ADVANCED OXIDATION PROCESSES OF XYLENOLS IN AQUEOUS SOLUTIONS

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Abstract. Xylenols form a significant part of the total phenols content in the oil-shale wastewaters. In the present study, the ozonation and advanced oxidation processes of xylenols were investigated. The process was conducted in a semi-batch reactor continuously supplied with ozone gas. The process was found to be pH dependent. Ozonation was quite effective in destroying xylenols, especially in basic media. The addition of H_2O_2 to the reaction mixture (O_3/H_2O_2 process) had no impact on the removal rate of xylenols. The O_3/UV process was found to have no advantages over ordinary ozonation. The formation dynamics of two oxidation by-products (quinone and hydrogen peroxide) was studied. Ozonation may be recommended as a posttreatment purification method for xylenols removal.

Key words: xylenols, advanced oxidation processes, ozonation, pH, aqueous solutions, purification.

INTRODUCTION

Oil-shale ash dump leachates contain up to 750–800 mg/l phenols. These include phenol (40–85 mg/l) and its substituted derivatives such as cresols (66–106 mg/l), xylenols (202–250 mg/l), trimethylphenols, thymol, etc. [1].

Ozonation and advanced oxidation processes (AOP) have been shown to be quite effective for the destruction of phenolic compounds. The kinetics of phenol and cresols ozonation has been widely investigated. The reaction rate constants and some oxidation by-products formation have been reported. However, there are only a few data available on the ozonation of other substituted phenols. This information is necessary for the development of ozonation reactors and wastewater treatment technologies. Xylenols form a significant part of phenols found in the

wastewaters of the oil-shale industry. Data concerning the effectiveness of AOPs in eliminating xylenols is of particular interest since a good posttreatment method for oil-shale wastewaters is lacking. The results of this investigation may prove to be of wider interest because xylenols are constituents in some other industrial wastewaters, too [2].

The mechanisms and kinetics of phenol ozonation have been studied by several researchers. They indicate that substituted phenols may react, depending on the substituent, with ozone many times faster than simple phenol [3–7]. The process of phenol ozonation is significantly influenced by pH. Ozone may react with solutes either via direct oxidation, in which case molecular ozone reacts at electron-rich sites of the solutes, or via indirect oxidation, when the hydroxyl radicals resulting from the decomposition of ozone serve as oxidants in a series of chain reactions [3]. The direct reactions take place in acidic solutions and are highly selective in respect to the solutes with which ozone reacts. The formation rate of the hydroxyl radicals increases with increasing pH [7]. Above a certain pH value, the hydroxyl radicals become the predominant oxidants. Direct and indirect routes may be equally important in case of many systems [6].

In many cases, the reaction rate is limited by the rate of mass transfer [7].

The products of phenols ozonation are hydroquinone, catechol, glyoxal, glycolic, glyoxylic, acetic, propionic, maleic, mesotartaric, oxalic, carbonic, furmaric, and formic acids [8–12]. p-Benzoquinone has been identified as an intermediate by-product [13–15]. Glycolic and oxyphthalic acids, diacetyl, and glyoxal are the ozonation products of 2,3-xylenol [8]. Hydrogen peroxide is formed as a by-product of phenol and resorcinol ozonation [12, 16].

The mass balance for the ozone and phenolic compounds indicates, for several experiments, a stoichiometric reaction factor of 1.0 [3, 17]. This is consistent with the hypothesis that the initial attack of phenol by one mole of ozone either breaks the benzene ring or results in the formation of a hydroxylated product, yielding, in both cases, a compound different from the parent phenol molecule [17]. For example, the ozonation of phenol, o-cresol, chlorophenol, etc. yields dihydroxybenzenes as first intermediates, which are as reactive towards ozone as the initial phenols [6, 9]. The initial stoichiometry of the reaction of ozone with resorcinol is reported to be 2:1 [18], and with phenol from 1:1 to 3:1 [3, 13, 14, 19].

There are only a few data available on the ozonation of substituted phenols [3, 5, 6]. The ozonation and UV-degradation of some substituted phenols were investigated by Gurol and coworkers [3, 5]. The experiments were conducted in phenol mixtures. The reaction rate of different phenols in mixtures was compared with the reaction of phenol to exclude the mass transfer influence, and the relative rate constants were evaluated. These experiments showed that in acidic media (pH = 2.5) the phenol ozonation and UV-degradation processes are dependent on the phenol structure, but at pH values of 7.0 and 9.0 the oxidation rates are nearly the same in case of different phenols, including dioxybenzenes, cresols, and xylenols.

