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**SORPTION  
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## **Study of the Effect of Technological Parameters of Extractive Wastewater Purification in Production of Bisphenols**

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**Abstract**—Effect of various technological parameters of the process in which wastewater formed in production of bisphenols is purified to remove phenol. The optimal parameters of the process were determined, with which a processed wastewater is obtained with phenol concentration that enables recycling of wastewater into the technological process and its partial delivery to treatment facilities.

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The environment protection is the most important requirement imposed on any chemical plant. Therefore, our new technology being developed for production of bisphenols (BPs) [1] assumes as a stage of the process the treatment of wastewater formed from the reaction water in the distillation stage and from the washing water in the stage of isolation and purification of the target product. The main component responsible for the toxicity of wastewater is phenol used as the main reagent in production of BPs. The overwhelming majority of the known BP syntheses are performed with an excess of phenol [2, 3], with its good solubility in water resulting in a high concentration of this substance in wastewater (up to 10 g L<sup>-1</sup>) even in the case of high-efficiency BP production processes providing the maximum conversion of the reagents.

Phenol is a highly toxic compound exerting a highly unfavorable influence on living organisms even at its insignificant amounts, which predetermines the maximally stringent sanitary regulations according to which the admissible concentration of phenol in water should not exceed 0.001 mg L<sup>-1</sup> [4].

Deep purification of industrial wastewaters to remove phenol is a rather complicated and labor-consuming task

because none of the known methods for detoxication of phenol can provide the required degree of purification at comparatively acceptable technological and economic parameters. The most effective way to preclude ingress of phenol into natural water basins is to recover this substance on local installations and recycle purified water into the close water supply system of a plant.

The methods for purification of wastewater to remove phenol can be divided into two groups: regenerative and destructive. However, in view of the high turnover of phenol in production of BPs, destructive methods lead to a dramatic rise in expenditure of raw materials, which makes the production of BPs economically unfeasible. Therefore, methods that enable recycling of phenol are employed in actual practice: extraction, distillation, rectification, and adsorption.

The most preferable method at high concentrations of phenol and large amounts of wastewater is, with consideration for the ability of phenol to form an azeotropic mixture with water, the extraction technique [5] based on the different solubilities of phenol and water in organic solvents. The choice of a suitable solvent satisfying such requirements as the high dissolving capacity for phenol and low solubility in

water, availability, chemical stability, nontoxicity, zero emulsifying capacity, etc. is the key factor determining the efficiency of the purification process. Thus, the problem of the optimal solvent for purification of industrial wastes formed in manufacture of BPs to remove phenol still remains topical, as also does the issue of the optimal technological implementation of the purification process for the chosen solvent.

It has been suggested previously to use a mixture of solvents as an extractive agent; however a substantial increase in the extraction efficiency has only been observed in isolated cases [6]. A highly economically attractive method is that in which the role of the extractive agent is played by a fraction based on isopropenylbenzene, formed in isolation and purification of bisphenol [7]. However, the minimum obtainable concentration of phenol in water substantially exceeds that required by regulations, which necessitates an additional purification. A high efficiency was exhibited by the method in which wastewater is purified in a counter current column with a mixture based on methylisobutyl ketone [8]. However, although technological solutions made it possible to reach large distribution coefficients, the choice of the extractive agent is not unquestionable because, first, its solubility in water exceeds that of some other solvents and, second, it has a rather high toxicity. In addition, there are no reliable data on the efficiency of this mixture at low phenol concentrations, which is particularly important in view of the tendency exhibited by most of solvents toward a decrease in the extractive capacity at lower concentrations of the substance being extracted.

Of particular interest among the compounds devoid of these shortcomings is butyl acetate having the largest distribution coefficient for phenol among all the available solvents [9]. The main hindrance to application of butyl acetate is in its ability to be hydrolyzed when the reaction of the medium differs from being neutral. However, the appearance of acid-alkaline admixtures can be avoided if solid heterogeneous cation-exchange resins are used as catalysts for synthesis of bisphenols. Therefore, this solvent is, in our opinion, the most suitable for wastewater purification to remove phenol in the technological process for synthesis of bisphenols with heterogeneous catalysts.

Various technological solutions aimed to extract phenol with butyl acetate are still being suggested

[10], but a deliberate implementation of the deepest purification process requires a more detailed analysis of the influence exerted by various parameters on the capacity of butyl acetate for extraction of phenol.

