Influence of pH on the degradation 4-chlorophenol by gamma radiocatalysis using SiO₂, Al₂O₃ and TiO₂

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Advanced oxidation process is a technology used in detoxification of residual water containing organic pollutants in small and medium scales. Radiocatalysis is a process that combines photocatalysis and radiolysis. An important experimental parameter in radiocatalysis is the pH because it influences the electrochemical system by modifying the electric charge on the surface of materials. This effect was investigated in the radiocatalytic degradation of 4-chlorophenol using titanium, silicium, and aluminum oxides. It was found that the degradation of 4-chlorophenol is enhanced at pH between 3 and 7.

Introduction

Nowadays, large amounts of wastes are released into the environment, resulting in pollution of water, air and soil. Chlorophenols are found in water wastes, because they are used in the manufacture of herbicides, plant growth regulators, disinfectants, and wood preservatives.[1] Chlorophenols are produced by chlorination of phenols during disinfection, in the reaction of hypochlorite with phenolic acids, such as biocides, or degradation products of phenoxy herbicides, and they are considered possible carcinogen.[2] There are several proposals to eliminate chlorophenols; incineration is an efficient way to treat these compounds, however, phenols and chlorophenols are precursors of formation of polychlorinated dibenzo p-dioxins (PCDD) during incineration processes.[3,4]

Advanced oxidation processes (AOP) are widely studied for the treatment of toxic compounds; photocatalysis and radiolysis have been used in mineralization of persistent organic compounds. These processes can be used separately or in combination with other AOP or conventional treatment methods. Heterogeneous photocatalysis is an AOP that uses an oxide excited by UV or visible radiation, and the radiolysis use gamma-radiation or electrons to generate •OH radicals in the water.[5]

The radiation chemistry of heterogeneous systems, called radiocatalysis, is presumed to be similar to photocatalysis.[6–8] In photocatalytic reactions, pH dependence is present during degradation of organic compounds.[9] Initial pH of the solution has a significant effect in the superficial properties of materials, such as TiO₂, Al₂O₃, and SiO₂.[10,11]

Metal oxides are affected by pH because some changes due to the union of protons to hydroxyl groups occurred in the hydrated surface. An amphoteric character of the surface is observed, for example: for SiO₂ at high pH, surface is charged negatively [Eq. (1)], and at low values, surface is charged positively [Eq. (2)]:[10–12]

$$\mathrm{SiOH + H^+ \rightleftarrows SiOH_2^+} \qquad (1)$$

$$\mathrm{SiOH \rightleftarrows SiO^- + H^+} \qquad (2)$$
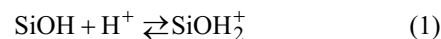
Since the recombination of the electron hole is fast (picoseconds), preadsorption is a prerequisite for an efficient degradation of organic compounds.

Both, the radiolytic and photocatalytic degradations of 4-chlorophenol (4-CP) have been widely studied.[13–15] For example, STAFFORD et al.[16] studied the degradation of 4-CP by radiolysis and by photocatalysis, similar results were obtained at pH 3 and 6; however, at pH 9.1, the degradation was smaller.

The present work will provide information on the nature of the radiocatalytic process, compared with photocatalysis.

Experimental

Materials

The following chemicals were used as received: TiO₂, SiO₂, and Al₂O₃ (Degussa Co.); 4-chlorophenol, 4-aminoantipirine, and Na–K-tartrate (Aldrich); ammonium chloride, potassium ferrocyanide (Baker), and ammonium hydroxide; NaOH and HNO₃ (Merck).

Gamma-irradiation and degradation measurement

Twenty milliliters of 4-CP solution (100 mg/l) and 20 mg of oxide were mixed to obtain dispersions of 1.0 g oxide/l; the initial pH values of 3, 5, 7, 9, and 11 were adjusted with NaOH and HNO₃ solutions. The dispersions obtained were bubbled with O₂ for 3 minutes at a flow of 90 cm³/min, and sealed in a vial.

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Sealed vials were gamma-irradiated with 3 kGy in a Transelektro LGI-01 irradiator with a dose rate of 4.07 kGy/h. After irradiation, the samples were filtered using 0.4 μm Millipore membranes. The 4-CP degradation data were recorded on a UV-vis Perkin–Elmer lambda 10 spectrophotometer, and color development was carried out using the 4-amino-antipirine method.

Results and discussion

The 4-CP 100 mg/l solution has an initial pH of 4.7. After the addition of oxides to the solution, a decrease of pH values in all samples was observed, this was evident for the relase of protons from the oxide surface.

The main products in the degradation process, such as HCl, 4-chlorochatechol, and hydroquinone had an acid character. These substances modify the pH of suspensions after irradiation and diminish the pH values (Fig. 1).

