A comparative study of efficiency of photooxidation of organic contaminants in water solutions in various photochemical and photocatalytic systems
1. Phenol photooxidation promoted by hydrogen peroxide in a flow reactor

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Abstract

Phenol photooxidation in a flow reactor of a cylinder shape was studied for systems H_2O_2 + UV and TiO_2 + H_2O_2 + UV. TiO_2 was prepared as cylinder granules 0.3 cm long and 0.2 cm in diameter. Limit liquid flows and concentrations of organics that can be converted in the reactors were estimated. The contributions of various reaction routes (direct photochemical action on the organic compound, OH generation from H_2O_2, photocatalytic decomposition of H_2O_2 and organics on TiO_2) were estimated and shown experimentally. It has been proved in experiment that in a designed photocatalytic reactor (length 15 cm, mercury lamp middle pressure 250 W) up to 98% of phenol can be decomposed at a concentration of 6×10^{-5} M phenol and a concentration of 10^{-2} M peroxide at a flow of 21 l h^{-1}. © 1997 Elsevier Science S.A.

1. Introduction

Light-driven water purification technologies open a promising way in some important areas of environmental control especially in the oxidative destruction of organic contaminants [1]. There are three main paths for the destruction of organic compounds. First, light can directly excite the molecules of the organic contaminants thus leading to their direct photochemical destruction. Second, light can activate some exogenic oxidants like $H_2O_2(O_3)$ added into the system to produce strong oxidizers like OH or O (such system herein after are denoted as 'photochemical H_2O_2 + UV systems'). And, third, light can be absorbed by some photocatalysts like TiO_2, etc., the photocatalysts either directly participate in the oxidation of organics or initiate the formation of OH radicals from water and hydrogen peroxide added (below we denote such systems as 'photocatalytic TiO_2 + UV systems'). Each of the mentioned systems can be used in practice and optimal under some particular conditions. However, these systems have also their drawbacks and limitations with use.

System H_2O_2 + UV offers now a wide practical application [1]. Its main and well-known drawback appears to be a weak absorption of light by hydrogen peroxide even in the UV-C region (ϵ_{250} equals only 18.5 M^{-1} cm^{-1}) [2]. As to the photocatalytic system TiO_2 + UV, it did not meet a wide use in practice. However, this photocatalytic system has some evident advantages compared with the H_2O_2 + UV system [3]. Indeed, TiO_2 can adsorb light in the wide region from near to far UV (at $\lambda < 400$ nm). Furthermore, the granules of TiO_2 are able to utilize the whole flux of light from this region.

In this paper, we tried to use the advantages of both TiO_2 + UV and H_2O_2 + UV systems by adding the granules of TiO_2 to H_2O_2 + UV system. The photooxidative activities of TiO_2 + UV, H_2O_2 + UV, TiO_2 + H_2O_2 + UV systems were compared in the process of phenol oxidation in the flow reactor.

2. Experimental

2.1. Reagents and materials

To prepare solutions, we used distilled water, 30% hydrogen peroxide solutions, phenol and sodium hydroxide (anal-

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ysis purity grade). TiO$_2$ granules of cylinder shape 0.3 cm long, 0.2 cm in diameter, were prepared by Dr. Zenkovets G.A.

2.2. Experimental

To oxidize organic compounds we used a flow reactor consisting of two coaxial cylinders. The inner cylinder (external radius $R_{ex} = 2.5$ cm) was made of quartz. External cylinder (inner radius $R_{in} = 3$ cm) was made of glass. If necessary, we placed the TiO$_2$ cylinder granules in the gap between the cylinders ($\Delta R = 0.5$ cm). A 250 W middle pressure mercury lamp DRL-250, installed into the quartz cylinder, served as a light source. Solutions were fed by a peristaltic pump SP 3 (MLW Labortechnic, GDR). The flow of liquid through the reactor was controlled with pinch-cocks on flexible hoses and monitored with a flowmeter 1 W 160 (Prufgerate Werk Medingen, GDR).

