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Determination of Iron (III) and Vanadium (IV) by Its Catalytic Effect on the Oxidation of some Environmental Pollutants with H_2O_2

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ABSTRACT

In this project the UV/H_2O_2, UV/H_2O_2/Fe (III) and UV/H_2O_2/V (IV) processes have a grate importance because of their high rates in eliminating the pollutants and can be used in purification of sewages of chemical industries. In this research, photo catalytic destruction of some environmental pollutants such as methyl orange, methyl green and methyl blue as organic samples in sewages of chemical industries in presence of photo catalysts was investigated. The effect of different parameters such as the period of photo radiation, amount of photo catalyst, pH and temperature were investigated. Results showed that these chromogenic organic materials are decomposable in presence of hydrogen peroxide and ultraviolet radiation (UV) from mercury lamp (400 W) and also photo destruction process. Elimination of methyl orange, methyl green and methyl blue in absence of hydrogen peroxide and in effect of direct photo destruction is low and in absence of ultraviolet radiation is very low. The effect of environment pH was also investigated in all reactions and in all cases the optimum amount of pH was 7. In all reactions, it was observed that temperature has no significant effect on these reactions and destruction reaction is carried out well in room temperature. The kinetic investigations showed that the kinetics of these reactions follows the modified model of Langmiur-Hinshel Wood and first order rate rule. Finally the first order rate constant of photo catalytic destruction reaction of these materials were compared using the UV/H_2O_2, UV/H_2O_2/Fe (III) and UV/H_2O_2/V (IV) photo catalyst. Results showed that in all cases, the rate constant of destruction reaction in presence of UV/H_2O_2/Fe (III) is very more than the rate constant of reaction in presence of UV/H_2O_2/V (IV) and UV/H_2O_2 so the method of photo catalytic oxidation of methyl orange, methyl green and methyl blue using the photo catalyst of UV/H_2O_2/Fe (III) can be applied as a practical and useful method for elimination of these pollutants from environment.

Keywords: UV/H_2O_2, photo catalysts; Photo catalytic destruction;

INTRODUCTION

In different industries such as chemical and weaving industries and etc, existence of environmental pollutants is a basic problem and a proper purification is needed for eliminating these compounds[1]. Today using of rapid methods with high efficiency and small process volume is an important issue. In this regard, the method of photo chemical decomposition by photo catalyst is applied vastly[2].

In this research, the UV/H_2O_2, UV/H_2O_2/Fe (III) and UV/H_2O_2/V (IV) processes have a special importance because of their high speed in eliminating the pollutant materials and they can be used in purification of chemical industries sewages[3]. In this project, the organic compounds such as methyl orange, methyl green and methyl blue have been selected as the existed organic sample in chemical industries sewages[4]. Results show that these chromogenic organic materials are decomposable in presence of hydrogen peroxide and UV radiation from mercury lamp (400 W) and also photo destruction process[5]. Elimination of methyl orange, methyl green and methyl blue were investigated in absence of H_2O_2 and in effect of photo destruction process and in absence of UV radiation and in UV/H_2O_2 process, deferent parameters such as the period of UV radiation, amount of H_2O_2 and the primary concentration of sample were studied [6]. In this regard the effect of various parameters such as the period of UV radiation, amount of H_2O_2, the primary concentration of dye and different amounts of UV/H_2O_2, UV/H_2O_2/Fe (Ⅲ) and UV/H_2O_2/V (Ⅳ) were investigated[7].

MATERIALS AND METHODS

Materials

All materials containing H_2O_2, $FeCl_3$, Fe $(NO_3)_3$, $VOSO_4$, vanadium nitrate, methyl orange ($C_{14}H_{14}N_3NaO_3S$), methyl green ($C_{26}H_{33}N_3Cl_2$), methyl blue ($C_{37}H_{27}N_3Na_2O_9S_3$), $NaH_2PO_4.2H_2O$ and NaOH were obtained from Fluka, Merck and Aldrich Companies. Double distilled water was used for preparing the buffers and all solutions were freshly prepared and used.