The goal of our study was to examine how the parameters describing the efficiency of butyl acetate in extraction of phenol from wastewater depend on the extraction conditions and to determine the optimal parameters of the process of purification of wastewater formed in BP synthesis at which the phenol concentrations approaching the maximum permissible concentration (MPC) to the greatest extent can be obtained.

## EXPERIMENTAL

The process was performed under vigorous dispersion. The extraction yielded two layers: upper layer of purified water and lower layer of spent butyl acetate. Then, samples were taken from both layers, the phenol concentration was measured in the samples, and the distribution coefficient  $K$ , the main parameter characterizing the efficiency of the extractive agent was calculated:

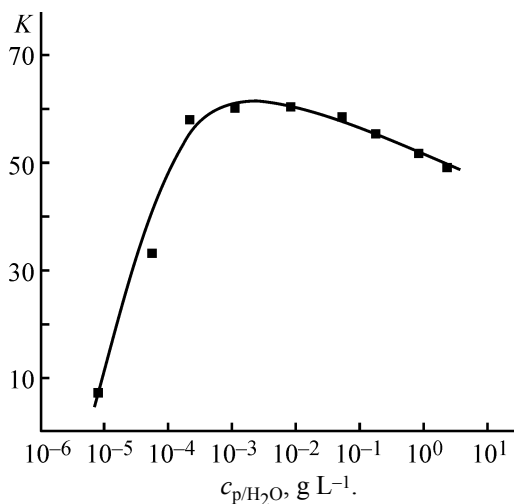
$$K = \frac{c_{p/ba}}{c_{p/H_2O}},$$

where  $c_{p/H_2O}$  and  $c_{p/ba}$  are the concentrations of phenol in the water and solvent layers, respectively.

The concentration of phenol in water was determined by photocolourimetry and titration.

The concentration of phenol in water at its concentrations lower than  $1 \text{ mg L}^{-1}$  was determined by the photocolourimetric method in which an aliquot of a solution being analyzed is taken, its volume brought with distilled water to 500 mL, and 5 mL of an ammoniac buffer solution with pH 10 was added. The resulting solution was poured into a separatory funnel and 3 mL of a 2% solution of 4-aminoantipyrine and 3 mL of a 8% solution of potassium(III) hexacyanoferrate were added. After that, 25 mL of chloroform was added, the mixture was thoroughly shaken-up and allowed to stay for 30 min. The extract was filtered and its optical density at 460 nm was measured. The concentration of phenol was found by using plots.

The content of phenol in water at high concentrations ( $>1 \text{ mg L}^{-1}$ ) was determined by titration. For this



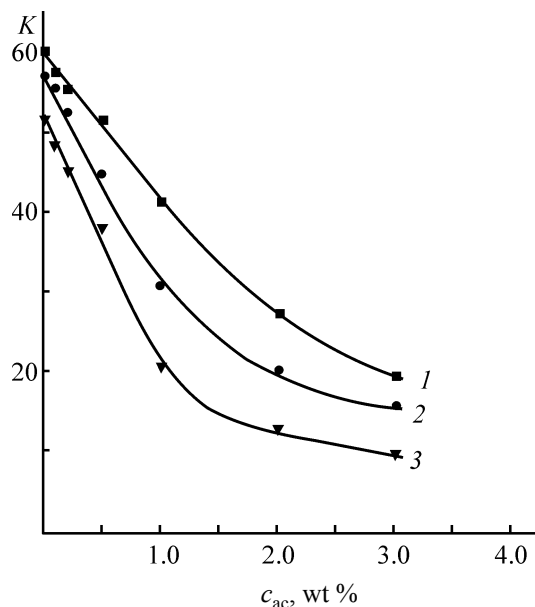
**Fig. 1.** Distribution coefficient  $K$  of phenol in butyl acetate and water vs. the equilibrium concentration of phenol in water,  $c_{p/H_2O}$ , at 20°C.

purpose, 25 mL of a bromide-bromate mixture (prepared by dissolution of 1.67 g of potassium bromate and 6 g of potassium bromide in 1 L of water) and 10 mL of a 25% sulfuric acid solution were added to 50 mL of a solution being analyzed. The resulting mixture was allowed to stay in a closed vessel for 30 min. Then, 1 g of potassium iodide was added and the solution was titrated with 0.05 N sodium thiosulfate in the presence of starch until its discoloration.

