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Studies on Pollutant Composition and Properties Changing While Physicochemical Purification of Diazodinitroquinone Manufacturing Wastewater

A. M. ZAYNULLIN[1], I. G. SHAYKHIEV[1], S. V. FRIDLAND[1], R. Z. MUSIN[2] and I. KH. RIZVANOV[2]

[1]*Kazan State Technological University,*
Ul. K. Marksa 68, Kazan 420015 (Russia)

E-mail: zainullin@list.ru

[2]*Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences,*
Ul. Arbuzova 8, Kazan 420088 (Russia)

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Absract

Basing on UV absorption spectroscopy and chromatography techniques, the composition and change in the properties of diazodinitroquinone manufacturing wastewater due to physicochemical wastewater treatment have been studied for the first time. It has been established that as the neutralization of acidic initial wastewater proceeding, an extension of the molecular chain occurs, whereas the further liquid processing results in the reduction of the molecular chain as well as in the formation of other compounds.

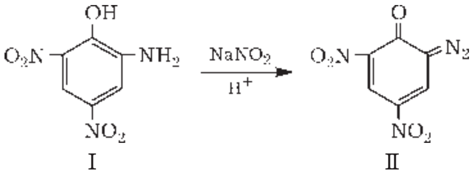
INTRODUCTION

A severe hazard for the environment is exhibited by heavy metals those are included, in particular, in the structure of priming explosives (initiators). The latter have found an extensive application in many industries. Standard priming explosives (mercury fulminate, lead trinitroresorcinate, lead azide, *etc.*) those are used during many years do not meet modern ecological requirements now, therefore an increasing attention of researchers is paid to the search for to find out the compounds with no heavy metals contained in the structure. Novel manufactures of environmentally safe initiator substances require for efficient local wastewater treatment, therefore the development and extensive application of closed cycles for water supply in the industry as well as the perfection of wastewater treatment are of currently central value.

Diazodinitroquinone (DDQ) represents a standard environmentally safe priming explosive whose production is developed by now at a number of enterprises of the industrial branch. However, the problem of local wastewater treatment in the manufacture of this compound has not been adequately investigated up till now, and it seems impossible to be solved without carrying out additional studies.

EXPERIMENTAL

The synthesis of DDQ (II) is carried out according to the following pattern:



I

II

The most economic method that allows one to obtain high quality DDQ consists in the reaction of picramic acid diazotisation in an aqueous solution of hydrochloric acid [1].

The parameters of DDQ wastewaters determined according to the techniques described in [2] are presented in Table 1.

TABLE 1

Physical and chemical parameters of initial wastewater

Parameter	Value
COD, mg O_2/L	18 750
pH	0.01
Contents of chloride ion, mg/L	60 236
Total contents of nitrites and nitrates, mg/L	190.6
Total acidity, mg-eq/L	2600
Content of solid residue, g/L	22.3
Content of calcinated residue, g/L	19.1
Optical density (absorbance) D	0.15
Transmittance (T), %	71.2
Content of aromatic hydrocarbons, mg/L	1830

Chromatography–mass spectrometry analysis

Chromatography–mass spectrometry studies were carried out with the use of a Perkin Elmer device supplied with a quadruple mass analyser and a Turbo Mass Gold 4.4 data processing system. Electron impact ionisation was used with the energy of ionising electrons amounting to 70 eV. A Perkin Elmer capillary column with grafted phase, 30 m length and 0.25 mm in diameter was used; helium being used as a carrier gas.

Chromatography conditions

1. Injector temperature being at 280 °C, flow split ratio 1 : 30.
2. The column was heated in a programming mode; initial temperature amounted to 120 °C (hold 1 min), and then heating was carried out with the rate of 6 °C/min up to 150 °C (hold 5 min). Further the heating rate was increased up to 10 °C/min during 10 min till a final temperature of 280 °C had been obtained (hold 6 min). Overall time of the analysis was 25 min.
3. Carrier gas flow rate amounted to 1 mL/min.
4. The temperature of the mass spectrometer interface unit was 250 °C.
5. Sample volume was equal to 1 μL.

RESULTS AND DISCUSSION

In order to develop the methods of wastewater treatment for DDQ manufacture, first of all it is necessary to ascertain the pollutant composition in wastewater.

As one can see from the data presented in Table 1, the initial wastewater is characterized by a higher COD value, which is caused first of all by the presence of organic compounds of the aromatic series. This fact is indicated by UV absorption spectroscopy data: the spectrum of initial waste water (Fig. 1) exhibits two peaks at the wavelength of 253 and 320 nm those are in a good correspondence with respect to the absorption bands of aromatic compounds and nitro-substituted derivatives of the latter [3].