Apparatuses

The spectra were recorded by Cary 100 Scan UV-Vis-NIR double beam spectrophotometer equipped by temperature regulation system. Weighing was carried out by an AE 160 balance from Mettler Company. Regulation of pH was carried out by an F-12 pH-meter from Metrohm Company.

Preparing the stock solution of methyl orange, methyl green and methyl blue

The 1mM solutions of methyl orange, methyl green and methyl blue in water were prepared and these solutions were used for preparing the standard solutions.

Efficiency of methods

The method of adding the standard was used in order to determining the efficiency of preparation methods of samples and the concentration of added standards in sample texture was determined and the efficiency of methods was calculated. In this regard, three 50 ml flask were charged with 25 ml of unknown solution and 10 ml of standard (20 µg/l) was added to second flask and 10 ml of standard (40 µg/l) was added to third flask and amounts of methyl orange, methyl green and methyl blue of samples for each method was determined.

Repeatability (Precision)

In order to investigating the precision of analysis method, the samples were analyzed in several successive days and for several times in a day and each solution were freshly prepared and used. Results showed that the instrument has a proper precision and repeatability (Figs. 1-3).

Preparing the 1mM buffer solution of phosphate

Ingredients of this buffer are K_2HPO_4 as basic salt and KH_2PO_4 as acidic salt. In order to preparing the 1 liter of this solution, a 1000 ml flask was charged with 0.676 gr K_2HPO_4 and 0.0414 gr KH_2PO_4 and the pH of solution was regulated at pH=7 using the concentrated solution of NaOH and HCl.

Experimental methods

In order to determining the maximum wavelength, the absorption spectrum of dye solution (20 mg/l) was plotted in limit of 200-850 nm by spectrophotometer. The absorption spectrum of methyl orange, methyl green and methyl blue solutions have the maximum wavelength at 631, 500 and 675 nm respectively. After determining the maximum wavelength, different solutions with different concentrations of methyl orange, methyl green and methyl blue were prepared and their absorptions were determined at 631, 500 and 675 nm and the calibration curve was plotted.

Photo destruction of methyl orange, methyl green and methyl blue in absence of photo catalyst

In order to investigating the amount of photo destruction of methyl orange, methyl green and methyl blue by UV radiation and in absence of photo catalyst, 50 ml of each solution with concentrations of $5*10^{-4}$ mM of methyl orange, methyl green and methyl blue were prepared. Distance of liquid surface from lamp was regulated at 14 cm. The pH of solution was 7 and the time of UV radiation was 40 minutes. For determining the photo destruction percent of methyl orange, methyl green and methyl blue, their absorption were determined before and after radiation at 631, 500 and 675 nm.

Photo destruction of methyl orange, methyl green and methyl blue in presence of photo catalyst

In order to investigating the amount of photo destruction of methyl orange, methyl green and methyl blue in presence of UV/H_2O_2/Fe (Ⅲ) and UV/H_2O_2/V (Ⅳ) photo catalysts, 50 ml of each solution with concentrations of $5*10^{-4}$ mM of methyl orange, methyl green and methyl blue were prepared. Distance of liquid surface from lamp was regulated at 14 cm. The pH of solution was 7 and the time of UV radiation was 40 minutes. 20 ml of V (Ⅳ) and Fe (Ⅲ) solutions with concentration of $2*10^{-2}$ mM were added separately as catalyst. For determining the photo destruction percent of methyl orange, methyl green and methyl blue in presence of UV/H_2O_2/Fe (Ⅲ) and UV/H_2O_2/V (Ⅳ) photo catalysts, their absorption were determined before and after photo destruction process at 631, 500 and 675 nm by spectrophotometer.