The concentration of phenol in butyl acetate was determined by gas chromatography on an HP-6890 chromatograph with a flame-ionization detector. This was done under the following conditions: HP-5 capillary column with length of 30 m and diameter of 0.32 mm; thickness of the immobile liquid layer thickness, 0.25  $\mu$ m; injector temperature 200°C; sample introduction with flow division 1 : 20; dose 1  $\mu$ L; column thermostat temperature programmed from 30 to 150°C; detector temperature 250°C; carrier-gas nitrogen.

We obtained dependences of the distribution coefficient on the concentration of phenol in water, content of impurities characteristic of wastewater formed in production of BPs, extraction temperature, and ratio between the flow rates of wastewater and the extractive agent.

The distribution coefficient of phenol among butyl acetate and distilled water as a function of the widely



**Fig. 2.** Distribution coefficient  $K$  of phenol in butyl acetate and water vs. the content of acetone in water,  $c_{ac}$ , at 20°C.

varied equilibrium concentration of phenol in water is shown in Fig. 1. It can be seen that, as the content of phenol in water becomes lower than 10<sup>-4</sup> g L<sup>-1</sup>, the degree of purification sharply falls, which gives no way of reaching a value of 0.001 mg L<sup>-1</sup>. However, with consideration for the fact that wastewater is, as a rule, subjected to several purification stages, the reachable phenol concentrations are comparable with the MPC.

However, wastewater formed in production of bisphenol may contain, in addition to phenol, acetone (the second main reagent in synthesis of bisphenol), bisphenol, trace amounts of its isomers (e.g., 2,4'-dihydroxy-2,2-diphenylpropane), and a number of intermediate compounds (primarily *para*-isopropylphenol).

Figure 2 shows how the distribution coefficient depends on the content of acetone in the solution of phenol in water at various initial concentrations of phenol. It can be seen that insignificant amounts of acetone (on the order of tenths of a percent) do not exert any strong influence on the extraction processes, but the distribution coefficient sharply falls with increasing content of acetone. In addition, the stratification of mixtures is deteriorated because of the unlimited solubility of acetone in both phases, which makes necessary a substantially longer contact of water with the extractive agent, or, in the case of a continuous purification process, substantially lower flow rates.

Distribution coefficient of phenol among butyl acetate and aqueous phase for various compositions of wastewater formed in production of BP ( $K_1$ ) and that for acetone and phenol solutions of similar concentrations in water ( $K_2$ ) at 20°C

Admixture	Admixture concentration, wt %, for indicated composition		
	no. 1	no. 2	no. 3
Phenol	0.15	0.44	0.60
Acetone	0.02	0.07	0.14
Bisphenol	0.07	0.19	0.25
2,4'-Dihydroxy-2,2-diphenylpropane	0.01	0.03	0.04
<i>para</i> -Isopropylphenol	0	0	0.01
$K_1$	57.1	51.9	49.8
$K_2$	57.3	51.9	49.9

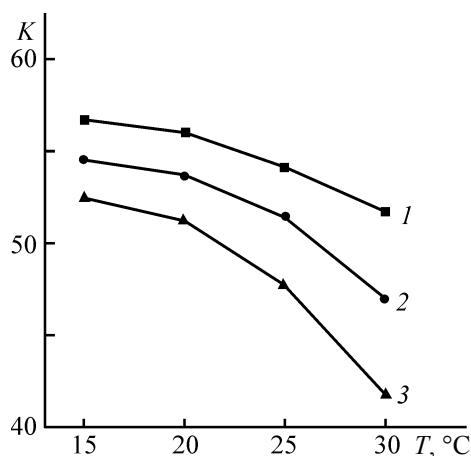
Thus, the presence of acetone in wastewater rules out its extractive purification to remove phenol. If, however, bisphenol is synthesized with a large degree of conversion of acetone and, accordingly, its low content in the sewage, butyl acetate demonstrates high extraction efficiency.

To determine the dependence of the distribution coefficient on other impurities, we extracted with butyl acetate various aqueous mixtures obtained as wastes in synthesis of BP. The composition of wastewater varied with the synthesis parameters and, accordingly, with the conversion of the reagents and selectivity. The distribution coefficients of three different mixtures were compared with the coefficients obtained for solutions prepared from phenol and acetone with similar concentrations. The results

