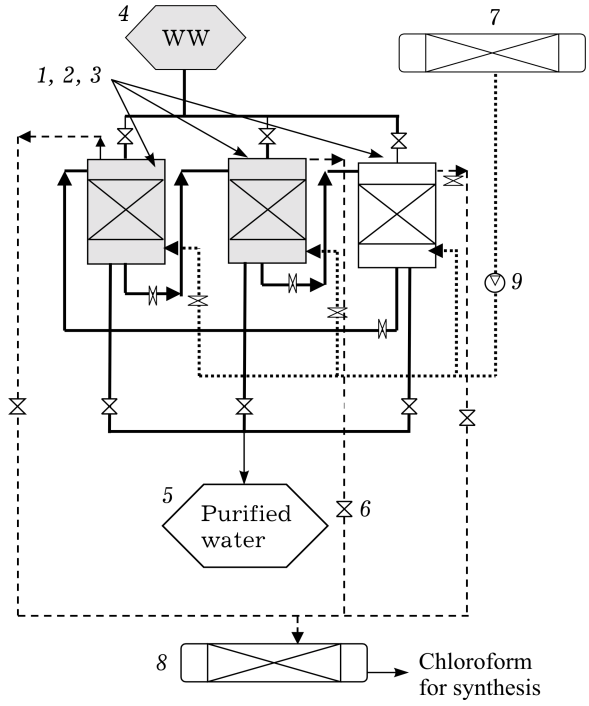

Fig. 7. Technological scheme of adsorption purification of wastewaters containing chloroform: *1–3* – adsorption filters, *4* – wastewater container, *5* – purified water container, *6* – pumps, *7* – heat exchanger, *8* – condenser, *9* – air pump.

Purified water that passed through the carbon layer is recycled to the washing stage of the process.

After the sorbent layer has been saturated, the adsorption filter is switched over to the regeneration stage. It is proposed that activated carbon be regenerated with an inert gas (nitrogen) heated to 150 °C. The use of this temperature is possible due to the low boiling temperature of chloroform (61.7 °C). Moreover, chloroform does not decompose under these conditions.

The following reaction takes place during regeneration:

$$[CHCl_3 - \text{SKD-515 AC}] + \text{inert gas (150 °C)} = \text{SKD-515 AC} + [CHCl_3 - \text{inert gas}]$$

The amount of the gas flow should be calculated with allowance for distillation of the adsorbed substance and heating of the sorbent. Regeneration starts with maximal possible removal of the water residue from the adsorption column. Then inert gas heated to 150 °C is fed to the column from bottom upward.

The gas flow spent on heating and chloroform extraction depends on the carbon temperature before the start of heating, on the amount of water remaining in the pores of the sorbent after the removal of the liquid from the adsorption column, on the temperature of the heating gas, on the mass and heat capacity of carbon and chloroform, *etc*. The exhaust gas released from the adsorption filter and containing chloroform is directed to the condenser, where chloroform is isolated from the gas phase. The purified inert gas is recycled to regeneration, and chloroform goes to synthesis.

The developed technology permits the creation of resource-saving and ecologically safe production processes due to recycling of water and chloroform.

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