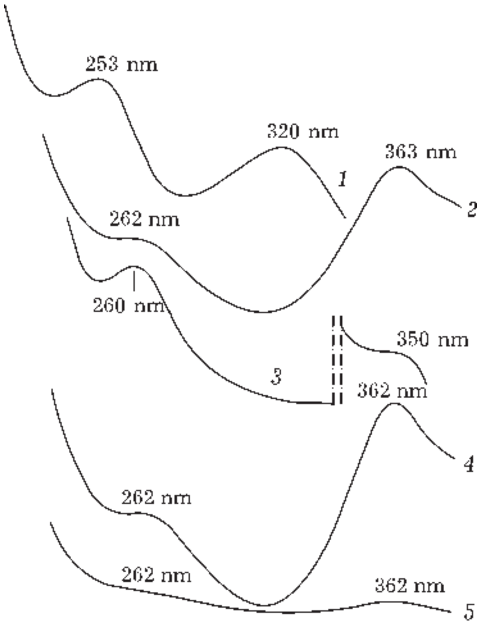


Fig. 1. UV absorption spectra of wastewater: *1* – initial, *2* – neutralized, *3* – ozonized, *4* – oxidized by atmospheric oxygen without catalyst, *5* – oxidized by atmospheric oxygen with a catalyst ($FeCl_3$).

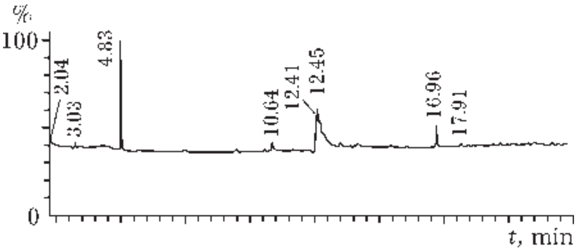


Fig. 2. Chromatographic profile of the extract of impurities (with respect to total ionic current).

As the result of the thin layer chromatography analysis performed it was established that the initial wastewater contain DDQ (II) (*Rf* = 0.3) (the eluent being a mixture such as benzene/ethyl acetate = 2 : 1) and, in addition, a number of products identified by means of the chromatography– mass spectrometry technique. For this purpose a hydrocarbon phase was extracted from the sample of a waste liquid with methylene chloride. The extract obtained was then subjected to a chromatographic separation.

As evident from Fig. 2, wastewater contains five main organic impurities with the retention time of chromatographic peaks amounting to 4.83, 10.64, 12.45, 16.96, and 17.91 min. The mass spectra of the impurities corresponding to these chromatographic peaks are presented in Fig. 3.

The analysis of *m*/*z* values and of peak intensity distribution in the mass spectra allowed us to determine and confirm the struc-