The aim of the present study was to investigate AOPs and the ordinary ozonation of different xylenols to obtain data on the behaviour of xylenols. AOPs were found to be more effective for the destruction of some organic compounds than simple ozonation due to the formation of hydroxyl radicals, which are very active oxidation agents.

EXPERIMENTAL

The AOPs of xylenols in aqueous solutions were studied in a semi-batch reactor constantly supplied with ozone gas. The experiments were conducted in a glass bubble column (4.35 cm in diameter and 21 cm in height). In the centre of the column, a quartz tube (1.9 cm in diameter and 17 cm in height) with a low pressure mercury lamp was placed. The UV-radiation intensity at $\lambda = 254$ nm was measured using actinometry [20] and its value was 1.17×10^{16} quantum/s during the experiments. A gas disperser (diameter 3.5 cm, the average pore size 0.1 mm) was located at the bottom of the reactor to disperse ozone gas into the aqueous solution. The gas flow rate was kept at 1.0 l/min, the concentration of ozone in the feed gas mixture at 0.5 mg/l. The concentrations of ozone in the inlet and outlet gas were measured by spectrophotometer (SPECORD UV/VIS, Carl Zeiss Jena, GDR) at 258 nm, the length of the quartz cell was 100 mm. The concentration of ozone dissolved in water was measured by the indigo method [21].

Analytical grade xylenols were purified by sublimation and their pre-measured amounts were dissolved in distilled water. The solutions were refrigerated and used within 24 h to prevent degradation. The temperature was kept at 20°C by means of water cooling. The ozonation lasted for 6 min. At least 50% xylenol conversion was achieved within this time in most runs.

The initial concentration of xylenols was 0.4 mM. The analyses were carried out immediately after the ozonation. A high pressure liquid chromatograph (HZ 1311, Belarus) with Separon C18 column, 0.5×300 mm, was used to separate phenols at ambient temperature. Xylenols were detected by the fluorescence detector (the excitation wavelength was 220 nm and the emission range over 280 nm). The isochratic method with a solvent mixture of 50% acetonitrile and 0.1% acetic acid in water was applied. The peak retention time (in minutes) for the compounds at a solvent flow rate of 5.0 µl/min was 26.3 for 2,3-xylenol; 26.3 for 2,5-xylenol; 28.2 for 2,6-xylenol; and 23.5 for 3,4-xylenol.

The formation dynamics of two by-products of xylenols ozonation was studied. Hydrogen peroxide was determined by visible spectrophotometry at 410 nm as a complex compound with Ti^{4+} [22], and the amount of p-quinone at 436 nm, using specific reaction with hydroxylamine hydrochloride in 50% ethanol [23].

The pH value of the phenol solutions was adjusted to the necessary level by adding 0.1 N sulphuric acid or 0.1 N potassium hydroxide.

RESULTS AND DISCUSSION

Ozonation and O_3/H_2O_2 process

Analytical grade individual 2,3-, 2,5-, 2,6-, and 3,4-xylenols were ozonated at the ozone concentration in feed gas of 0.5 mg/l at pH 3.5, 6.5, and 9.5 in aqueous solutions. The kinetic curves of xylenols removal are described adequately by the first order reaction rate equations (correlation coefficients $r > 0.98$). The corresponding rate constants k_1 are displayed in Table 1. The rate constants were calculated using the integral method. This process enables to remove about 50% or even more of the initial xylenols in 6 min of ozonation. The reaction rate is strongly dependent on pH of the initial solution. In general, the reaction rate increases when the solution pH changes from acidic to neutral and basic. In acidic media, the rate of xylenols removal was from 4.4 (2,3-xylenol) to 8.2 (2,6-xylenol) times lower than in basic solutions. The removal rate of 3,4-xylenol was the highest and that of 2,3-xylenol the lowest at any pH. The selectivity of ozone towards xylenols decreased, as a rule, when pH was raised (Figs. 1, 2). At the same time, the impact of pH on the removal rate of xylenols depended on the compound. This can be explained by the predominant role of the hydroxyl radicals in the neutral and, especially, in the basic media. Since the ozone self-decomposition is quite slow in the neutral media, xylenol itself must be activating ozone decomposition and free radicals formation [5].

