The vanadium-substituted heteropolytungstate catalyzed oxidation of the organic dye by H_2O_2 in an aqueous solution

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Abstract

The main objective of this work is to study the oxidation of the acid orange 7 (AO7) in an aqueous solution by using the hydrogen peroxide in the presence of vanadium substituted heteropolytungstate ($\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62}$)^{6−} as a catalyst. The effects of various experimental parameters on the oxidation reaction of the dye were investigated. And they are as follow: The H_2O_2 concentration, the mass of the catalyst, and the dye concentration. The optimum conditions were determined. In addition, it was found that the efficiency of the degradation is obtained after 80 min of reaction, and it was about 100%. The optimal parameters were: initial pH = 4; $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$; catalyst mass = 0.05 g; for a concentration of the dye $[\text{AO7}]_0 = 2 \text{ mg/L}$. The kinetic oxidation of the AO7 by this catalytic system was also elucidated and based on experimental data. The oxidation of the AO7 follows a pseudo second-order Kinetic model. The activation energy, as well as the activation enthalpy and the entropy were calculated by using respectively the Arrhenius and the Eyring equations. The oxidation of the AO7 by the H_2O_2 and the ($\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62}$)^{6−} requires a small amount of energy and has an endothermic nature.

Keywords The Vanadium-substituted heteropolyanions · A homogeneous catalysis · The azo dyes · The hydrogen peroxide · A kinetic and thermodynamic study · The water treatment

1 Introduction

The metal-substituted heteropolyanions (HPAs) which is based on the Well-Dawson [1] and the Keggin structures [2] are of a great interest in the catalysis and other applications in different areas such as medicine, materials science, separation and imaging [3, 4].

And among the various metal-substituted heteropolyanions, vanadium-substituted heteropolyanions is extensively investigated in terms of synthesis, characterizations and applications [5]. In addition, a possible role of polyoxovanadates as an anti-tumor and anti-viral agents is being investigated [3]. The Vanadium-substituted heteropolyanions are good catalysts; they have proved their effectiveness in many reactions of the oxidation. For example,

the Dawson-type vanadium-substituted heteropolyanions: $[\text{P}_2\text{V}_2\text{W}_{16}\text{O}_{62}]^{8-}$ ($\text{P}_2\text{V}_2\text{W}_{16}$), $[\text{P}_2\text{MoV}_2\text{W}_{15}\text{O}_{62}]^{8-}$ ($\text{P}_2\text{MoV}_2\text{W}_{15}$) and $[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{9-}$ ($\text{P}_2\text{V}_3\text{W}_{15}$) is used as electrocatalysts for oxidation of the L-cysteine on a glassy carbon [6].

The vanadium-substituted heteropolyacids $\text{H}_4\text{PMo}_{11}\text{VO}_{40} \cdot 12\text{H}_2\text{O}$ is also used as a catalyst for the oxidation of the benzene, the toluene, and the phenol [7].

In this study, the oxidation of the Acid Orange 7 dye (AO7) by H_2O_2 , is studied by using the vanadium-substituted heteropolyanion ($\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62}$)^{6−} (V(IV)-HPA) as a catalyst. This species which having been the subject of an effective use in the electrocatalytic oxidation of the NADH [8]. In fact, this reaction is a part of the depollution of water, and in particular to the treatment of the

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discharged water by the textile industry which is soiled by the organic dyes.

In the textile industry, the main pollution source of waste water comes from dyeing and finishing. At present, there are several methods such as the adsorption, the chemical flocculation, the UV photooxidation, and the ozonation that are for the treatment of the textile pollutants [9].

The application of the biological process in the treatment of the textile waste water is reported extensively. However, there is a practical limit to the degree of the organic removal and the colour removal in addition to the inability of the biological treatment processes in removing the nonbiodegradable substances. The Catalytic oxidation, using a Dawson type heteropolyanion, is an alternative for the treatment of the industrial waste water containing non-biodegradable organic pollutants. The Fe(III)-substituted heteropolyanions " $\text{HFe}_{2.5}\text{Mo}_6\text{P}_2\text{W}_{18}\text{O}_{62}\cdot 23\text{H}_2\text{O}$ " and the " $\text{HFe}_{2.5}\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}\cdot 22\text{H}_2\text{O}$ " are used as catalysts in Fenton-like oxidation of the methyl violet dye, although the reaction is favored in the acidic medium. The same catalysts were used for the oxidation of the Acid yellow 99 and the acid orange 7 by H_2O_2 [10, 11]. However, there were no research reports done before on application of the vanadium-substituted heteropolyanion $(\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62})^{6-}$ as a catalyst for the oxidation of the organic compounds by the hydrogen peroxide.