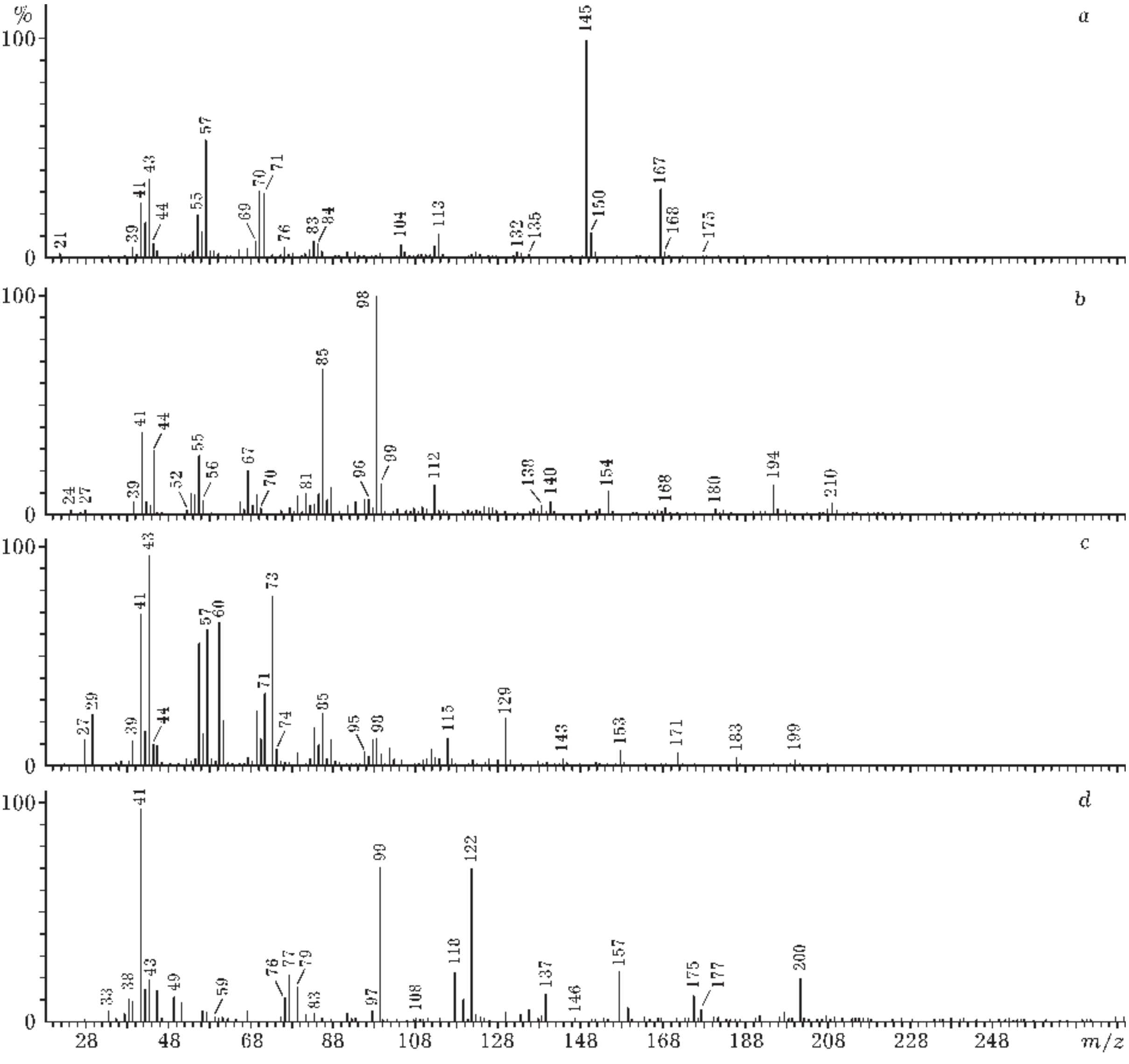


Fig. 3. Mass spectra of the impurities contained in wastewater under investigation: *a* – 2,6-dichloro-4-nitrophenol (IV), *b* – DDQ (II), *c* – 2,4-dinitro-6-aminophenol (I), *d* – 2,4-dinitropyrocatechin (III).

ture of compounds those are contained in the waste liquid. The chromatographic peak with the retention time of 4.83 min corresponds to 2,4-dinitropyrocatechin (III), which is supported by the presence of a molecular ion $M^{+\bullet}$ with the value of m/z 200 in the mass spectrum. Moreover, in the mass spectrum the peaks of fragmental ions are observed with m/z values equal to 137, 122, 108, 118 whose formation could be presented reasoning from the molecule (III).

The chromatographic peak with the retention time of 12.45 min corresponds to 2,4-dinitro-6-aminophenol (I). In support of this interpretation it could be pointed to the presence of a molecular ion $M^{+\bullet}$ with the value of m/z 199 in the mass spectrum. Furthermore, there are peaks of fragmental ions with m/z value equal to 183, 153, 74, 73 observed in the mass spectrum whose formation could be presented reasoning from the molecule (I).

The chromatographic peak with the retention time of 16.96 min corresponds to diazodiniroquinone (II), which is confirmed by the presence of a molecular ion $M^{+\bullet}$ with the value of $m/z = 210$ in the mass spectrum. Moreover, in the mass spectrum the peaks of fragmental ions are observed with m/z values equal to 194, 180, 138, whose formation could be presented basing on the molecule (II).

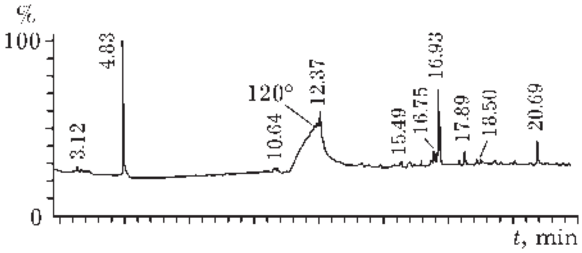


Fig. 4. Chromatographic profile of the extract of impurities contained in neutralized wastewater.

The chromatographic peak with the retention time of 17.91 min corresponds to 2,6-dichloro-4-nitrophenol (IV). In support of this interpretation it could be pointed to the presence of a molecular ion $M^{+\bullet}$ with the value of m/z 208 in the mass spectrum. In addition, there are peaks of fragmental ions with m/z value equal to 175, 145, 135 observed in the mass