Table 1

Ozonation of xylenols

| Compound	Initial pH	Δ pH after 6 min of ozonation	Quinone (maximum), mg/l	H_2O_2, mg/l after 6 min of ozonation	Rate constant k_1, s^{-1}
2,3-Xylenol	3.5	0.41	0.14	12.7	0.0019
	6.5	2.61	1.64	19.5	0.0022
	9.5	3.11	1.12	27.5	0.0083
2,5-Xylenol	3.5	0.04	0.43	6.8	0.0012
	6.5	2.15	0.34	9.5	0.0025
	9.5	3.15	0.56	23.7	0.0079
2,6-Xylenol	3.5	0	0.75	8.45	0.0011
	6.5	1.77	1.75	9.3	0.0037
	9.5	3.81	0.42	20.7	0.0091
3,4-Xylenol	3.5	0.13	0	7.62	0.0022
	6.5	2.32	0	8.03	0.0034
	9.5	3.13	0	13.6	0.0103
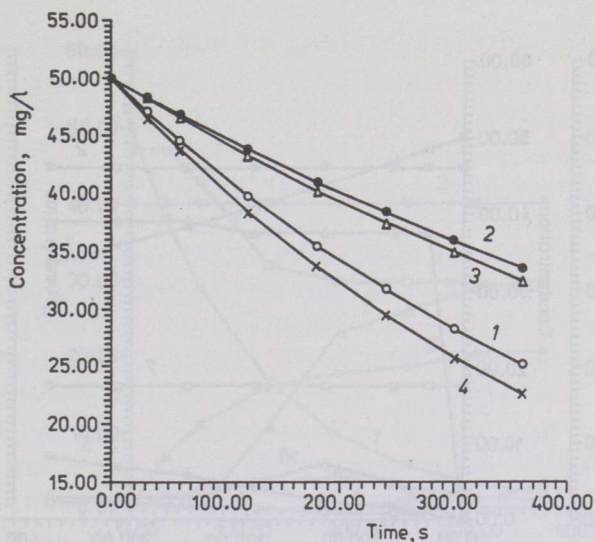
Fig. 1. Ozonation of xylenols at pH 3.5. *1* – 2,3-xylenol; *2* – 2,5-xylenol; *3* – 2,6-xylenol; *4* – 3,4-xylenol.
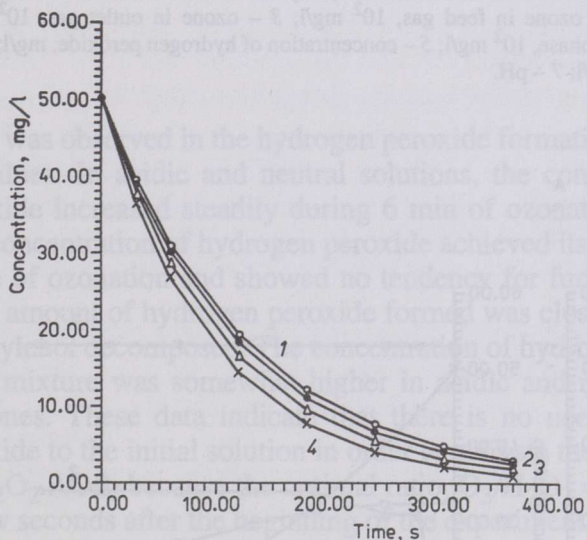

Fig. 2. Ozonation of xylenols at pH 9.5. (Legend of curves see Fig. 1.)

