

TWO-PHASE OZONATION PROCESS FOR THE DESTRUCTION OF PHENOLIC POLLUTANTS

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Abstract. A liquid–liquid ozonation technique was applied for the destruction of phenol, 4-methylphenol, and 4-chlorophenol from aqueous solution. The ozonation process was carried out in a reactor–absorber system with a circulating ozone carrier. Simultaneously with the oxidation of phenol in the reactor the saturation of the carrier by ozone in the absorber occurred. The two-phase ozonation of phenolic compounds is a mass transfer process accompanied by a surface reaction. The overall process rate is increasing in the order phenol–4-chlorophenol–4-methylphenol.

Key words: ozonation, fluorinated solvent, waste water, phenol, 4-methylphenol, 4-chlorophenol.

INTRODUCTION

Ozonation has been widely employed as a method for the destruction of hazardous organic compounds in several waste waters. However, the conventional gas–liquid ozonation process is characterized by low solubility of ozone in water and low ozone concentration in the gas phase. Therefore the rate of the mass transfer from gas to the aqueous phase remains relatively low. Furthermore, ozone is unstable in aqueous solution and hence decomposes partially before reacting with an organic pollutant. The inorganic compounds occurring in water also consume ozone or inhibit the formation of OH· radicals [1]. Therefore the efficiency of ozone with regard to the destruction of organic pollutants remains low in a conventional ozonator.

These problems may partially be overcome by using a liquid ozone carrier. The ozonation process can be realized in a liquid–liquid system consisting of an inert organic solvent saturated with ozone and an aqueous phase containing the pollutant. The process is referred to as two-phase ozonation [1, 2].

Bhattacharyya et al. [1] in their study of two-phase ozonation of chlorinated organics suppose that the organic pollutant is being extracted from the aqueous phase into the solvent where the oxidation by ozone occurs. The selectivity of the

process results from the inability of inorganic and dissociated compounds to partition to the nonpolar solvent phase and high solubility of ozone in the solvent as compared with water. The ozone solvent must be insoluble in water and have an extended O_3 stability. As ozone solvents nonpolar completely fluorinated hydrocarbons FC 40 and FC 43 were used. The process was realized in a batch stirred tank reactor.

Other authors [3] studied the destruction of 2,4-dichlorophenol with ozone in aqueous solution, in fluorinated solvent FC 77, and in a combined gas-liquid-liquid system. They established the superiority of the combined system as compared with the homogeneous phase ozonation.

Differently from the previous authors we carried out the two-phase ozonation process in a reactor-absorber system with a circulating ozone solvent (carrier) at a practically permanent ozone concentration and fixed interfacial area, thus being able to assess the role of mass transfer in the overall process kinetics. In addition to previously used FC 40 perfluorodecalin was applied as the ozone carrier.

EXPERIMENTAL

The scheme of the experimental equipment is shown in Fig. 1. The ozonation process was carried out in a system consisting of a reactor for the oxidation of an organic pollutant (phenol, 4-methylphenol, 4-chlorophenol) and an absorber for the saturation of an inert organic solvent (ozone carrier) with ozone. In this system the ozone carrier was circulating by means of a peristaltic pump.

In the reactor interfacial mass transfer occurred simultaneously with the oxidation reaction. The water soluble oxidation products went into the aqueous phase. In the case both the phases were stirred with small paddle stirrers, due to high density of the solvent (1.95 g cm^{-3}), the interfacial contact area of 10.75 cm^2 remained practically constant at the stirring speeds used. In the case a turbine stirrer was used the interfacial area was significantly larger due to the phase dispersion.

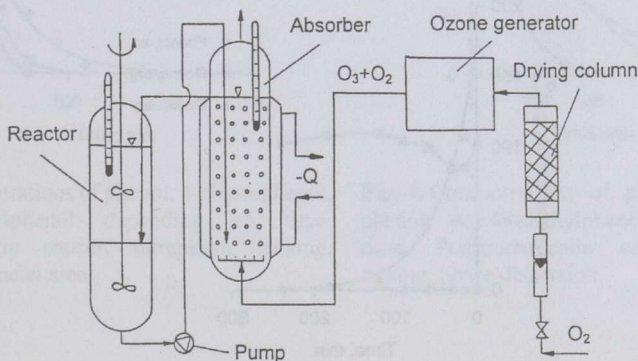


Fig. 1. Scheme of the experimental equipment.