Fig. 1 views the setup. It consists of the reactor, peristaltic pump, T-joint, pinch-cocks, refrigerator (20 °C), vessels of 1 l and 2 l volume '1' and '2', respectively. At the beginning, vessel 1 contained 1 l of distilled water, while vessel 2 contained 2 l of distilled water with the required amounts of phenol and hydrogen peroxide. The initial temperature of the solutions in the vessels 1 and 2 was ca. 20 °C. pH of the second solution was adjusted using sodium hydroxide. After this the output reactor hose was placed into vessel 1, and T-joint was turned to vessel 1. Then the pump, lamp and refrigerator were switched on. After 5 min of operation, needed to heat the lamp, T-joint was returned to vessel 2, containing the working mixture. Then 1.5 l of the solution was pumped through the reactor, 50 ml of the solution was taken and the concentration of phenol in this sample was measured.

As the working mixture goes through the reactor with a switched-on lamp, phenol decomposes, as is evidenced by a spectrum of phenol luminescence excitation at $\lambda = 270$ nm. Luminescence excitation were registered by a Shimadzu UV-300 (Japan) spectrophotometer. A BC-4 glass cutoff filter served to quench the samples scattering and simultaneously to measure the integral intensity of the sample luminescence at $\lambda > 300$ nm.

Phenol concentration was calculated as follows: the luminescence intensity of the sample was measured just at the
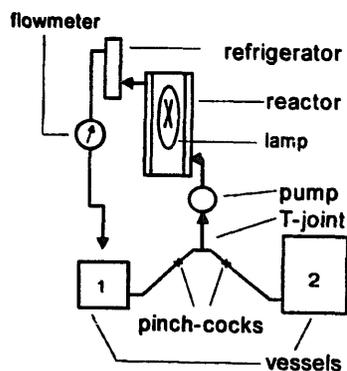
reactor exit. Then, we added phenol into the sample in the amount required to obtain the initial concentration of phenol as in the vessel before the reactor. We recorded the luminescence intensity again. Phenol amounts in the sample were calculated as follows: the ratio of the luminescence intensity before phenol addition and the difference of luminescence intensities before and after phenol addition was multiplied by the phenol concentration added into the sample. This procedure enables to take into account a plausible quenching of phenol luminescence by the products of its oxidation.

2.3. Evaluation of regions of efficient operation of the reactor

Before measuring the operation efficiency of a flow photoreactor of a definite geometry equipped with a light source, one should evaluate the ranges of the liquid flows and the concentration of the oxidized organic material in which all organics can be converted in the reactor. The limitations may be related to the light source power, a slow diffusion of reagents to the photocatalyst surface, flow overheating and low reaction quantum yield.

Therefore, the reactor with TiO$_2$ photocatalyst granules is able to photocatalytically oxidize the flows of organic compounds, if the following three conditions are met: (1) The number of photoactive light quanta radiated by the lamp in time unit should exceed the number of organic molecules fed into the reactor during the same time. This condition results from the fact that usually the photocatalytic oxidation quantum yield does not exceed 1 (Here, we have neglected chain processes). (2) Each organic molecule entering the reactor should at least once collide with a photocatalyst granule. This condition follows from the fact that the photocatalytic oxidation of organic molecules proceeds only near the photocatalyst surface. The OH radical which can oxidize organics is active, but is a short living particle and it cannot diffuse deeply from the surface of the photocatalyst into a solution. (3) The temperature of an oxidized solution should not be raised up to 100 °C, so as it will promote a precipitation of salts from the solution at the surface of the photocatalyst, and deactivation of the last one.

Fig. 2 shows a domain of the expected efficient operation of the reactor under study, that is where all three conditions are met. These calculations were performed on the basis of standard formulas reported in [4].

2.4. Phenol oxidation in the reactor

The reactor was tested under conditions close to those expected at a practice. We measured the concentration of phenol, oxidized during a single run, $\Delta [Ph] = [Ph]_i - [Ph]_f$, where $[Ph]_{i,f}$ are the phenol concentrations before and after the reactor. The phenol concentration at the reactor inlet was the main variable. To elucidate the effect of H$_2$O$_2$, dependence $\Delta [Ph]$ versus $[Ph]_i$ was determined for four different concentrations of H$_2$O$_2$, namely 0, 10^{-4}, 10^{-3} and 10^{-2} M.