The effect of methyl orange, methyl green and methyl blue concentration

In order to investigating the effect of methyl orange, methyl green and methyl blue concentration on the apparent rate of photo destruction, different solutions of methyl orange, methyl green and methyl blue with different concentrations of $1*10^{-4}$, $2*10^{-4}$, $3*10^{-4}$, $4*10^{-4}$ and $5*10^{-4}$ mM were prepared. The photo destruction percent of pollutant versus concentration of pollutant were investigated in similar conditions of lamp distance to solution surface, amount of photo catalyst, the period of radiation and the volume of pollutant solution.

The effect of photo catalyst amount on the elimination of methyl orange, methyl green and methyl blue

In order to investigating the effect of photo catalyst amount on the elimination of methyl orange, methyl green and methyl blue, different concentrations of photo catalysts were used while other conditions were constant.

The effect of pH on the photo destruction of photo catalysts

In order to investigating the effect of pH on the photo destruction of photo catalysts, solutions of methyl orange, methyl green and methyl blue with concentration of $5*10^{-4}$ mM were prepared in presence of UV/H_2O_2/Fe (Ⅲ) and UV/H_2O_2/V (Ⅳ) photo catalysts at different pHs of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13 and other conditions were kept constant. Results showed that the optimum pH for photo destruction of photo catalysts in order to elimination of methyl orange, methyl green and methyl blue was 7.

The effect of temperature on the photo destruction of photo catalysts for elimination of methyl orange, methyl green and methyl blue

In this regard, the solutions of methyl orange, methyl green and methyl blue pollutants with concentration of $5*10^{-4}$ mM in presence of UV/H_2O_2/Fe (Ⅲ) and UV/H_2O_2/V (Ⅳ) photo catalysts were prepared and other conditions were kept constant. The photo destruction of photo catalysts was carried out at different temperatures of 20, 25, 30, 35, 40 and 45°C. Results showed that these reactions have a low dependence on temperature and destruction process is performable in room temperature.

RESULTS AND DISCUSSION

Investigating the effect of photo catalysts on the photo destruction process of methyl orange, methyl green and methyl blue

In this regard, photo destruction of methyl orange, methyl green and methyl blue was carried out in absence and in presence of photo catalyst for 60 minutes. Their results are shown in Figs. 1-3 and table 1. We can calculate the apparent rate constant of photo destruction process from relation stated as below:

$$\text{Ln}([C]/[C_0]) = -k_{ap}\, t$$

Where $[C_0]$ is primary concentration of pollutant, $[C]$ is concentration of pollutant after radiation, t is the time of radiation and k_{ap} is apparent rate constant of photo destruction process. With monitoring the changes of Ln([C]/[C_0] in absence and in presence of photo catalysts, the apparent rate constant (k_{ap}) of photo destruction of methyl orange, methyl green and methyl blue was calculated in absence and in presence of photo catalyst in 60 minutes (see Fig. 3 and Table 2). The results of rate constant indicate the photo catalytic effect.

The efficient role of UV ray and H_2O_2 solution was investigated separately and contemporary in UV/H_2O_2 process. As we see in Figs. 1-3, when the photo destruction solutions of methyl orange, methyl green and methyl blue containing H_2O_2 are placed in dark place, the photo destruction is very low and when a solution of dye without H_2O_2 is placed exposed to the UV radiation, the photo destruction process increased slightly and when the solutions of methyl orange, methyl green and methyl blue containing H_2O_2 are placed exposed to the UV radiation, the elimination percent increased highly (table 1). The reason is related to creating of hydroxyl radicals in effect of H_2O_2 photolysis under the UV radiation. Fig. 4 shows that with increasing the H_2O_2 amount, the elimination efficiency increased so that methyl orange, methyl green and methyl blue solutions with concentration of 40 ppm and in presence of 20 mM $H_2O_2$are eliminated completely during 50 minutes. Also according to this Figure, increasing the concentration of H_2O_2 from a special limit does not have so much effect on the dye elimination and reason of this issue is due to further composition of hydroxyl radicals so the optimum amount of H_2O_2 in UV/H_2O_2 process is 20 mM. According to Fig. 4, with constant amount of H_2O_2 and when the other conditions are constant, with increasing the dye concentration, amount of dye elimination decreased highly and its reason is due to equal amount of produced hydroxyl for all samples so for samples with low concentration of pollutant, the rate of decomposition is high.