The remaining concentrations of 4-CP after irradiation are presented in Table 1. Among the oxides used, Al_2O_3 was the most efficient. These results were normalized, as relative concentration (C_i/C_0) i.e., the ratio of the remaining concentration after treatment (C_i) and initial concentration (C_0), plotted versus initial pH (Fig. 2). High degradation of 4-CP occurred at initial pH=5, and among the tested oxides, Al_2O_3 presented the highest ratio.
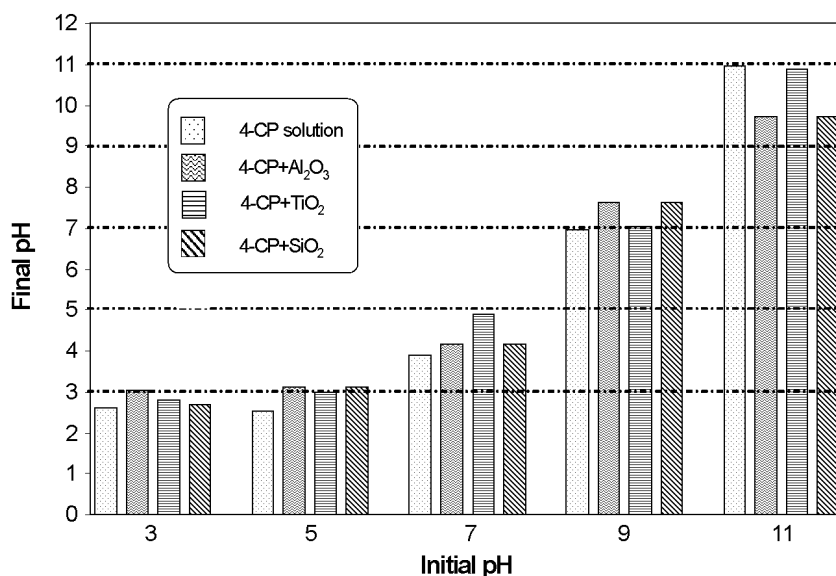

Fig. 1. Final pH values in solutions of 4-CP (100 mg/l) after 3 kGy of gamma-irradiation from a ^{60}Co source. To notice variations they were marked with a doted line level of initial pH values

Table 1. Remaining concentration of 4-CP (in mg/l) after 3 kGy of gamma-irradiation at a different initial pH values and 1 g/l of oxide concentration

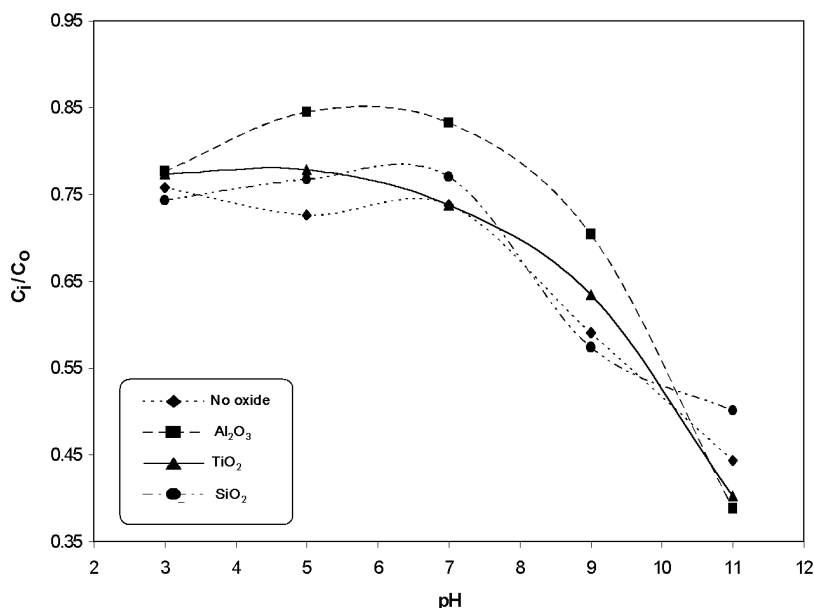| Initial pH	Radiolysis	Radiocatalysis		
		Al_2O_3	TiO_2	SiO_2
3	23.49 ± 1.73	20.79 ± 1.36	21.75 ± 1.24	24.13 ± 2.23
5	26.52 ± 3.77	15.46 ± 0.37	21.14 ± 0.74	23.21 ± 1.67
7	25.22 ± 1.73	16.65 ± 2.41	24.11 ± 0.37	22.83 ± 2.04
9	39.95 ± 2.72	28.71 ± 4.08	35.80 ± 2.66	41.34 ± 4.21
11	50.78 ± 1.18	53.84 ± 1.86	53.62 ± 2.17	43.56 ± 1.73