The Acid Orange 7 was chosen as a dye model, as it displays the «core-structure» of a number of commercial dyes and thus having similar physicochemical properties as more complex dye compounds [9]. The Acid Orange 7 (also known as Orange II) is one of the dyes that are produced in large amounts in the world. It is commonly used in pharmaceutical, food, and cosmetics industries. The Acid Orange 7 is an azo dye; it is used in the dyeing of silk and wool. For these characteristics, the Acid Orange 7 is much used in the textile industry. The molecular structure of the azo-dye Orange II is shown in Fig. 1.

The main objective of this study is the investigation of the oxidation efficiency of the Acid Orange 7 by H_2O_2 by using $(\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62})^{6-}$ as a catalyst. Many important variables such as the solution pH, the catalyst mass, the concentration of H_2O_2 and the initial dye concentration were examined. And for better understanding the phenomena, the Kinetic and the thermodynamic are studied.

Fig. 1 Chemical structure of orange II

2 The material and the method

2.1 The synthesis of the heteropolyanion $(\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62})^{6-}$

The substituted heteropolyanion $(\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62})^{6-}$ were prepared according to the method presented in the literature [10] starting from the lacunary compound $(\alpha_1\text{P}_2\text{W}_{17}\text{O}_{62})^{6-}$ according to the following protocol:

To 160 mL of 0.5 M HCl it was added 10 mL of 0.5 M NaVO_3 , (5 mmol) of $(\alpha_1\text{P}_2\text{W}_{17}\text{O}_{62})^{6-}$. In some times, the solution was not quite clear so that it was filtered on a filter paper. Then 25 g of KCl was added to the filtrate. The precipitate was filtered off and then recrystallized from the minimum amount of 0.1 M HCl.

The anal Calcd for $(\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62})^{6-}$: K, 5.67; V, 1.06; W, 64.7. It was found that: K, 5.80; V, 1.1; W, 63.3.

$(\alpha_1\text{P}_2\text{W}_{17}\text{O}_{62})^{6-}$ and $(\alpha\text{P}_2\text{W}_{18}\text{O}_{62})^{6-}$ were prepared according to the methods described in the literature [11, 12]. Figure 2 shows the step of the synthesis of $(\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62})^{6-}$ from $(\alpha\text{P}_2\text{W}_{18}\text{O}_{62})^{6-}$.

2.2 The reagents of the oxidation

The 4-(2-hydroxy-1-naphthylazo) the benzene sulfuric acid sodium salt, which is commonly named the orange II or the acid orange 7 (AO7) (90%) was obtained from the Aldrich. H_2O_2 the latter was purchased from the Aldrich Chemical Company. All the other reagents (NaOH or H_2SO_4) used in this study were of an analytical grade.

2.3 The procedure: analysis

In all the reactions 0.1 L of the aqueous (AO7) solution containing the appropriate quantity of the catalyst and the H_2O_2 was magnetically stirred at a room temperature. pH solution was adjusted by using the 0.1 N H_2SO_4

Fig. 2 Preparation of $(\alpha_1 P_2W_{17}VO_{62})^{6-}$ from $(\alpha P_2W_{18}O_{62})^{6-}$ [10]

or the NaOH aqueous solutions. The initial concentration of the (AO7) solution was of 10 mgL^{-1} for all the experiments, except for those carried out to examine the effect of the initial dye concentration. The degradation process of the azo dye solution was monitored and based on the decay of the absorbance (A) at a maximum wave-length ($\lambda_{\text{max}} = 486 \text{ nm}$) [13] of AO7 by measuring the absorbance with 6705 UV visible spectrophotometer JENWAY.

2.4 The effects of the operational parameters on the AO7 oxidation

The oxidation of the AO7 by H_2O_2 using the $(\alpha_1 P_2W_{17}VO_{62})^{6-}$ as a catalyst is studied according to the following factors: the initial pH of the solution, the H_2O_2

concentration, the catalyst mass, and the dye concentration. The oxidation efficiency (discolouration) was determined as it is shown below:

$$DE = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

DE: The discoloration efficiency, C_i : the Initial dye concentration, C_f : the final dye concentration.

3 The results and the discussion

3.1 The characterization of the complexes by the infra-red spectroscopy

The vibrational spectroscopy infrared is a means of a quick check of the structure of a given heteropolyanion compound [13].