The behaviour of xylenols differs in acidic, neutral, and basic solutions (see Figs. 3–5). The curves of xylenol and pH reduction (due to aromatic breakdown and acids formation) as well as the curves of some oxidation intermediates (quinone and hydrogen peroxide) serve to illustrate this. It is seen that, in neutral and acidic media, the concentration of ozone in the liquid phase differs from zero since the very beginning of the process. In basic media, the concentration of ozone in the liquid phase remains zero up to the second or even the third minute of ozonation, and begins to increase quite rapidly when the bulk of xylenol (80% or more) is removed. This means that during the first minutes of oxidation the reaction takes place in the liquid boundary layer.
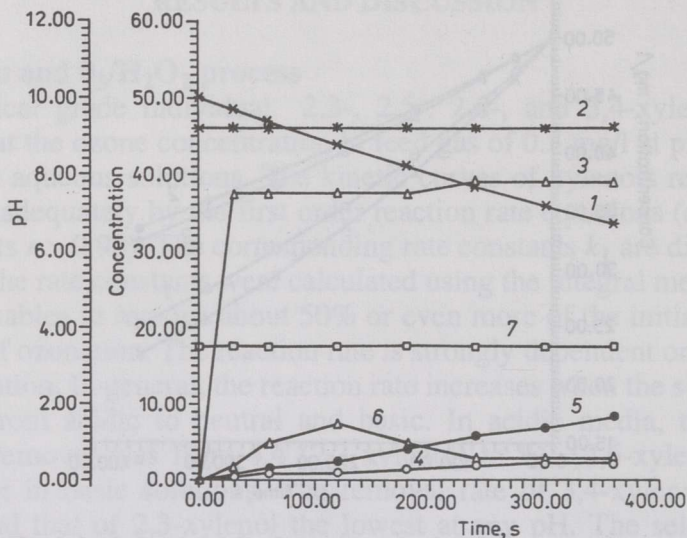
Fig. 3. General picture of the ozonation of 2,6-xylenol in acidic media. 1 – concentration of 2,6-xylenol, mg/l; 2 – ozone in feed gas, 10^2 mg/l; 3 – ozone in outlet gas, 10^2 mg/l; 4 – ozone dissolved in liquid phase, 10^2 mg/l; 5 – concentration of hydrogen peroxide, mg/l; 6 – concentration of quinone, 10^1 mg/l; 7 – pH.
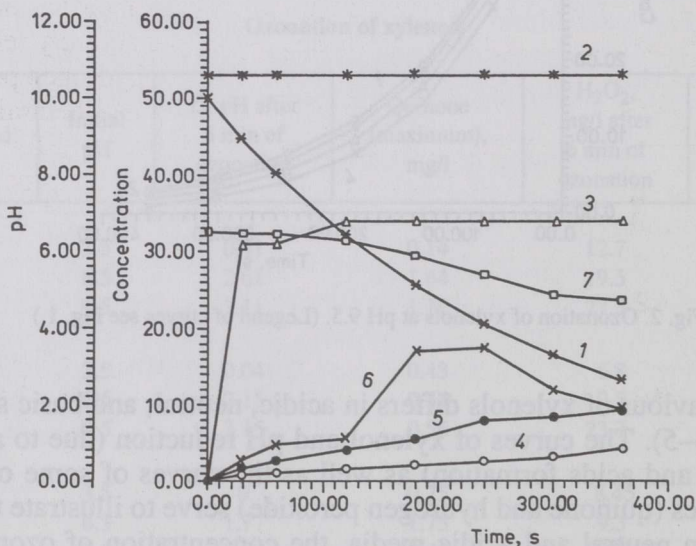

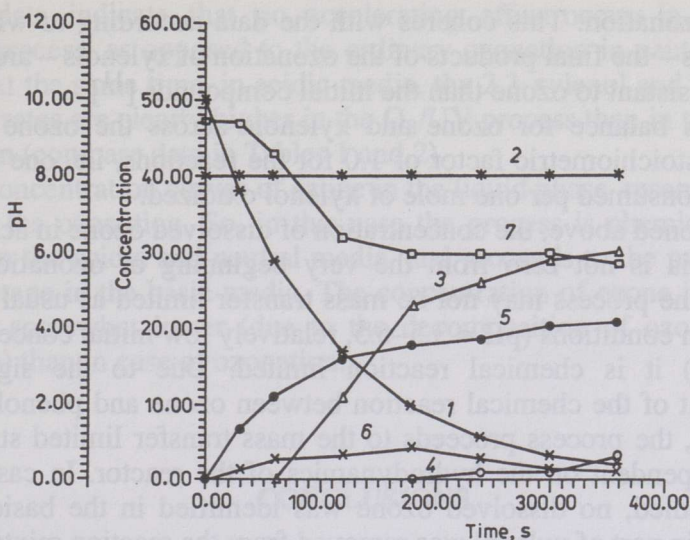Fig. 4. General picture of the ozonation of 2,6-xylenol in neutral media. (Legend of curves see Fig. 3.)

