Kinetic study of the catalytic decomposition of H_2O_2 in phosphoric acid medium

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ABSTRACT

The kinetics of hydrogen peroxide decomposition in phosphoric acid media containing ferrous ion was investigated. The results indicated that this reaction followed the pseudo-first-order kinetic model. The decomposition rate of H_2O_2 was accelerated by increasing Fe^{2+} concentrations and temperature. However, higher levels of H_2O_2 inhibited the reaction kinetics. Based on the rate constants obtained at different temperatures, the empirical Arrhenius expression of H_2O_2 decomposition was derived. The derived activation energy for H_2O_2 decomposition by ferrous ions is 57.1 kJ/mol.

Introduction

Tunisian industrial phosphoric acid is produced by the wet process from phosphate rock. It consists in converting the raw phosphate ore into phosphoric acid and calcium sulfate (gypsum) by the addition of sulfuric and phosphoric acids to the reactor.

Although this method is known by its adaptability to all grades of phosphate, its ease of operation, low capital cost and maintenance, as well as its good performance, it produces nevertheless a phosphoric acid which can contain many organic and inorganic impurities [1,2]. Organic impurities are responsible for many problems in the acid digestion of the rock [3–5], the crystallization of gypsum [2,3] and affect seriously the quality of the produced phosphoric acid [3,6].

Among the proposed solutions, the use of hydrogen peroxide seems promising. It is known as a clean oxidant because its oxidation by-products are oxygen and water. Currently, it is widely used in the field of water treatment to combat against the action of organic pollution by hydroxyl radicals which hydrogen peroxide may give rise in the presence of catalyst especially iron (Fenton's reagent) [7–10]. These radicals are known by their powerful oxidizing power towards organic compounds. Hydrogen peroxide is used in several studies to reduce the content of organic impurities in the industrial phosphoric acid [11–14]. However, no study has focused on the mode of action of H_2O_2 on organic matter in phosphoric midium. The presence of metal ions (iron,

copper…) in the industrial phosphoric acid can catalyze the decomposition of hydrogen peroxide to generate hydroxyl (OH$^{\bullet}$) and hyperoxyles (HO$_2$$^{\bullet}$) radicals which then react on organic matter. Since iron is the most active and most abundant metal in phosphoric acid, it can intervene with H$_2$O$_2$ to form Fenton's reagent.

To test this hypothesis, the effect of some operating parameters on the kinetics of H$_2$O$_2$ decomposition in aqueous solutions of phosphoric acid (28% wt P$_2$O$_5$) containing ferrous ion as a catalyst at concentrations similar to the ones naturally present as impurities in industrial phosphoric acid (28% P$_2$O$_5$) and in absence of organic matter was investigated.

Material and methods

The experimental set up is given in Fig. 1. It contains: (1) Sort ball neck (reactor) borosilicate glass 500 ml volume. (2) A condenser to prevent evaporation of the reaction medium and maintaining constant the content of P$_2$O$_5$. (3) A heater thermally regulated flask to set the desired temperature. (4) Thermometer. (5) A syringe to introduce the oxidant and take samples.

The experiments are performed on 200 ml of an aqueous solution of pure phosphoric acid. After heating the solution to the desired temperature, a well-determined amount of powdered iron salt is added with magnetic stirring. After dissolution of the iron salt, hydrogen peroxide is introduced progressively at a definite dose. During the reaction, the samples shall be made to dose the residual H$_2$O$_2$ by iodometric method. This method is designed for the determination of low levels of hydrogen peroxide (0.1%–5%) in aqueous solutions. Hydrogen peroxide in the sample reacts with excess potassium iodide in the presence of an ammonium molybdate catalyst to produce triiodide ions, which are subsequently titrated with a standard thiosulfate solution.

Results and discussion

In this section, we determined, first, the order of the reaction, and second, the effect of some operating parameters on the catalytic decomposition of H$_2$O$_2$ in the presence of Fe^{2+}. The choice of ca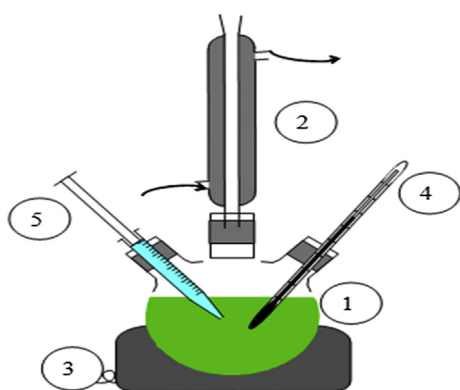talyst is justified by the fact that iron salts are most commonly used to catalyze the decomposition of H$_2$O$_2$ and are among the most abundant metals in industrial phosphoric acid.

Kinetic order

Although the decomposition of H$_2$O$_2$ is very complex, it has been shown that under certain operating conditions, the kinetics of decomposition of H$_2$O$_2$ can be described by a kinetic of pseudo-first order [15,16]: Eq. (1).

$$\frac{d[H_2O_2]}{dt} = -k_{apexp}[H_2O_2] \tag{1}$$

here k_{apexp}: the apparent rate constant of the first order t: reaction time and [H$_2$O$_2$]: the concentration of hydrogen peroxide at time t. After integration we obtain Eq. (2):

$$\ln\left(\frac{[H_2O_2]_0}{[H_2O_2]}\right) = k_{apexp}t \tag{2}$$

where [H$_2$O$_2$]$_0$: initial concentration of hydrogen peroxide.

Moreover, this approach is also used to describe the kinetics of catalytic oxidation of organic compounds by H$_2$O$_2$ [15,16].

Monitoring the concentration of H$_2$O$_2$ over time is presented in Fig. 2 under the following operating conditions: [H$_2$O$_2$] = 0.1 mol/L, [Fe^{2+}] = 0.037 mol/L, T = 60 °C.

The use of this figure can draw ln([H$_2$O$_2$]$_0$/[H$_2$O$_2$]) versus time is shown in Fig. 3.

The curve is a straight line with a correlation coefficient R^2 = 0.99 implying that the kinetics of decomposition of H$_2$O$_2$ in the presence of ferrous ion is pseudo-first order.

The role of Fe^{2+} concentration

The level of concentrations of Fe^{+2} used in this study is similar to the ones naturally present as impurities in industrial phosphoric acid (28% P$_2$O$_5$). As shown in Fig. 4, the decomposition of hydrogen peroxide is very sensitive to the concentration of Fe^{2+}. A significant increase in the rate of decomposition was observed by increasing the dose of iron. In fact, 50 min is sufficient to completely decompose hydrogen
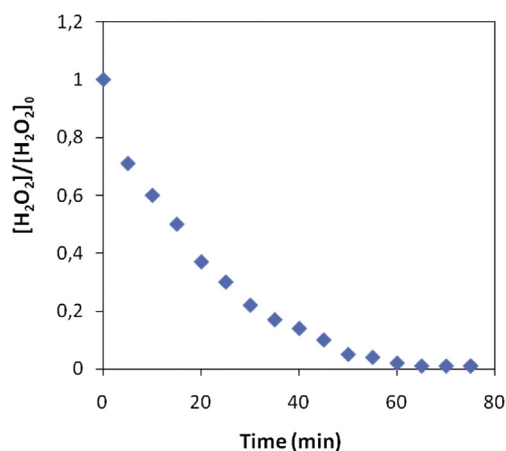

Fig. 1 – Experimental setup.

Fig. 2 – Evolution of the H$_2$O$_2$ concentration versus time ([H$_2$O$_2$] = 100 mmol/L, [Fe^{2+}] = 37 mmol/L and T = 60 °C).