IR spectra were recorded on KBr pellets using a Shimadzu FTIR-8400s spectrophotometer. Figure 3 shows a comparison of the IR characteristics of a main heteropolyanions synthesized in this work. The lacunary compound spectra is characterised by the presence of a weak supplementary located at 1100 cm^{-1} . *Deltchev* and *Thouvenot* have shown that the existence of a band corresponds to a major disturbance in a direction of the tetrahedron PO_4 : And here is the direction of the vacancy [14]. This band disappears for the complex $\alpha_1\text{P}_2\text{W}_{17}\text{V}$; the region of the P–O band becomes similar to that observed in the spectrum of the saturated species $\alpha\text{P}_2\text{W}_{18}$. This leaves a suggestion that the vanadium fills the gap.

Fig. 3 IR spectra of synthesized heteropolyanions

3.2 The oxidation of the AO7 by the H_2O_2 in presence of the $(\alpha_1\text{P}_2\text{W}_{17}\text{VO}_6)^{6-}$ as a catalyst

3.2.1 The effect of the solution pH

In order to find the optimum pH for the oxidation of the AO7, a series of experiments was conducted at an initial pH values in the range 3–10. For more acidic pH (< 3) there is a risk of the dimerization of the catalyst [4], while for the pH above 10, the catalyst is likely to deteriorate [4]. Figure 4 shows the variation of the discoloration efficiency over time and under the following experimental conditions: (the AO7 concentration is 10 mg L^{-1} , $[\text{H}_2\text{O}_2] = 1\text{ mM}$, catalyst mass = 0.08 g).

Figure 4 illustrates the effect of the pH on the discoloration efficiency of the AO7 in water. It was found that the discoloration efficiency of the AO7 is strongly dependent pH. The optimal pH is about 4 giving discoloration efficiency equal to 54.67%. This result can be explained by the stability of the catalyst at this pH [5]. And at a neutral pH, the discoloration efficiency decreases (23.44% is reached after 25 min of treatment).

In addition, the H_2O_2 molecules are unstable in alkaline solution therefore, the degradation of dye decreases in alkaline solution [15]. In alkaline solution, the degradation of the dye decreases (12.56% is reached after 25 min of the treatment at pH = 8 and 08.25% is reached after 25 min of treatment at pH = 10). This result can be explained by the instability of the H_2O_2 , so the molecules are unstable in the alkaline solution [16–18] therefore, the degradation of dye decreases in the alkaline solution. And the optimal value chosen is pH = 4.

Fig. 4 Effect of solution pH on AO7 oxidation ($C_0 = 10\text{ mg L}^{-1}$, $m(\alpha_1\text{P}_2\text{W}_{17}\text{V}) = 0.08\text{ g}$, $[\text{H}_2\text{O}_2] = 1\text{ mM}$, $T = 25^\circ\text{C}$)

3.2.2 The effect of the catalyst mass and the possible reaction mechanism

The effect of the catalyst mass was investigated, keeping the operational parameters identical to those of the experiment mentioned above. The influence of different catalyst mass $[m(\alpha_1P_2W_{17}VO_{62})^{6-}] = [0\text{ g} - 0.2\text{ g}]$ on the decolorization efficiency of the (AO7) is illustrated in Fig. 5.

These results show that the discoloration efficiency of the AO7 oxidation increase when increasing the catalyst mass up to 0.05 g where the decolorization efficiency is optimal. Beyond this value, there is a decrease of the discoloration efficiency. The reaction of the mechanism

proposed for this type of reaction is based on the initial formation of the hydroperoxy radical $HO_2\cdot$ and $V(IV)$ -HPA by the hemolytic cleavage of H_2O_2 at the vanadium atom inside the HPA (Eq. 2), the reaction of H_2O_2 with $V(IV)$ -HPA leads to the formation of the $OH\cdot$ and the $V(V)$ HPA (Eq. 3).