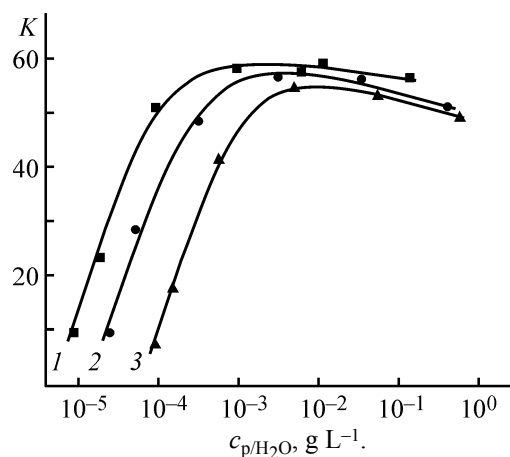
obtained are listed in the table. If the impurities characteristic of wastewater formed in production of bisphenol appeared in water in the given amounts, the distribution coefficient was hardly affected.

As already noted, the main and, presumably, the only disadvantage of butyl acetate as extractive agent used to purify phenol-containing water is that it tends to be hydrolyzed in non-neutral media and at elevated temperatures. Use of heterogeneous catalysts rules out an acid-alkaline hydrolysis, and the temperature factor was examined in the next stage of the study, the more so that temperature is one of the main parameters determining the extraction efficiency.

Temperature strongly affects the solubility of phenol in both water and butyl acetate; however, the



**Fig. 3.** Distribution coefficient  $K$  of phenol in butyl acetate and wastewater formed in production of BP vs. temperature  $T$ . (1–3) Composition numbers in the table; the same for Fig. 4.



**Fig. 4.** Distribution coefficient  $K$  of phenol in butyl acetate and wastewater vs. the equilibrium concentration of phenol in water,  $c_{p/H_2O}$ , at 20°C.

temperature dependence of the distribution coefficient is unobvious. To examine this dependence, we used three compositions (see table) of wastewater obtained in synthesis of bisphenol. The results obtained are presented in Fig. 3. Raising the temperature to more than 20°C, impairs the extraction, with this effect being more noticeable at an increased content of acetone in the mixture.

As follows from Fig. 3, the optimal temperature range for the extraction process is 10–20°C.

We also determined the possible degree of purification of the given wastewater compositions. For this purpose, we performed successive iterations of purification of the mixtures obtained. The results are presented in Fig. 4. It can be seen from these dependences that presence of acetone complicates the extraction processes by noticeably

raising the minimum reachable concentration of phenol, and, therefore, it is exceedingly important to control its content in water being purified. On the whole, the continuous counter-current extraction with butyl acetate provides a sufficiently high purification efficiency of wastewater characteristic of the BP production process.

Another parameter important for the continuous purification process tested in a counter-current column with glass packing is the ratio between the flow rates of water and the solvent. Apparently, raising the amount of butyl acetate makes smaller the number iterations necessary for reaching the lowest possible concentration of phenol. However, it follows from the results we obtained that, at flow ratios larger than 1 : 10, the obtainable concentrations of phenol vary only lightly as the flow rate of butyl acetate is raised further:

Lowest reachable concentration of phenol in the aqueous layer in relation to the ratio between the butyl acetate and water flow rates at 20°C for wastewater of composition no. 2

Ratio between flow rates of butyl acetate and water	1 : 2.5	1 : 5	1 : 10	1 : 20
Reachable phenol concentration in the aqueous layer, mg L <sup>-1</sup>	0.024	0.024	0.027	0.049

The results we obtained noticeably surpass those commonly reported in the literature [11].

Thus, we found the solvent and the conditions in which wastewater can be purified in a single extraction stage to a phenol content comparable with the MPC and be recycled into the technological process with partial delivery to treatment facilities.

## CONCLUSIONS

(1) Butyl acetate is the most effective extractive agent for purification of wastewater formed in production of bisphenol to remove phenol. This agent provides in a single stage of processing under the technological conditions found in the study a phenol concentration suitable for recycling of wastewater into the technological cycle, with partial delivery to treatment facilities.

(2) Admixtures of bisphenol and by-products of its synthesis in wastewater do not exert any significant influence on the efficiency of its purification to remove phenol, whereas presence of acetone in concentrations exceeding 0.5–1% not only diminishes the distribution

coefficient, but also hinders stratification of a mixture of water and butyl acetate.

(3) The optimal extraction temperature for maintaining the largest distribution coefficient is in the range from 10 to 20°C.

(4) The optimal ratio between the flow rates of butyl acetate and wastewater for reaching the maximum degree of purification in a continuous counter-stream extractor is in the range from 1 : 5 to 1 : 10.

## ACKNOWLEDGMENTS

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