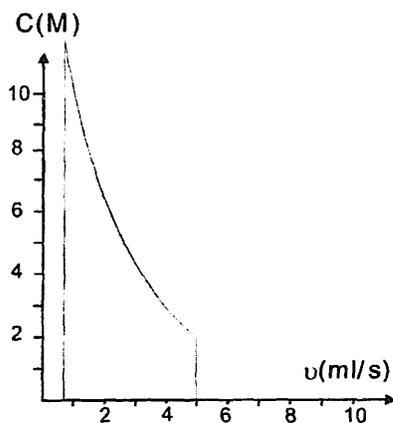Fig. 1. Scheme of the experimental setup.

Fig. 2. Domain of a plausible efficient operation of the reactor in coordinates: v: the flow, C: concentration of organic.

It should be pointed out that the rate of the dark oxidation of phenol was well below the rate of phenol oxidation under light. So, the dark oxidation processes may be ignored.

Without the photocatalyst, the concentration of phenol $\Delta[Ph]$ oxidized in the reactor depends linearly on $[Ph]_i$ (the lamp is switched on). Besides, the dependence slope rises, as the concentration of H_2O_2 increases (Fig. 3). In the presence of H_2O_2 some critical phenol concentration $[Ph]_i^{cr}$ does exist. If the initial concentration of phenol is below this critical value, then almost all phenol, fed to the reactor, is oxidized and $[Ph]_f$ measured does not exceed the experimental error. This critical concentration of phenol rises with the increase of the H_2O_2 concentration. For $[H_2O_2] = 10^{-4}$, 10^{-3} and 10^{-2} M, $[Ph]_i^{cr}$ equals 1×10^{-5}, 3×10^{-5} and 5×10^{-5} M, respectively.

In photocatalyst presence the dependence $\Delta[Ph]$ versus $[Ph]_i$ is different (Fig. 4). As $[Ph]_i$ increases from 1×10^{-5} to 4×10^{-5} M, $\Delta[Ph]$ rises linearly with $[Ph]_i$. Besides, extrapolation of these dependencies to zero gives a zero value of $\Delta[Ph]$. As $[Ph]_i$ rises, $\Delta[Ph]$ becomes independent of it. For $[H_2O_2] = 0$, 10^{-4} and 10^{-3} M, all observed dependencies $\Delta[Ph]$ versus $[Ph]_i$ are similar. At $[H_2O_2] = 10^{-2}$ M the dependence reaches a plateau at somewhat higher than
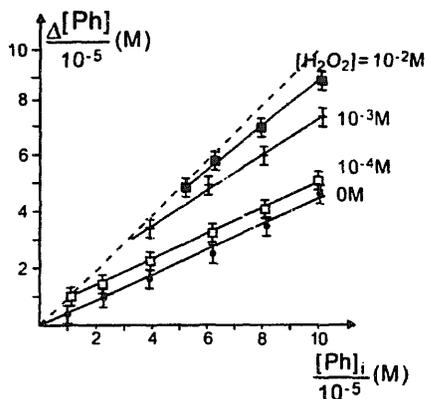

Fig. 3. Concentration of phenol decomposed, $\Delta[Ph]$, in the reactor vs. its initial concentration $[Ph]_i$ at the inlet of the reactor without TiO_2 photocatalyst upon four concentrations of hydrogen peroxide added to the solution. $v=6$ ml s^{-1}, initial temperature 20 °C, pH 5.6, $[H_2O_2] = 0$, 10^{-4}, 10^{-3} and 10^{-2} M.