The lower degradation efficiency ($\alpha_1P_2W_{17}VO_{62})^{6-}$ at a small mass is probably due to the lowest amount of the $OH\cdot$ radicals are producing a variable for oxidation. The

Fig. 5 Effect of catalyst mass on AO7 oxidation ($pH = 4$, $C_0 = 10\text{ mgL}^{-1}$, $[H_2O_2] = 1\text{ mM}$, $T = 25^\circ\text{C}$)

Fig. 6 Effect of initial H_2O_2 concentration on AO7 oxidation ($C_0 = 10\text{ mgL}^{-1}$, $pH = 4$, $m(\alpha_1P_2W_{17}V) = 0.05\text{ g}$, $T = 25^\circ\text{C}$)

negative influence of the higher catalyst mass on the discoloration efficiency can be explained by the fact that, when the mass of the catalyst is high, it can react with the $\text{HO}_2\cdot$ and finally reduce the consumption of the very reactive $\text{OH}\cdot$ radicals according to the following reaction:

3.2.3 The effect of the H_2O_2 concentration

The initial concentration H_2O_2 plays an important role in the catalytic oxidation of the AO7. The effect of the H_2O_2 concentration on the discoloration efficiency was investigated by varying the H_2O_2 dosage from 0.8 mM to 1.5 mM and the results are represented in Fig. 6.

The results show that the discoloration efficiency increases with the increase of H_2O_2 concentration up to a value equal to 1 mM, but above it ($C_{\text{H}_2\text{O}_2} = 1.5 \text{ mM}$) the discoloration efficiency decreases. In general, the degradation rate of the organic compounds increases as the H_2O_2 concentration increases until the critical H_2O_2 concentration is achieved. However, when a concentration is higher than the critical concentration is used, the degradation rate of organic compounds decreases, and as a result this is called the scavenging effect [15].

The high concentrated H_2O_2 solution undergoes a self quenching of the $\text{OH}\cdot$ radicals, with the formation of the hydroperoxyl radicals $\text{HO}_2\cdot$. Although the $\text{HO}_2\cdot$ is an effective oxidant in itself, its potential oxidation is much lower than that of $\text{OH}\cdot$ the radicals [19, 20].

According to the results shown above, the critical H_2O_2 concentration is about 1 mM.

3.2.4 The effect of the initial dye concentration

The study of the initial concentration effect of the acid orange 7 dye on the discoloration efficiency was carried out from a concentration of 2–30 mg/L.

The results are represented in Fig. 7. From Fig. 7, we can notice that the discoloration efficiency decreases with the increase of the initial concentration of the dye. This result is in good agreement with the literature [21, 22].

This phenomenon can be explained by the fact that increasing the initial concentration of the dye leads to an increase in the number of molecules of the (AO7), while the number of the hydroxyls radicals remain constant (H_2O_2 concentration and the catalyst kept constant), thereby causing a decrease in the discoloration efficiency [16, 17, 23, 24].

3.3 The UV–Vis absorbance spectra of the dye before and after oxidation

The degradation of the AO7 by H_2O_2 catalysed with $(\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62})^{6-}$ heteropolyanion can be well supported by the change in the UV–Vis absorption spectrum over the course of degradation (Fig. 8). The AO7 spectrum was characterized by the chromophore that contains the azo linkage [18] in the visible range at 484 and 430 nm corresponding

Fig. 7 Effect of initial dye concentration on AO7 oxidation (pH = 4, $m(\alpha_1\text{P}_2\text{W}_{17}\text{V}) = 0.05 \text{ g}$, $[\text{H}_2\text{O}_2] = 1 \text{ mM}$, $T = 25^\circ\text{C}$)

Fig. 8 UV-Vis spectra of AO7 water solutions during the oxidation of AO7 with $\alpha_1P_2W_{17}V/H_2O_2$ system ($C_0 = 2 \text{ mgL}^{-1}$, $\text{pH} = 4$, $m(\alpha_1P_2W_{17}V) = 0.05 \text{ g}$, $[H_2O_2] = 1 \text{ mM}$, $T = 25^\circ\text{C}$)

Fig. 9 Plot of first-order

to the hydrazone and the azo form. In the ultraviolet region, the absorbance, which peaks at 230 and 310 nm, are due to respectively the benzene and the naphthalene rings. These four characteristic bands were markedly weakened during the degradation reaction, tending to disappear completely after 80 min, without the appearance of new absorption bands in the visible or the ultraviolet regions and this is due to the destruction of the chromophoric and the auxochromic structures of the oxidation reaction.

3.4 The kinetics oxidation and a thermodynamic study

3.4.1 The kinetics oxidation

In order to investigate the kinetics reaction, the oxidation reaction of the AO7 by H_2O_2 and the $(\alpha_1P_2W_{17}VO_{62})^{6-}$ was conducted with three different initial concentrations of the dye concentration ($C_1 = 5 \text{ mgL}^{-1}$; $C_2 = 10 \text{ mgL}^{-1}$; $C_3 = 20$

mgL⁻¹), and each one at three different temperatures (25 °C, 35 °C and 45 °C). The catalyst mass and the H₂O₂ concentration were maintained constant (0.05 g, 1 mgL⁻¹); and the pH was adjusted to 4.