As ozone carriers octadecafluorobicyclo[4,4,0]-decane, perfluorodecalin (Perfloran, Moscow), and a completely fluorinated hydrocarbon solvent Fluorinert FC 40 (Sigma Chemical) were used.

The saturation of the carrier with ozone proceeded in the bubble column absorber. In order to increase the solubility of ozone, enhance the gas-liquid mass transfer, and simultaneously reduce the vapour pressure of the solvent, the absorber was cooled to keep the solvent temperature below -4°C . The volumes of the aqueous and organic phases were 70 and 60 cm^3 respectively.

The mixture of ozone gas and oxygen was generated by conducting oxygen through a drying column and a laboratory Ozon-K generator (Medinfot, Moscow) and then the mixture was entered into the absorber. The gas flow was kept at 0.5 l min^{-1} , the ozone concentration in the gas was about 80 g m^{-3} . The circulation rate of the carrier was kept at about $40 \text{ cm}^3 \text{ min}^{-1}$. Before pouring the aqueous phase into the reactor the carrier was saturated with ozone. The samples for analysis were taken from the aqueous and organic phases at fixed time intervals after receiving steady-state temperatures of both phases.

The concentration of the phenolic compound in the aqueous solution was measured with a high performance liquid chromatograph LC 1311 (USSR) equipped with a fluorometric detector. The wavelength used was 220 nm. A reverse phase column, packed with Separon C18, was applied. As solvent a mixture of acetonitrile and water (10%) was used. The concentration of the phenolic compound in the organic phase was measured using a gas chromatograph. The concentration of ozone in both phases was measured by the indigo method [4] using an automatic photocolormeter KFK-2MP at a wavelength of 580–600 nm.

Typical curves describing phenol and ozone concentration depending on time are shown in Fig. 2. The concentration of ozone in the organic phase was kept roughly constant, an insignificant minimum at the beginning of the experiment could not be avoided. During the experiment no presence of phenol was discovered in the organic phase. Ozone occurred in the aqueous phase at the end of the experiment when the bulk of phenol had been practically consumed.

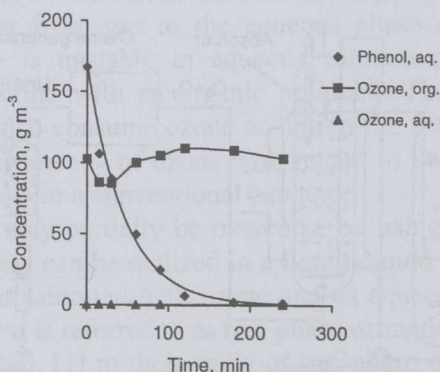


Fig. 2. Concentrations of phenol and ozone depending on time.

RESULTS AND DISCUSSION

Our experiments were carried out at different stirring speeds using both paddle and turbine stirrers and different phenolic pollutants in the aqueous phase. In Fig. 3 the concentrations of phenol, 4-chlorophenol, and 4-methylphenol depending on time are shown. The curves were obtained roughly at the same physical conditions (perfluorodecalin carrier, paddle stirrer with stirring speed $n = 375$ rpm, ozone concentration in the organic phase $2.0 \pm 0.2 \text{ mol m}^{-3}$, and temperature in the reactor $14 \pm 1^\circ\text{C}$). Figure 4 shows analogous concentration curves obtained approximately under the same conditions but at turbulent mixing (turbine stirrer $n = 200$ rpm) and a significant phase dispersion. As can be seen, in both cases the overall process rate of phenolic compounds increases in the order phenol, 4-chlorophenol, 4-methylphenol. This order corresponds to the values of the reaction rate constants obtained at the ozonation of these compounds in an organic solution [5].

Figure 5 shows the concentration curve of 4-chlorophenol obtained in the case a fluorinated solvent FC 40 was used as the carrier (paddle stirrer $n = 375$ rpm, ozone concentration in the organic phase 2.5 mol m^{-3} , temperature 15.5°C). As can be seen the oxidation of 4-chlorophenol in the FC 40 solution proceeds approximately at the same rate as in the case of perfluorodecalin carrier (Fig. 4).

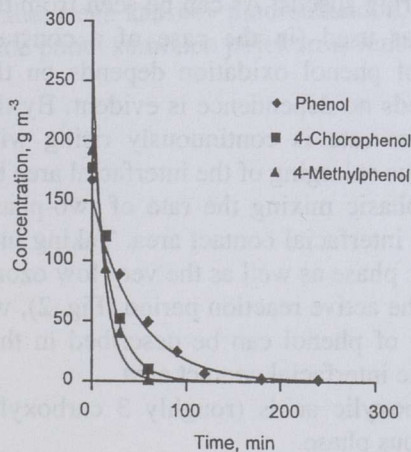


Fig. 3. Concentrations of phenol, 4-chlorophenol, and 4-methylphenol depending on time. Perfluorodecalin carrier, intraphasic mixing, constant interfacial area.