Fig. 5. General picture of the ozonation of 2,6-xylenol in basic media. (Legend of curves see Fig. 3.)

A difference was observed in the hydrogen peroxide formation profiles at different pH values. In acidic and neutral solutions, the concentration of hydrogen peroxide increased steadily during 6 min of ozonation, while in basic ones the concentration of hydrogen peroxide achieved its maximum at the fifth minute of ozonation and showed no tendency for further increase. In all cases, the amount of hydrogen peroxide formed was closely related to the amount of xylenol decomposed. The concentration of hydrogen peroxide in the reaction mixture was somewhat higher in acidic and neutral media than in basic ones. These data indicate that there is no need for adding hydrogen peroxide to the initial solution in order to activate the process (the so-called O_3/H_2O_2 AOP) because the optimal ratio, $O_3/H_2O_2 = 1.0–1.66$, is reached in a few seconds after the beginning of the experiment.

Our experiments confirmed this supposition. The addition of 5.0, 10.0, and 15.0 mg/l of hydrogen peroxide (0.15–0.45 mM H_2O_2) to the reaction mixture (O_3/H_2O_2 process) did not affect the removal rate of xylenols.

The concentration of one of the intermediates, quinone, increased during 2–3 min from the beginning of ozonation and then started to decrease. Such quinone concentration profiles were typical for 2,3-, 2,5-, and 2,6-xylenols. The maximum measured amount of quinone was small, from 0.14 to 1.75 mg/l in case of different xylenols. It follows that quinone is also quite reactive towards ozone and undergoes further conversion very rapidly. The ozonation of 3,4-xylenol did not lead to quinone formation.

The formation of a significant amount of acidic products was observed. The decrease in pH ranged from 3.11 to 3.81 when the process took place in a basic medium, and from 1.77 to 2.61 when the initial solution of xylenols was neutral. The decrease in pH practically stopped at the sixth

minute of ozonation. This coheres with the data according to which the organic acids – the final products of the ozonation of xylenols – are a great deal more resistant to ozone than the initial compounds [11].

The mass balance for ozone and xylenols across the ozone reactor indicated a stoichiometric factor of 1.0 for the reactions, i.e. one mole of ozone was consumed per one mole of xylenol oxidized.

As mentioned above, the concentration of dissolved ozone in acidic and neutral media is not zero from the very beginning of ozonation. This means that the process may not be mass transfer limited as usual [6], but under certain conditions (pH = 3.5–6.5, relatively low initial concentration of xylenols) it is chemical reaction limited. Due to the significant enhancement of the chemical reaction between ozone and phenols in the basic media, the process proceeds to the mass transfer limited stage and becomes dependent on the hydrodynamics of the reactor. In case of all xylenols studied, no dissolved ozone was identified in the basic media until the main part of xylenol was removed from the reaction mixture.

O₃/UV process

The picture of the xylenols removal in the O₃/UV process as well as the profiles of ozone and by-products were in general the same as in simple ozonation. The process was also found to be pH dependent. The first order rate constants for the O₃/UV degradation process are presented in Table 2.

Table 2

O₃/UV process of the degradation of xylenols

Compound	Initial pH	Δ pH after 6 min of ozonation	Quinone (maximum), mg/l	H_2O_2, mg/l after 6 min of ozonation	Rate constant k_1, s⁻¹
2,3-Xylenol	3.5	0.48	0.56	11.2	0.0028
	6.5	2.28	0.34	14.4	0.0036
	9.5	3.40	1.13	23.3	0.0072
2,5-Xylenol	3.5	0.03	0	7.6	0.0016
	6.5	2.32	0	11.0	0.0024
	9.5	3.34	0.56	24.6	0.0060
2,6-Xylenol	3.5	0.01	0	7.6	0.0012
	6.5	2.00	0.85	11.0	0.0037
	9.5	3.78	0.70	17.0	0.0092
3,4-Xylenol	3.5	0.26	0	9.3	0.0033
	6.5	2.49	0	11.9	0.0030
	9.5	3.13	0	11.9	0.0110

The data indicate that no accelerating effect occurs in case of the O_3/UV process, as opposed to the ordinary ozonation in neutral or basic media. At the same time, in acidic media, the 2,3-xylenol and 3,4-xylenol removal rates are clearly higher in the O_3/UV process than in the ordinary ozonation (compare data in Tables 1 and 2).