For each experiment the absorbance is measured by a spectrophotometer, and then the dye concentration in the solution was calculated. The general law of the reaction rate is defined as:

$$V = \frac{dC}{dt} = k[C]^n \quad (8)$$

where k is the rate constant and n refers to the order of the reaction.

And, by integration, the law rate of the first-order reaction can be written as follows:

$$\ln C = \ln C_0 - kt \quad (9)$$

The law rate of the second-order reaction can be written as follows:

$$\frac{1}{C} = \frac{1}{C_0} + kt \quad (10)$$

A plot of $\ln C$ in function of time for the three concentrations is shown in Fig. 9.

A plot of $1/C$ in function of time for the three concentrations is shown in Fig. 10.

We draw the curves for the three concentrations to define the order of the reaction.

The results from Figs. 9 and 10 of R^2 show that the oxidation of the AO7 by H₂O₂ catalysed by $(\alpha_1P_2W_{17}VO_{62})^{6-}$ follows the second-order kinetics.

3.4.2 The thermodynamic study

To understand the effect of the temperature on the degradation of the studied dye, the different thermodynamic parameters were calculated including the activation energy E_a , enthalpy ΔH^* , ΔS^* entropy.

The activation energy was calculated by using the Arrhenius equation:

$$k = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (11)$$

or

k is the coefficient rate, E_a is the activation energy of the reaction, R is the ideal gas constant (8.314 J/mol K), T is the temperature and A is the frequency factor.

The reactions do not obey all to the Arrhenius relation, before using this relation, it is important to check it. And to do this, the equation is transformed by taking the logarithm of each member:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad (12)$$

$\ln k$ is the plotted versus $1/T$ stands for the three temperatures (25 °C, 35 °C, 45 °C).

We observe that the points are well aligned, so the Arrhenius law is verified for this reaction, and the activation energy is calculated from the slope.

The activation enthalpy and the entropy were calculated using the Eyring equation in the thermodynamic formulation [25, 26]:

Fig. 10 Plot of second-order Fenton reaction

$$k = \frac{k_b \cdot T}{h} \exp\left(-\frac{\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right) \quad (13)$$

where ΔH^* is the activation enthalpy; ΔS^* is the activation entropy; k_b = the boltzman constant; h = the plank constant.

The Eq. (5) can be linearized as follows:

$$\ln \frac{k}{T} = \ln \frac{k_b}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R} \cdot \frac{1}{T} \quad (14)$$

The graph is plotted $\ln k/T = f(1/T)$ (Fig. 11).

The value of the apparent activation energy estimated from the linear regression in Fig. 11 is $E_a = 43.42$ kJ/mol. The linear regression of the $\ln k/T = f(1/T)$, which is shown in Fig. 12, allows the calculation of the activation enthalpy and the entropy values as $\Delta H^* = 40.86$ kJ/mol

and, $\Delta S^* = 103.17$ J mol⁻¹ K⁻¹, the Δ^* the positive value indicates that the uptake is endothermic.

4 Conclusion

This study introduces a simple homogenous catalytic approach for the degradation of the azo dye pollutants. The prepared Dawson heteropolyanion vanadium substituted, $(\alpha_1P_2W_{17}VO_{62})^{6-}$ was successfully used as a catalyst for the oxidation of the acid orange 7 dye (AO7) by H_2O_2 in an aqueous solution.

It is approximately 100% dye which is eliminated after 80 min on the following operating conditions: The optimal parameters were: initial pH=4; $[H_2O_2]_0 = 1$ mM; catalyst mass = 0.05 g; for a concentration of the dye

Fig. 11 Plot of $\ln k/T = f(1/T)$

Fig. 12 Lineaire regression of experimental data

[AO7]₀ = 2 mg/L. The oxidation of the AO7 follows pseudo second-order the Kinetic model.

The value of activation energy ($E_a = 43.42$ kJ/mol), activation enthalpy ($\Delta H^* = 40.86$ kJ/mol), and the entropy ($\Delta S^* = 103.17$ J mol⁻¹ K⁻¹). The oxidation of the AO7 by H₂O₂ and the ($\alpha_1\text{P}_2\text{W}_{17}\text{VO}_{62}$)⁶⁻ requires a small amount of energy and has an endothermic nature.

These data are in line with those previously reported, [27, 28]. The ΔS positive sign shows that the generation of the hydroxyl radicals is oriented to the catalyst-solution area.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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