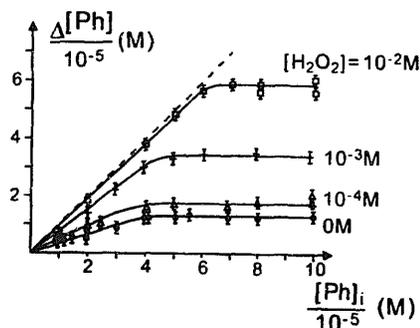

Fig. 4. Concentration of phenol decomposed, $\Delta[Ph]$, in the reactor vs. concentration of phenol entering the reactor upon four concentrations of hydrogen peroxide added to the solution. Reactor is filled with TiO_2 granules of C-4 type, $v=6$ ml s^{-1}, initial temperature 20 °C, pH 5.6, $[H_2O_2] = 0$, 10^{-4}, 10^{-3} and 10^{-2} M.
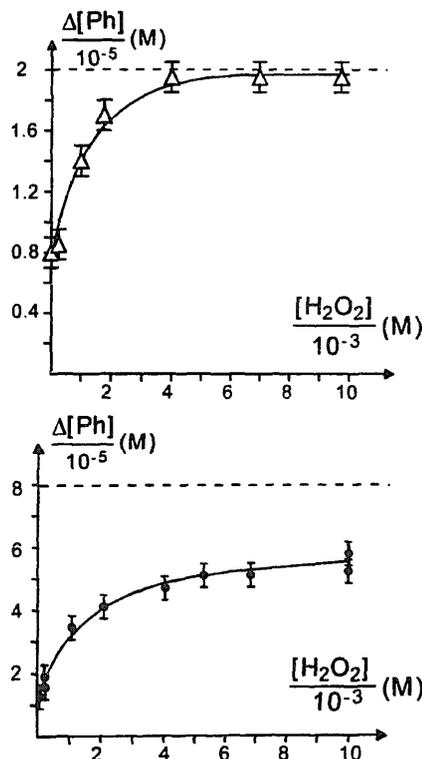

Fig. 5. Concentration of phenol decomposed, $\Delta[Ph]$, in the reactor as a function of concentration of hydrogen peroxide added. Reactor is filled with TiO_2 granules of C-4 type. Initial phenol concentration is 2×10^{-5} M (a) and 8×10^{-5} M (b). $v=6$ ml s^{-1}, initial temperature 20 °C, pH 5.6.

for $[H_2O_2] = 0$, 10^{-4} and 10^{-3} M phenol concentrations. Fig. 5a–b exhibit the effect of H_2O_2 addition. The figures show $\Delta[Ph]$ versus $[H_2O_2]$ at two fixed concentrations of phenol, i.e., 2×10^{-5} and 8×10^{-5} M. That correspond to typical parts of the curves presented on Fig. 4. Note, that when the concentration of hydrogen peroxide is raised up to $[H_2O_2] = 10^{-3}$ M, $\Delta[Ph]$ increases markedly (by a factor of 2).

3. Discussion

Let us discuss the above experimental data concerning the oxidation of phenol in the flow photocatalytic reactor.

First, consider the oxidation of phenol without the photocatalyst. Here, the reaction can go in two paths:

(a) A light quantum is absorbed by a phenol molecule. The photoexcited molecule then decays.

(b) A light quantum is absorbed by a H_2O_2 molecule. The photoexcited H_2O_2 molecule decomposes to produce OH radicals:

$$H_2O_2 \xrightarrow{h\nu} 2\,OH\cdot$$
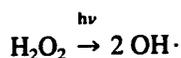
which later oxidize the phenol molecule.

Let us evaluate the rate of phenol oxidation regarding paths (a) and (b). For this purpose we should determine the number of light quanta absorbed by the molecules of phenol and hydrogen peroxide. For phenol let us use

$$I_{Ph} = \int_\lambda I_0(\lambda)\,[1 - 10^{-(D_{Ph}(\lambda)+D_{H_2O_2}(\lambda))}]\,\frac{D_{Ph}}{D_{Ph}+D_{H_2O_2}}\,d\lambda$$

and for hydrogen peroxide:

$$I_{H_2O_2} = \int_\lambda I_0(\lambda)\,[1 - 10^{-(D_{Ph}(\lambda)+D_{H_2O_2}(\lambda))}]\,\frac{D_{H_2O_2}}{D_{Ph}+D_{H_2O_2}}\,d\lambda$$

where $I_0(\lambda)$ is the light intensity at wavelength λ, $D_{Ph}(\lambda)$, $D_{H_2O_2}(\lambda)$ are the optical densities of phenol and hydrogen peroxide at wavelength λ, respectively. It is possible to show that under experimental conditions I_{Ph} depends linearly on $[Ph]$, while $I_{H_2O_2}$ does not practically depend on $[Ph]$.