According to linearity of Ln ([C]/ [C_0]) variations versus time and high linear correlation of diagram we can conclude that the equation of dye decomposition rate in UV/H_2O_2 process is first order. The results of rate constant in table 2 indicate the photo catalytic effect. Obtained results show that UV/H_2O_2, UV/H_2O_2/Fe (Ⅲ) and UV/H_2O_2/V (Ⅳ) processes are able to elimination of methyl orange, methyl green and methyl blue from pollutant waters and this action is due to production of oxidant factors such as hydroxyl radicals. Amount of dye decomposition is in effect of H_2O_2, Fe (Ⅲ) and V (Ⅳ) amount, primary concentration of dye and period of UV radiation.

Table1. Photo destruction amount of pollutants in absence and in presence of photo catalyst

Kind of process	Photo destruction of methyl orange	Photo destruction of methyl green	Photo destruction of methyl blue
UV/H_2O_2	15%	10%	5%
UV/H_2O_2/V(Ⅳ)	25%	15%	10%
UV/H_2O_2/Fe(Ⅲ)	45%	35%	25%

Table2. Apparent rate constant (k_{ap}) of photo destruction reaction of pollutants in absence and in presence of photo catalyst

Kind of process	k_{ap} of methyl orange (min^{-1})	k_{ap} of methyl green (min^{-1})	k_{ap} of methyl blue (min^{-1})
UV/H_2O_2	0.0631	0.0539	0.0249
UV/H_2O_2/V(Ⅳ)	0.2156	0.1590	0.0985
UV/H_2O_2/Fe(Ⅲ)	0.3314	0.2263	0.1638

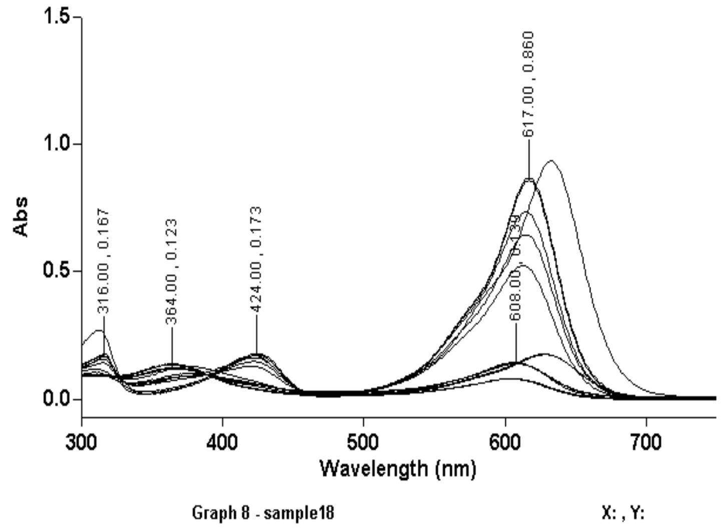

Fig1. The absorption spectrum of methyl green in 1 mM buffer (pH=7) and in 25°C using UV/H_2O_2/V (Ⅳ) photo catalyst