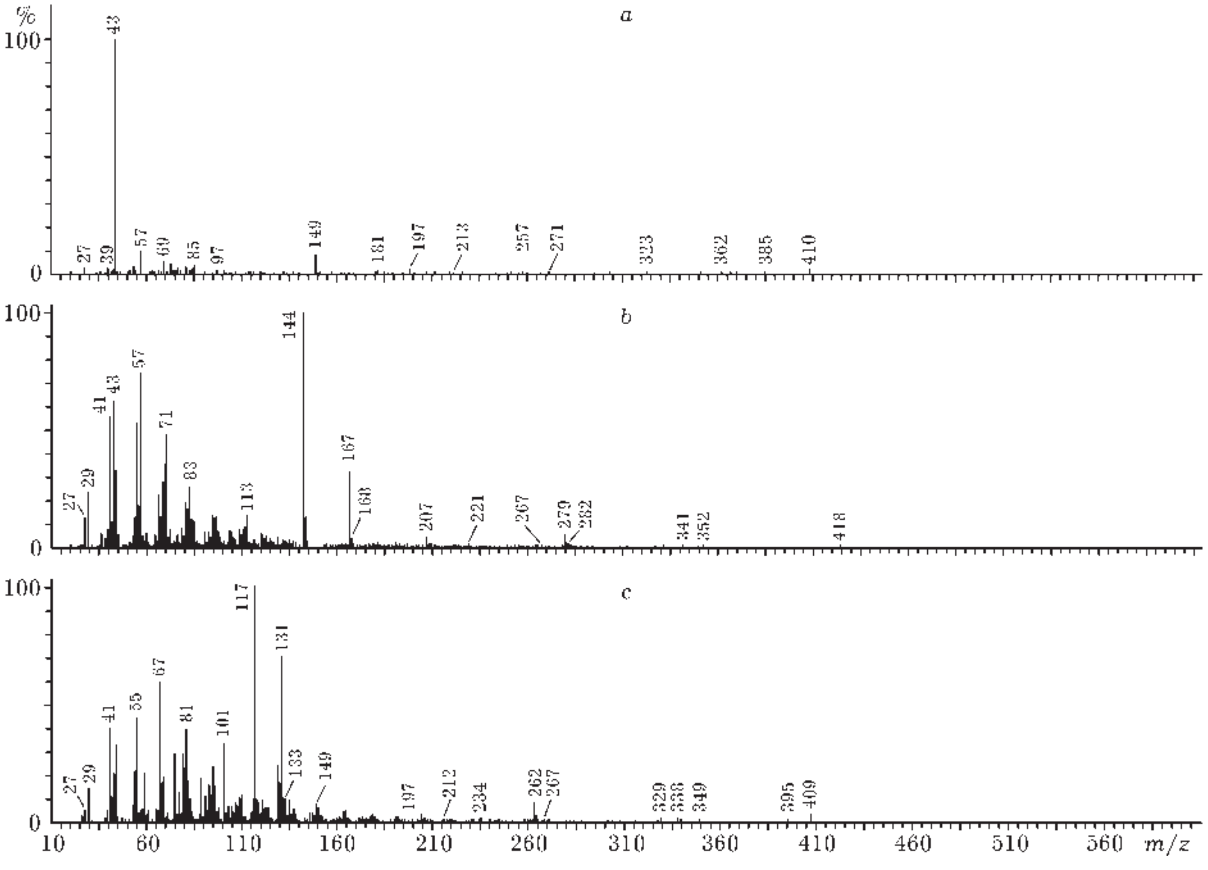


Fig. 5. Mass spectra of the impurities contained in neutralized wastewater: *a*–*c* – compounds V–VII, respectively.

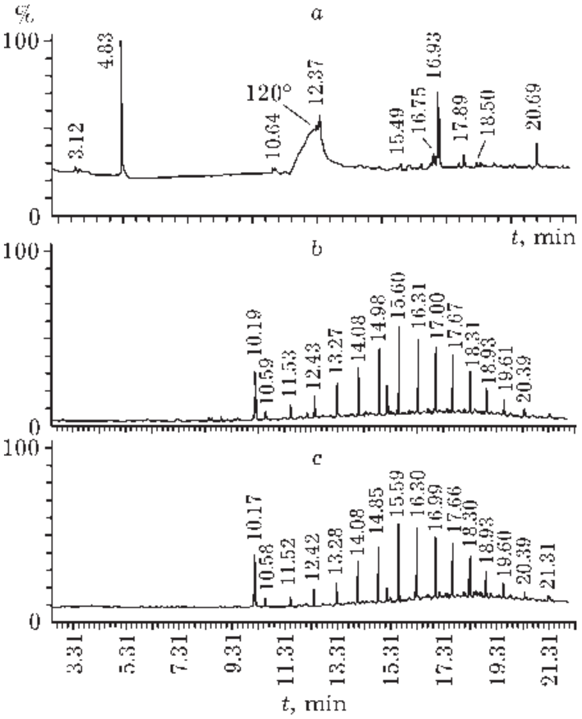


Fig. 6. Chromatographic profiles of neutralized wastewater (*a*) as well as of one oxidized by atmospheric oxygen in the presence of catalyst ($FeCl_3$) (*b*) and by ozone (*c*).

spectrum whose formation could be presented reasoning from the molecule (IV).

Thus, in the initial wastewater of DDQ manufacture the following organic compounds have been revealed: 2,4-dinitro-6-aminophenol (I), diazodinitroquinone (II), 2,4-dinitropyrocatechin (III), and 2,6-dichloro-4-nitrophenol (IV).

There is NaCl among inorganic components of wastewater formed due to sodium nitrite interaction with hydrochloric acid.

When the discharge of industrial wastewater is carried out either into a reservoir or into a city sewer collecting system, it is customary to assume the solutions with pH 6.5–8.5 to be almost neutral. Consequently, wastewaters with pH < 6.5 and pH > 8.5 are necessary to be neutralized. Reasoning from the conditions of the discharge of industrial wastewater, a greater hazard comparing to alkaline wastes is posed by extensively distributed acidic wastewaters. Furthermore, the volumes of industrial wastewaters with pH > 8.5 use to be insignificant.

From the data presented in Table 1 one can see that the wastewater of DDQ manufacture is characterized by a low pH value (0.01) due to a significant surplus of hydrochloric acid. Such an acidic corrosive medium can causes a severe corrosion of metal surfaces of any equipment; therefore the initial development cycle of the wastewater treatment technology should consist in choosing a cheap efficient neutralizing agent. As the latter, lime milk ($CaO \cdot H_2O$), calcium hypochlorite ($Ca(ClO)_2 \cdot 2H_2O$), dolomite flour, sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) were investigated.

It is established that as the result of wastewater neutralization the colour of the liquid changes from orange to give dark brown. This fact, to all appearance, could be caused by the processes of resinification and formation of new compounds. There is a so-called azocoupling process occurring in the system: the auxochrome groups (OH, NH_2 *etc.*) included in the structure of compounds donate electrons playing the role of electron donors, whereas the chromophor group such as N=N in the molecule manifests itself as an acceptor of electrons. Being in a conjugated chain, the chromophor and auxochrome groups can cause a molecule to be polarized and the mobility of π-electrons to increase; these groups use to less energetic long-wave light rays, thus the colour of a substance tending to become more saturated [4].