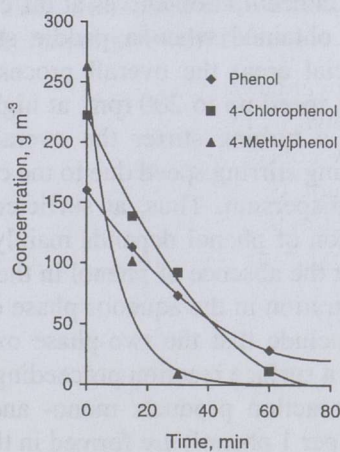


Fig. 4. Concentrations of phenol, 4-chlorophenol, and 4-methylphenol depending on time. Perfluorodecalin carrier, turbulent mixing, phase dispersion.

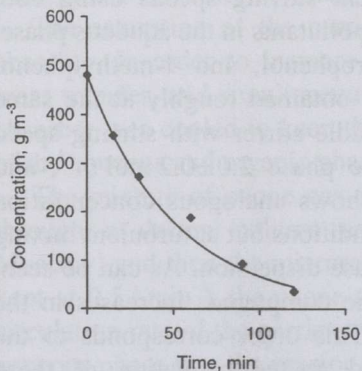


Fig. 5. Concentration of 4-chlorophenol depending on time. FC 40 carrier, intraphasic mixing, constant interfacial area.

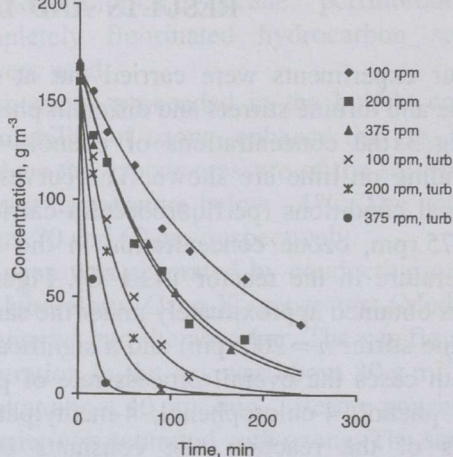


Fig. 6. Phenol concentration curves at different mixing speeds.

The overall process rate may be limited by the rates of both the chemical reaction and the diffusional mass transfer. In the case of a diffusion-controlled process the overall process rate depends on the stirring speed. Figure 6 presents phenol concentration curves at different stirring speeds. As can be seen from the curves obtained when a paddle stirrer was used (in the case of a constant interfacial area) the overall process rate of phenol oxidation depends on the stirring speed up to 200 rpm, at higher speeds no dependence is evident. By the use of a turbine stirrer the overall process rate is continuously rising with increasing stirring speed due to the continuous enlarging of the interfacial area by phase dispersion. Thus, at sufficient intraphasic mixing the rate of two-phase ozonation of phenol depends mainly on the interfacial contact area. Taking into account the absence of phenol in the organic phase as well as the very low ozone concentration in the aqueous phase during the active reaction period (Fig. 2), we can conclude that the two-phase ozonation of phenol can be described in that case as a surface reaction proceeding near the interfacial contact area.

As reaction products mono- and dicarboxylic acids (roughly 3 carboxylic groups per 1 phenol) are formed in the aqueous phase.

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KAHEFAASILINE OSOONIMISPROTSESS FENOOLSETE HEITMETE LAGUNDAMISEKS

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Vedelik–vedelik-osoonimise tehnoloogiat kasutati fenooli, 4-metüülfenooli ja 4-klorofenooli lagundamiseks vesilahuses. Osoonimisprotsess viidi läbi reaktorist ja absorberist koosnevas süsteemis, milles tsirkuleeris osoon kandur. Samaaegselt fenooli oksüdeerimisega reaktoris toimus absorberis kanduri küllastamine osooniga. Leiti, et fenoolsete ühendite kahefaasiline osoonimine on massi vahetusega kaasnev pindreaktsioon, kus protsessi üldine kiirus erinevate reagentide puhul suureneb järjekorras fenool, 4-klorofenool ja 4-metüülfenool.