Actually, the emission spectrum of lamp $I_0(\lambda)$ dramatically drops, if λ decreases below 300 nm. Thus, λ from the long-waved absorption band of phenol, namely $\lambda = 270$ nm, contributes to the integral determining I_{Ph}. For our set up, $\Delta R = 0.5$ cm $D_{H_2O_2}$ almost equals zero at such a wavelength, if $[H_2O_2] \leq 10^{-2}$ M. For the phenol concentrations in use, $[Ph] < 10^{-4}$ M, $D_{Ph}(\lambda = 270$ nm$) = \epsilon_{Ph}(\lambda = 270$ nm$)\cdot\Delta R[Ph] < 0.1$, where $\epsilon_{Ph}(\lambda = 270$ nm$) = 2470$ nm^{-1} M^{-1} is the phenol extinction coefficient at $\lambda = 270$ nm [5], ΔR is the length of optical path (gap between the cylinders). Then

$$I_{Ph} = \int_\lambda I_0(\lambda)\ln 10\,\epsilon_{Ph}(\lambda)\,[Ph]\Delta R d\lambda \approx k[Ph]$$

where

$$k = \int_\lambda I_0(\lambda)\ln 10\,\epsilon_{Ph}(\lambda)\Delta R d\lambda$$

Second, using the fact that the spectrum of the lamp $I_0(\lambda)$ dramatically drops if λ decreases below 300 nm one can find that wavelengths $\lambda > 230$ nm mostly contribute to $I_{H_2O_2}$. In addition, in this region $D_{Ph} < 0.1$ and consequently $I_{H_2O_2}$ depends on D_{Ph}, i.e., on the phenol concentration only slightly. This means that the concentration of phenol is so low that it does not shield H_2O_2 at the wavelengths mainly contributing to $I_{H_2O_2}$. Summing up both reaction routes, we find:

$$-\frac{d[Ph]}{dt} = aI_{Ph} + bI_{H_2O_2} = ak[Ph] + bI_{H_2O_2}$$

where a, b are the efficient quantum yields in each path. Integrating, one can find $\Delta[Ph]$ as the concentration of phenol oxidized during time τ:

$$\Delta[Ph] = [Ph]_i - [Ph]_f = (1 - e^{-ak\tau})\left[[Ph]_i + \frac{bI_{H_2O_2}}{ak}\right]$$

$[Ph]_{i,f}$ are the initial and final concentrations of phenol. For the flow reactor, these values correspond to the concentration of phenol at reactor inlet and outlet, τ is the residence time of mixture passing through the illuminated space.

Thus, $\Delta[Ph]$ depends linearly on $[Ph]_i$. Besides, if the phenol concentration is below its critical value $[Ph]_i^{cr}$:$[Ph]_i < [Ph]_i^{cr}$, this relation gives that $\Delta[Ph] > [Ph]_i$. In fact it means that phenol is almost completely oxidized in the reactor: $\Delta[Ph] = [Ph]_i$. The above ratio describes at least qualitatively the experimental dependence between $\Delta[Ph]$ and $[Ph]_i$ (Fig. 3).

Now, let us consider phenol oxidation with the photocatalyst granules.