From the UV absorption spectrum of the neutralized wastewater (see Fig. 1) one can observe that after the processing with a neutralizing agent a bathochromic shift of $\Delta\lambda$ absorption bands occurs amounting to 9 and 43 nm, respectively.

The investigation by means of chromatography–mass spectrometry technique (Fig. 4) has demonstrated, that the neutralization resulted in the formation of larger molecules (with the molecular mass >300), which adds considerable support for our assumption of the fact that the azocoupling reaction occurs.

As evident from Fig. 4, the neutralized wastewater contains six main organic impurities with the retention time values equal to 4.83, 10.64, 12.37, 15.49, 16.93, and 20.69 min. Figure 5 exemplifies a chromatogram of the neutralized wastewater. The analysis of m/z values indicates that after the neutralization of the waste liquid an azocoupling reaction of nitro-substituted aromatic hydrocarbons occurs; the product with the retention time value equal to 10.64 min is corresponding to the product of the initial liquid such as dinitropyrocatechin (III) that did not entered into the reaction.

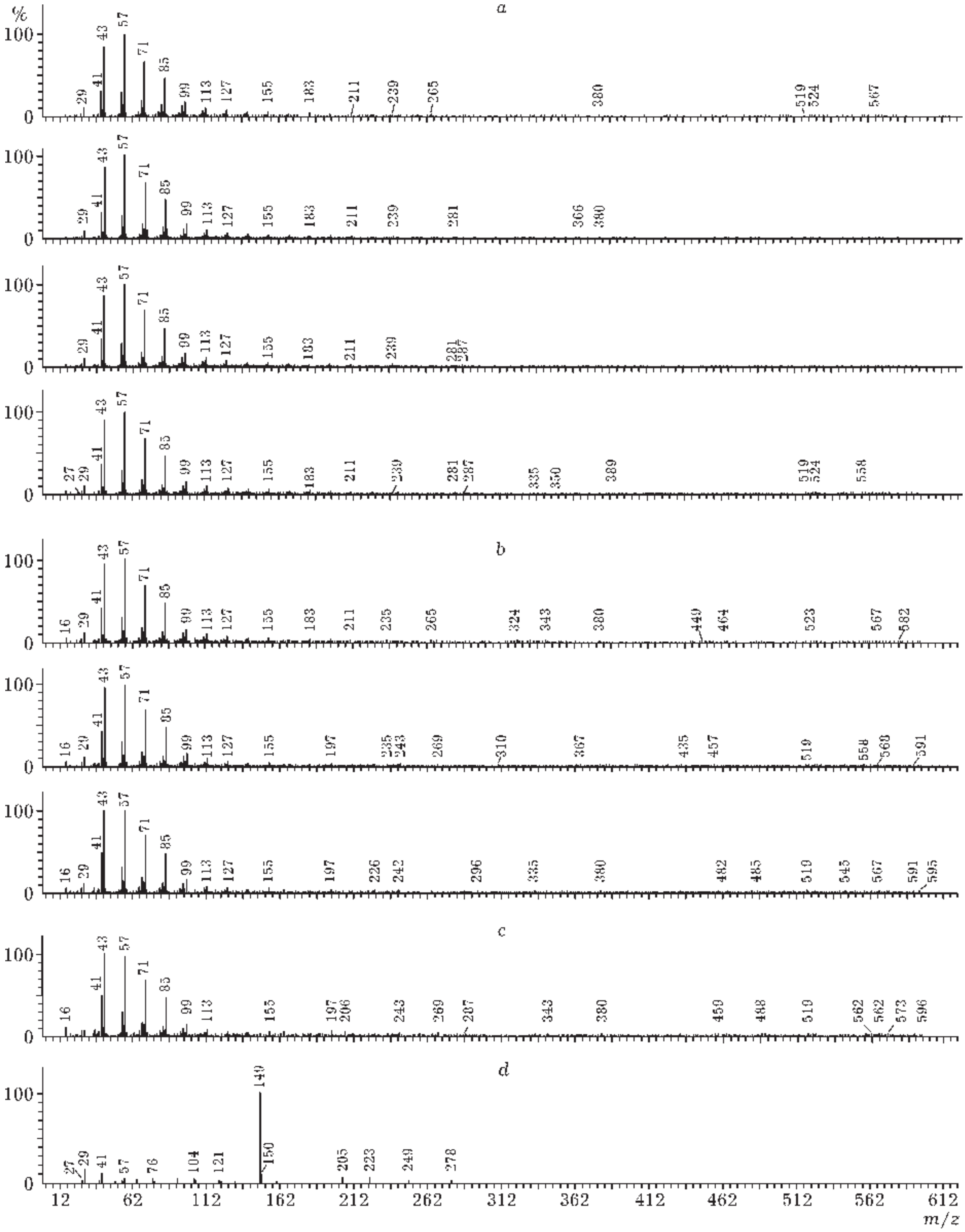
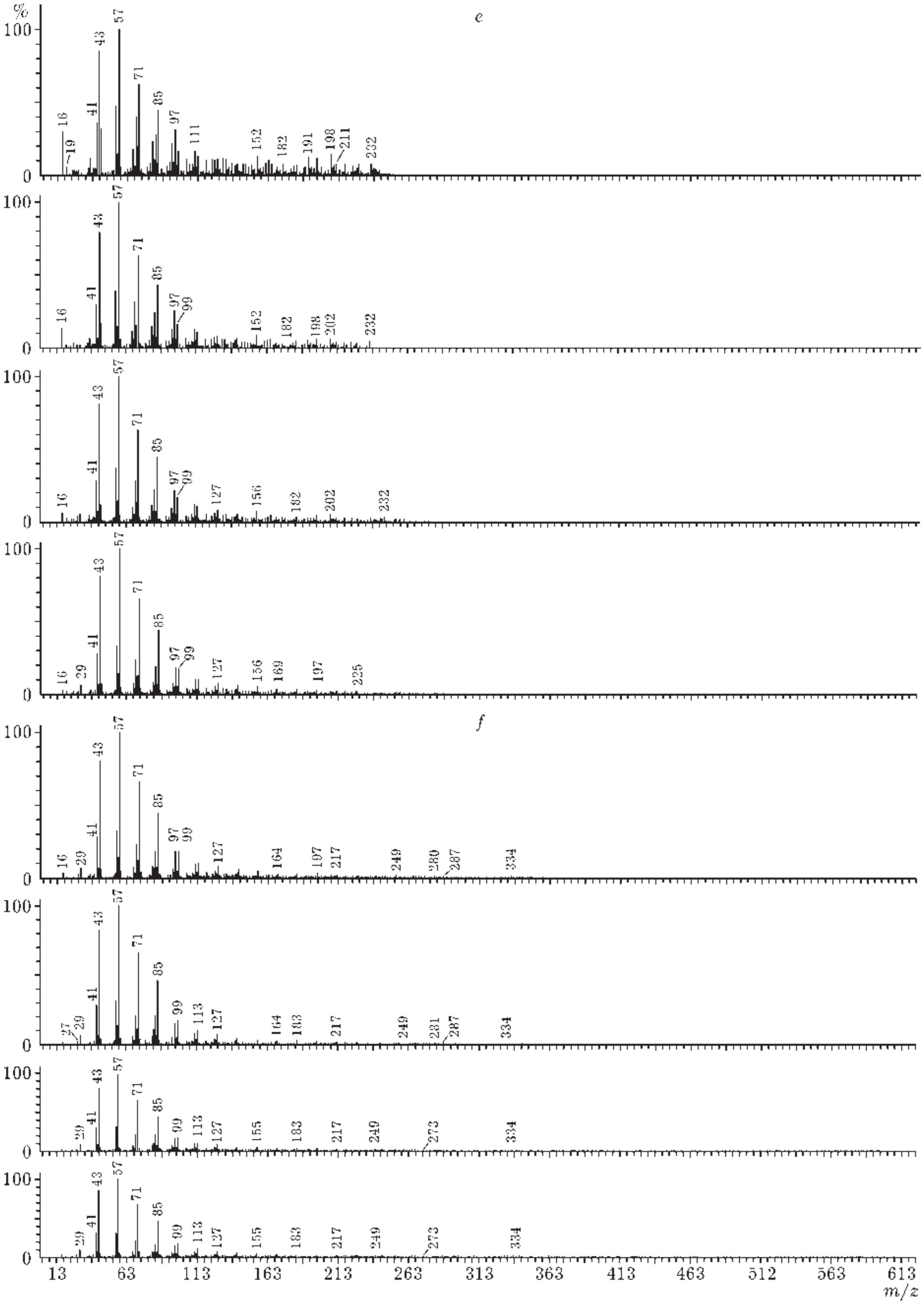
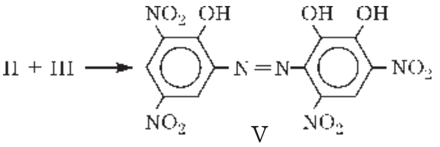


Fig. 7. Mass-spectra of the impurities contained in oxidized wastewater: *a* – dioctyl ester of orthoptalic acid (IX), acid (XIII), *f* – dihexyl ester of orthophtalic acid (XIV).



b – dibutyl ester of decanedioic acid (X), *c* – nonadecane (XI), *d* – dibutyl phthalate (XII), *e* – dinitrohexadienedioic

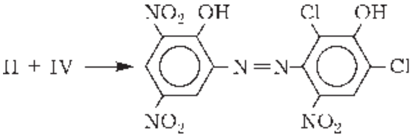
The chromatographic peak with the retention time value equal to 12.37 min corresponds to 2-hydroxy-3,5-dinitro-2′,3′-dihydroxy-4′,6′-dinitroazobenzene (V) that is formed, to all appearance, resulting from the azocoupling reaction between diazodinitroquinone (II) and 2,4-dinitropyrocatechin (III) according to the scheme



V

This fact may be evidenced by the presence of a molecular ion $M^{+\bullet}$ with the value of m/z 410 in the mass spectrum corresponding to azo compound such as (V). Moreover, in the mass spectrum the peaks of fragmental ions are observed with m/z values equal to 213, 197, 271, 149 whose formation could be presented basing on the molecule (V).