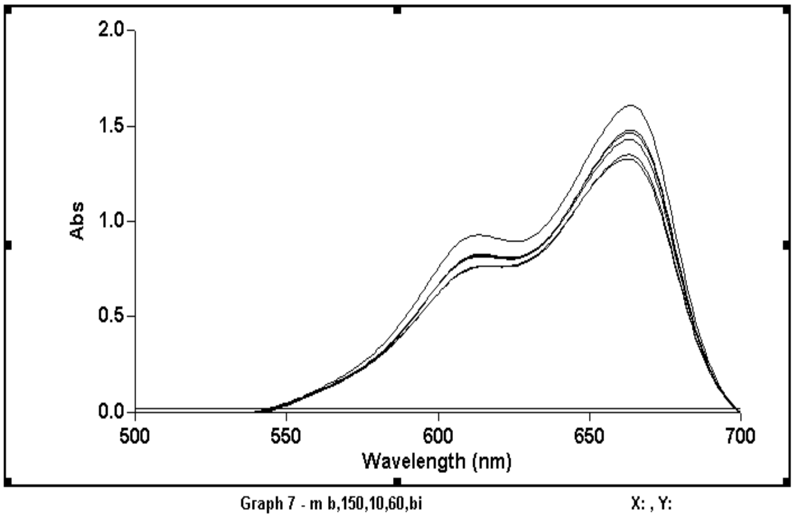

Fig2.The absorption spectrum of methyl blue in 1 mM buffer (pH=7) and in 25°C using UV/H_2O_2/V (IV) photo catalyst

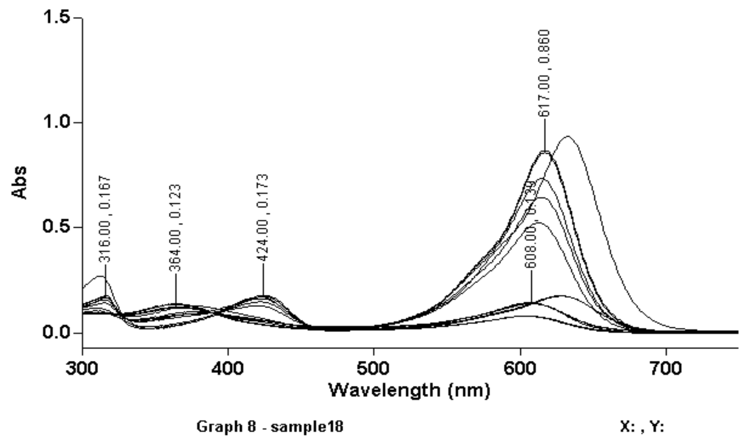

Fig3.The absorption spectrum of methyl orange in 1 mM buffer (pH=7) and in 25°C using UV/H_2O_2

The effect of different parameters such as period of photo radiation, amount of photo catalyst, pH and temperature was investigated and results showed that this chromogenic organic materials are decomposable in presence of hydrogen peroxide and ultraviolet radiation (UV) from mercury lamp (400 W) and also photo destruction process. Elimination of methyl orange, methyl green and methyl blue in absence of H_2O_2 and in effect of direct photo destruction is low and in absence of UV radiation is very insignificant. The effect of environment pH was investigated in all reactions and the optimum pH was 7. About the effect of temperature on the photo catalytic destruction of methyl orange, methyl green and methyl blue, it was observed that these reactions have a very low dependence on temperature and destruction reaction can be also carried out in room temperature very well. The kinetic investigations showed that the kinetics of these reactions follows the modified model of Langmiur-Hinshel Wood and first order rate rule. Finally a comparison was carried out between first order rate constant of photo catalytic destruction reaction of these materials using the UV/H_2O_2, UV/H_2O_2/Fe (III) and UV/H_2O_2/V (IV) photo catalyst. Results showed that in all cases, the rate constant of destruction reaction in presence of UV/H_2O_2/Fe (III) is very more than the rate constant of reaction in presence of UV/H_2O_2/V (IV) and UV/H_2O_2 so the method of photo catalytic oxidation of methyl orange, methyl green and methyl blue using the photo catalyst of UV/H_2O_2/Fe (III) can be applied as a practical and useful method for elimination of these pollutants from environment.

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