Fig. 2. Degradation of 4-CP in solutions of relative concentration (C_i/C_0) [i.e., the ratio of remaining concentration (C_i) and initial concentration (C_0)] versus different initial pH values after 3 kGy of gamma-irradiation
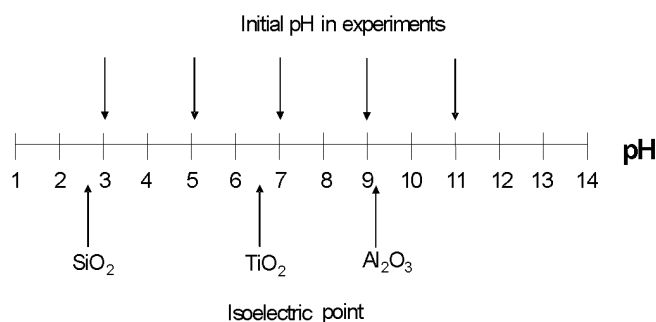

Fig. 3. Isoelectric point of oxides tested compared with initial pH during the experiments

The radiocatalytic degradation of 4-CP can be influenced by two factors related to pH; first, the modification of surface oxide properties; and second, that different pH promotes different pathways reactions.[16]

The charge at the surface is related to the isoelectric point of the oxide and the initial pH in the suspension. If pH is small at that isoelectric point, the surface is charged positively; therefore, at high pH the surface is negatively charged. The 4-CP was more efficiently oxidized at low pH because it was attracted toward the positively charged surface and this allows the electronic transfer due to the radicals formed by gamma-radiation. For SiO_2, the surface was negatively charged at all pH values used during experiments and, therefore, it had a smaller efficiency among the three oxides. On the other hand, Al_2O_3 was positively charged showing the best degradation efficiency (Fig. 3). This explains the differences of degradation among the oxides, where the ratio of degradation decrease in the order $Al_2O_3 > TiO_2 > SiO_2$.

According to STAFFORD,[16] the routes of degradation are different: at high pH, the degradation occurs via 4-chlorophenoxide radical, which does not produce aromatic compounds. When the 4-CP is oxidized in weak acidic conditions, the main intermediate formed is the 4-chlorodihydroxycyclohexadienyl radical (4-CDHCHD•), later forming 4-chlorocatechol and hydroquinone. The theorical pathway of degradation is showed in Fig. 4.
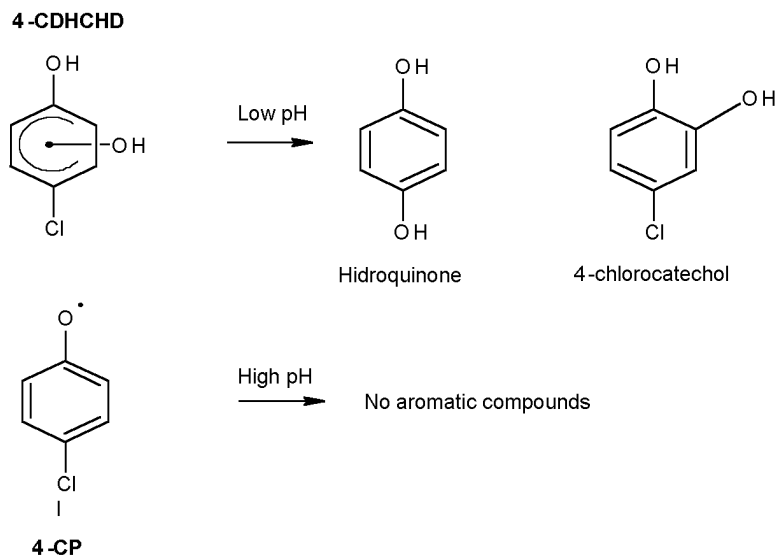
4 -CDHCHD

Fig. 4. Routes of degradation of 4-CP at low and high pH values

The $^\bullet$OH is the main radical that participates in the 4-CP degradation, but other radicals and reactive species that allow the degradation are produced also; the perhydroxy radical is generated by the radiolysis of water with oxygen, at pH>4 it is dissociated into the superoxide ion; and at pH>11 the radical hydroxide and the peroxide of hydrogen are dissociated in oxide and peroxide ions, respectively. During water radiolysis, the yield of formation of $^\bullet$OH is almost constant at pH 1–10, and it decreases at pH 11,[17] so, under the tested experimental conditions, no influence of the amount of radicals was expected.

Conclusions

The pH influences the radiocatalytic degradation of 4-CP, therefore, the mechanism of degradation on the surface of oxide is similar to photocatalysis, with a high predomination of radiolysis. The differences in degradation ratios were attributed to the surface properties of oxides, by variations in the patways due to pH.

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