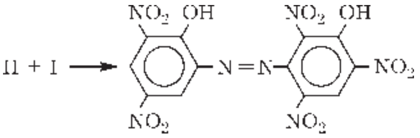
The chromatographic peak with the retention time value amounting to 15.49 min corresponds to 2-hydroxy-3,5-dinitro-2′,4′-dichloro-3′-hydroxy-6′-nitroazobenzene (VI), formed due to the azocoupling reaction between diazodinitroquinone (II) and 2,6-dichloro-4-nitrophenol (IV) according to the scheme



VI

This fact is also indicated by the presence of a molecular ion $M^{+\bullet}$ with the value of m/z 418, corresponding to azo compound such as (VI). Furthermore, in the mass spectrum the peaks of fragmental ions with m/z values equal to 221, 207, 167, 144 are observed whose formation could be presented reasoning from the molecule (VI).

The chromatographic peak with the retention time value equal to 20.69 min corresponds to 2-hydroxy-3,5-dinitro-2′-amino-3′-hydroxy-4′,6′-dinitroazobenzene (VII), formed in the course of the azocoupling reaction between diazodinitroquinone (II) and 2,4-dinitro-6-aminophenol (I) according to the scheme



VII

This consideration can be confirmed by the presence of a molecular ion $M^{+\bullet}$ with the value of m/z 409 corresponding to azo compound such as (VII). In addition, in the mass spectrum the peaks of fragmental ions with m/z equal to 212, 197, 149, 133 are observed whose formation could be presented reasoning from the molecule (VII).

Thus, basing of the data obtained a conclusion could be drawn that there are so-called azocoupling reactions occurring in the course of the neutralization process. As a result, there are compounds formed in the wastewater, such as the three azo products (according to formulae V–VII) and nitro-substituted aromatic hydrocarbon (dinitropyrocatechin (III)) not entered into azocoupling reactions; in addition, there is such inorganic compound as NaCl.

Prior to be supplied to biological treatment facilities, the wastewaters containing nitro products must be subjected to preliminary chemical purification. At present time a widespread application and development in the technology of wastewater treatment has been found by such chemical method of waste liquid treatment as an oxidation process with the use of ozone, H_2O_2 and atmospheric oxygen. This fact is caused, first of all, by profound transformations of complex organic molecules occurring due to the effect of oxidizers resulting in the formation of simple compounds those could be easily digested by microorganisms either in the course of biochemical purification or in the process of water self-purification in aquatic reservoirs. In this connection, the method of oxidation was studied in the present work in order to remove from water the impurities (including azo and diazo dyes) those impart coloration to water.

For the determination of the changes occurred as the result of oxidation, an appropriate analysis of the wastewater under treatment was performed. With this purpose a sampling was carried out from the wastewaters after the treatment by the most efficient and cheap oxidizers such as atmospheric oxygen with a ferriferous catalyst as well as by ozone that was used as a reference.

The analysis of UV absorption spectra of ozonized wastewater (see Fig. 1) has demonstrated that after the purification a bathochromic shift of Δλ absorption bands took place equal to 7 and 20 nm, respectively.

The UV absorption spectrum of wastewater oxidized by means of atmospheric oxygen was almost identical to the UV absorption spectrum of neutralized wastewater. Also it has been established that the UV absorption spectra of wastewater oxidized by atmospheric oxygen in the presence of the catalyst exhibit peaks of a lower intensity, which indicate a decrease in the amount of aromatic hydrocarbons. For the identification of the products formed during oxidation of the impurities, the analysis of wastewater samples was performed with the use of chromatography–mass spectrometry technique.

The chromatographic profile of the waste liquid subjected to oxidation is presented in Fig. 6. One can see that the chromatograms differ from each other insignificantly and, consequently, the process of oxidation by atmospheric oxygen and ozone results in the formation of identical products.

Figure 7 demonstrates mass spectra of wastewater oxidized with the use of atmospheric oxygen in the presence of a heterogeneous ferriferous catalyst.

Basing on a comparative analysis of the experimentally obtained mass spectra with mass - spectra available from the computer catalogue of the TurboMassGold 4.4 data processing system, the following compounds were identified in wastewaters: dibutyl phthalate XIII (retention time value amounting to 10.19 min), nonadecane XI (10.59 and 11.53 min), dibutyl ester