Note, that photocatalyst absorbs the main portion of light. As it was mentioned in the experimental section, the photocatalyst granules used are cylinders of 0.2 cm in diameter and 0.3 cm long. If the gap between the reactor tubes is simply loaded with the photocatalyst granules, the light will pass at a distance smaller than the granule radius, somewhat about 0.02 cm, before TiO_2 will absorb it. For this path and $\lambda > 230$ nm, the optical densities of phenol and hydrogen are $D_{Ph} < 2.4 \times 10^3 \times 10^{-4} \times 0.02 \approx 0.005$ and $D_{H_2O_2} < 100 \times 10^{-2} \times 0.02 \approx 0.02$, respectively. Thus, the photocatalyst granules rather than bulk phenol or hydrogen peroxide absorb the main portion of light.

If the optical path for phenol and hydrogen peroxide decreases from 0.5 to 0.02 cm (by a factor of 25) at the weak absorption, the portion of light absorbed by phenol and hydrogen peroxide also reduces by a factor of 25. Assuming that photodecomposition and photochemical oxidation are the single-quantum processes, i.e., their rate decreases linearly with the light intensity, we should state that the contribution of non-catalytic reactions in the presence of photocatalyst granules decreases by nearly a factor of $(1 - e^{-ak\tau}/1 - e^{-ak\tau/25}) > 15$. Moreover, phenol conversion in the catalyst presence is of the same order as without it (compare Figs. 3 and 4). This evidences that in system $TiO_2 + H_2O_2 + UV$ under study, the decomposition of phenol occurs mainly over the photocatalysis since the rate of non-photocatalytic paths of destruction of phenol are negligible.

Fig. 4 shows $\Delta[Ph]$ versus $[Ph]_i$ when the photocatalyst granules are placed in the reactor. One can readily see that $\Delta[Ph]$ versus $[Ph]_i$ cannot be determined by the frequency of phenol molecules collision with the photocatalyst, ν, since it is proportional to $[Ph]$, and $\Delta[Ph]$ versus $[Ph]_i$ attains the plateau at some particular concentration of phenol,

depending on the concentration of hydrogen peroxide. Moreover, a linear growth at low concentrations and the plateau at high concentration of compounds in the solution are typical for adsorption isotherms. Thus, one can suggest that the reaction rate and, consequently, the Δ[Ph] dependence on [Ph]$_i$ are determined mainly by the adsorption of phenol molecules over the TiO_2 photocatalyst surface.

However, at $v = 6$ ml s^{-1} and [Ph]$_i < 10^{-4}$ M, used in this work, collision frequency of molecule of organic material and the surface unit of the photocatalyst granule $\nu < 10^{-9}$ mol cm^{-2} s^{-1} (see [4]). The average intensity of light is known to be $I \approx 10^{-6}$ Einstein cm^{-2} s^{-1}. This means that for each collision of phenol molecule with the surface unit of irradiated photocatalyst surface $I/\nu = 1000$ light quanta are absorbed by TiO_2. At such a I/ν ratio, the photocatalyst operation regime, when the rate of the chemical reaction is not determined by the frequency of phenol molecules collision with the photocatalyst (see above), can be realized in two intercrossing cases: (a) the photocatalyst exhibits a low activity and (b) those parts of photocatalyst granules where $I/\nu < 1$, give the main contribution to the oxidation reaction.

Note, that if the concentration of hydrogen peroxide equals 10^{-2} M and the initial concentration of phenol is lower than 6×10^{-5} M, practically all phenol (98%), fed to the reactor, is oxidized. So, the photocatalytic reactor under study can neutralize about 6000 phenol TPC (phenol TPC is 10^{-8} M [6]) at a 6 ml s^{-1} flow rate (360 ml min^{-1}, 21 l h^{-1}, 518 l day^{-1}) and at 20 °C of the initial solution.

4. Conclusion

In conclusion, one can say that the $H_2O_2 + UV$ system has shown better operational features than the $TiO_2 + H_2O_2 + UV$ system in the reaction of phenol oxidation in the flow reactor under study. Actually, the $H_2O_2 + UV$ system can oxidize practically all phenol fed in to reactor, if its concentration is below the critical one. But the activity of the $H_2O_2 + UV$ system is fixed, while that of the $TiO_2 + H_2O_2 + UV$ system appears to enhance with increasing activity of the TiO_2 photocatalyst.

Acknowledgements

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