The concentration curves of ozone in the liquid phase resemble closely those of the ozonation. So, in this case the process is chemical reaction limited in the acidic and neutral media, and proceeds to the mass transfer limited stage in the basic media. The concentration of ozone in the outlet gas was somewhat lower (due to the decomposition of ozone by UV-radiation) than in case of ozonation.

CONCLUSIONS

Ozone is quite effective for the removal of xylenols. The reaction is of first order with respect to the phenolic compound and depends strongly on the pH value of the initial solution. The selectivity of ozone towards xylenols decreases with the increase in pH. The ozonation process is chemical reaction limited in the acidic and neutral media and mass transfer limited in the basic media.

The amount of hydrogen peroxide formed during the reactions is closely related to the amount of the destructed xylenol. There is no need to add hydrogen peroxide in order to activate oxidation because the optimal ratio (O_3/H_2O_2 = 1.0–1.66) is reached in a few seconds after the beginning of the experiment.

There is no accelerating effect in case of the O_3/UV process as opposed to the ordinary ozonation in the neutral or basic media. In the acidic media, 2,4-xylenol and 3,4-xylenol removal rates are remarkably enhanced in the O_3/UV process.

The initial concentration of xylenols reported in the experiments (0.4 mM) corresponds to the average concentration of xylenols in the phenolic effluents from oil-shale chemical industry undergoing biological oxidation at the Kohtla-Järve Central Wastewater Treatment Plant. The results of ozonation at pH 6.5 and 9.5 show that the final concentration of all different xylenols is 0.1 mM and less, i.e. they will be removed to the extent of 75% and more if the contact time of ozonation lasts for 6 min or more.

The application of AOPs (O_3/UV; O_3/H_2O_2, etc.) does not lead to a higher efficiency as compared to ordinary ozonation, except for the O_3/UV process in acidic media. Taking into account that AOPs are usually more expensive than ozonation, there is no doubt that ordinary ozonation is to be recommended as an effective posttreatment process for the biologically treated phenolic effluents.

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KSÜLENOOLIDE LAGUNDAMINE VESILAHUSTES OKSÜDATSIOONI TÄIUSTATUD MEETODITEGA

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On uuritud ksülenoolide osoonimist ja täiustatud oksüdatsiooniprotsesse. Ksülenoolid moodustavad märkimisväärse osa põlevkivitööstuse heitvetes sisalduvatest üldfenoolidest. Oksüdatsiooniprotsessid viidi läbi poolperioodses barbotaažkolonnis ja need sõltusid suurel määral lahuse pH-st. Osoonimine osutus ksülenoolide lagundamisel väga efektiivseks, eriti leelises keskkonnas. Vesinikperoksiidi lisamine reaktsioonisegule (nn. O_3/H_2O_2-protsess) ei avaldanud mingit mõju ksülenoolide lagunemiskiirusele. Ka O_3/UV-protsessi efektiivsus ei erinenud märgatavalt tavalise osoonimisprotsessi omast. On jälgitud ka oksüdatsiooni kahe vaheprodukti (kinooni ja vesinikperoksiidi) teket. Põlevkivitööstuse heitvete puhastamiseks ksülenoolidest võib soovitada tavalist osoonimist.

РАЗЛОЖЕНИЕ КСИЛЕНОЛОВ В ВОДНЫХ РАСТВОРАХ КОМБИНИРОВАННЫМ МЕТОДОМ ОКИСЛЕНИЯ

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Ксиленолы составляют значительную часть загрязнений сточных вод сланцехимической промышленности. Исследование посвящено изучению разложения различных ксиленолов в водных растворах озоном, а также их комбинированного окисления озоном с перекисью водорода и УФ-облучением. Процессы окисления проводились в полупериодическом барботажном реакторе, и их протекание в большой мере зависело от величины pH среды. Установлено, что озонирование водных растворов ксиленолов позволяет значительно снизить их концентрацию. Особенно успешно этот процесс протекает в щелочной среде. В то же время комбинированное озонирование не дает существенного эффекта по сравнению с простым озонированием. Изучена также динамика образования таких полупродуктов озонирования фенолов, как хинон и перекись водорода. Полученные результаты подтверждают возможность использования озонирования как метода очистки сточных вод сланцехимических предприятий от ксиленолов.