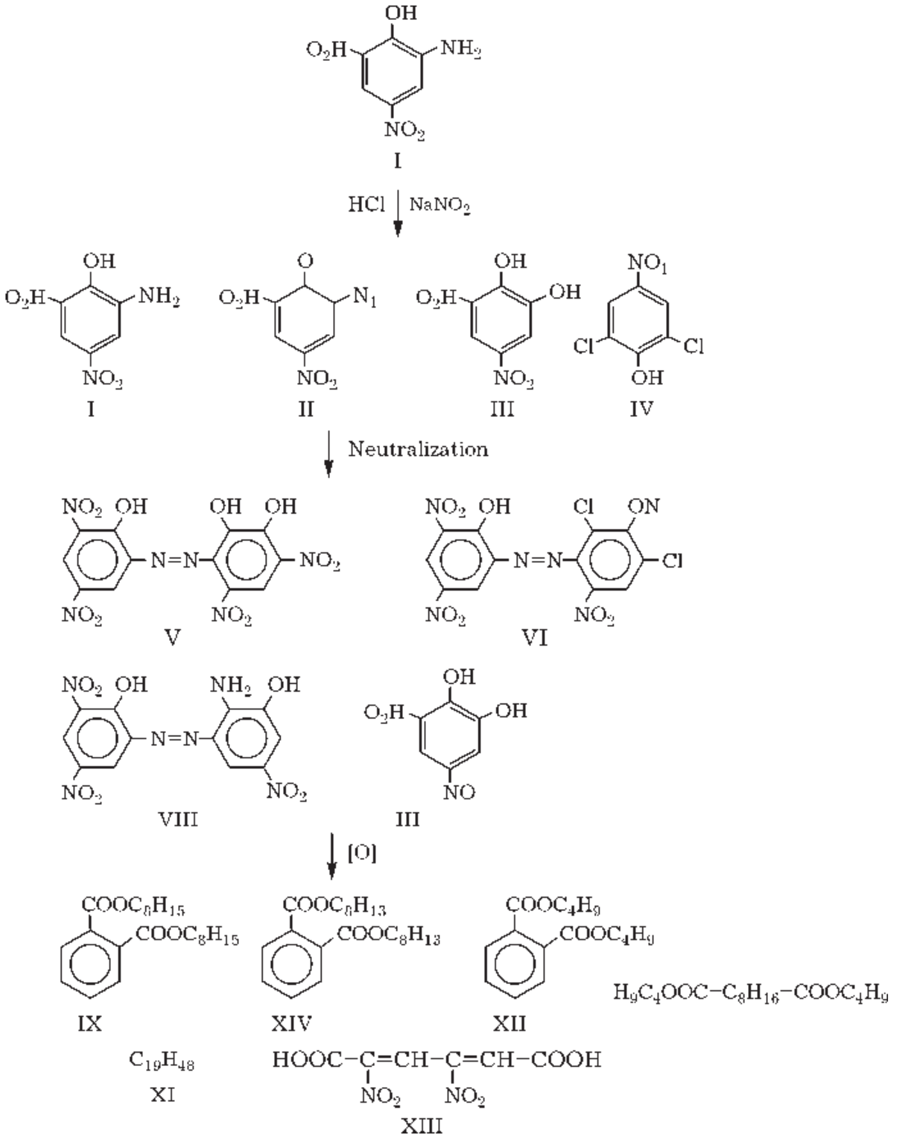
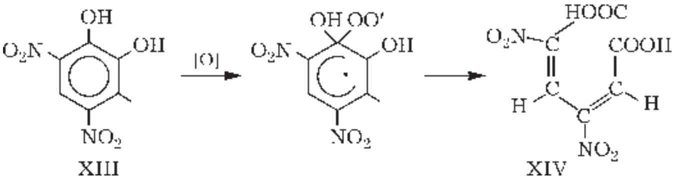


Fig. 8. Scheme of the transformation of impurities contained in the wastewaters from diazodinitroquinone manufacture.



Scheme 1.

of decanedioic acid X and its isomers (12.43, 13.27 min), dioctyl ester of orthophthalic acid IX and its isomers (14.08, 14.85, 15.59, 16.30 min). In the course of the further analysis of m/z values it was established, that the chromatographic peaks with the retention time value amounting to 16.99, 17.66, 18.30, 18.93 min, are corresponding to dinitrohexadiendioic acid (XIII), which is confirmed by the presence of a molecular ion $M^{+\bullet}$ with the value of m/z 232 in the mass spectrum. In addition, in the mass spectrum the peaks of fragmental ions with m/z values equal to 198, 182, 152 are observed whose formation could be presented basing on the molecule (XIII).

The chromatographic peaks with the retention time value amounting to 19.60, 20.39, 21.31 min correspond to dihexyl ester orthophthalic acid (XIV), which is confirmed by the presence of a molecular ion $M^{+\bullet}$ with the value of m/z 334 in the mass spectrum. Furthermore, in the mass spectrum the peaks of fragmental ions with m/z values amounting to 249, 217, 164 are observed whose formation could be presented basing on the molecule XIV. The formation of the product such as XIV may be presented by Scheme 1.

Thus, the studies on the composition of wastewater after the treatment by oxidizers demonstrated the wastewater to contain less toxic products. A mineralization of nitro derivatives of aromatic hydrocarbons has occurred, one part of these derivatives forming carbonic acids, whereas another part yielding linear molecules.

Basing on the results of the analysis of changing in the characteristics of the impurities those are contained in DDQ manufacturing wastewater, a hypothetical mechanism may be suggested for the transformation of these impurities (Fig. 8).

CONCLUSION

Thus, basing on the studies carried out, the following conclusion may be drawn: using the oxidation method only for diazodinitroquinone manufacturing wastewater treatment can not provide any achievement of COD level allowable for the discharge of the wastewater into biological purification facilities. We have offered a technology for wastewater treatment in DDQ manufacturing that includes the following three stages: the first stage is neutralization, the second one is oxidation by atmospheric oxygen in the presence of a ferriferous heterogeneous catalyst (a waste after ferrous metal processing), the third one consists in sorption by diatomite.

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