



ELSEVIER

Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

## Comptes Rendus Chimie

[www.sciencedirect.com](http://www.sciencedirect.com)

Full paper/Mémoire

# Wells–Dawson polyoxometalates $[\text{HP}_2\text{W}_{18-n}\text{Mo}_n\text{O}_{62}]\text{Fe}_{2.5}$ , $x\text{H}_2\text{O}$ ; $n = 0, 6$ : Synthesis, spectroscopic characterization and catalytic application for oxidation of dyes

Ouahiba Bechiri<sup>a,\*</sup>, Mostefa Abbessi<sup>a</sup>, Robila Belghiche<sup>a</sup>, Lahcène Ouahab<sup>b</sup><sup>a</sup> Laboratoire de recherche génie de l'environnement, département de génie des procédés, faculté des sciences de l'ingénieur, université Badji Mokhtar, BP 12, Annaba, Algeria<sup>b</sup> Organométalliques et matériaux moléculaires, UMR 6226 CNRS – université de Rennes-1, sciences chimiques de Rennes, avenue du Général-Leclerc, 35042 Rennes cedex, France

## ARTICLE INFO

## Article history:

Received 26 March 2013

Accepted after revision 8 July 2013

Available online 3 September 2013

## Keywords:

Heteropolyanions  
Wells–Dawson-type  
Synthesis  
Characterizations  
Dyes  
Hydrogen peroxide  
Oxidation

## ABSTRACT

The synthesis, IR, <sup>31</sup>P NMR and cyclic voltammetry characterizations of new Wells–Dawson-type heteropolyanions that contain iron,  $\text{HFe}_{2.5}\text{P}_2\text{W}_{18}\text{O}_{62}$ ,  $23\text{H}_2\text{O}$  and  $\text{HFe}_{2.5}\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$ ,  $22\text{H}_2\text{O}$ , are reported. The catalytic activity of these compounds was evaluated through the oxidation of methyl violet dye, by hydrogen peroxide. The influence of different parameters such as the initial pH, the initial  $\text{H}_2\text{O}_2$  concentration, the catalyst mass, and the initial dye concentration have been studied.

© 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## 1. Introduction

Polyoxometalates (POMs) constitute a diverse class of inorganic oxo-metal clusters composed of early transition metals in their highest oxidation state [1]. They have a great deal of structural diversity and various applications in different areas, including catalysis, material sciences, medicine, and biology. Several types have been characterized, and each of them is defined by the M/X ratio used in the polycondensation under acidic conditions. The two best-known heteropolyanions are the Keggin-type  $[\text{X}^{\text{VI}}\text{M}_{12}\text{O}_{40}]^{(8-n)-}$  [2] and the Wells–Dawson type  $[(\text{X}^{\text{VI}})_2\text{M}_{18}\text{O}_{62}]^{(16-2n)-}$  [3] (Fig. 1).

Polyoxometalates with Dawson structure may be promising catalysts in homogeneous and heterogeneous

systems because their redox and acidic properties can be controlled at atomic and molecular levels. They are used not only in acid-catalyzed [4] reactions, but also in many oxidations of organic compounds [5,6]. Recently, the Dawson-type Fe(III)-substituted heteropolyanion  $(\alpha_2\text{P}_2\text{W}_{12}\text{Mo}_5\text{O}_{61}\text{Fe})^{7-}$  was successfully used as a catalyst for the oxidation of methyl orange dye (MO) by  $\text{H}_2\text{O}_2$  in aqueous solution [7]. This compound was synthesized by addition of iron on the lacunary heteropolyanion  $(\alpha_2\text{P}_2\text{W}_{12}\text{Mo}_5\text{O}_{62})^{10-}$  [8]. In this work, we have synthesized and characterized new heteropolyanions that contain iron  $\text{HFe}_{2.5}\text{P}_2\text{W}_{18}\text{O}_{62}$ ,  $23\text{H}_2\text{O}$  and  $\text{HFe}_{2.5}\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$ ,  $22\text{H}_2\text{O}$ , by addition of  $\text{Fe}^{3+}$  ions to the Dawson acid forms  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}24\text{H}_2\text{O}$  or  $\text{H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}24\text{H}_2\text{O}$ .

The catalytic activity of these compounds was evaluated through the oxidation of an aqueous dye, methyl violet (its structure is shown in Fig. 2) [9,10] by hydrogen peroxide.

Methyl violet (MV), of molecular formula  $\text{C}_{24}\text{H}_{28}\text{ClN}_3$ , is a triphenylmethane dye, soluble in water, ethanol,

\* Corresponding author.

E-mail address: [bechirio@yahoo.fr](mailto:bechirio@yahoo.fr) (O. Bechiri).

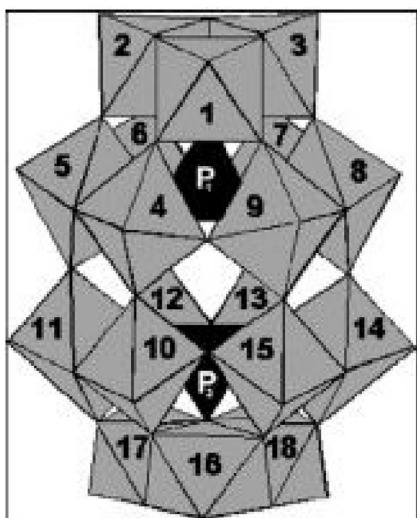


Fig. 1. Polyhedral representation of the polyanion Dawson structure.

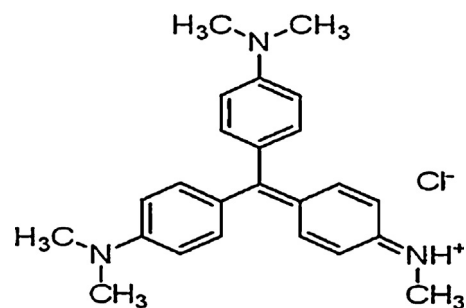


Fig. 2. Chemical structure of methyl violet.

methanol, diethylene glycol and dipropylene glycol. It is a dark green powder [11]. Methyl violets are the mixture of tetramethyl, pentamethyl, hexamethyl, and pararosani-lines. These dyes are chiefly used in heterogray and printing inks. They impart a deep violet colour in paint and printing ink. They are also used to obtain shades of deep colours that can be applied for the dyeing of cotton, silk, paper, bamboo, weed, straw and leather. Methyl violet dye is widely used in analytical chemistry laboratories as a pH indicator to test pH ranges from 0 to 1.6. The toxic information reveals that the dye may cause hard skin and eye irritation – it means that in case of physical contact with the dye, this causes an irritation with redness and pain. The dye is harmful if it is swallowed. Also, the inhalation of methyl violet may cause an irritation to the respiratory tract, whereas its ingestion causes an irritation to gastrointestinal tract [12]. Therefore, it is necessary to remove it from the waste water. The influence of different parameters such as initial pH, initial  $\text{H}_2\text{O}_2$  concentration, catalyst mass, and initial dye concentration has also been studied.

## 2. Experimental part

### 2.1. Preparation and characterization of catalysts

The heteropolyanions precursors  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$  and  $\text{H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62} \cdot 24\text{H}_2\text{O}$ , as well as their acids forms, were synthesized according to the published procedures [13,14], and their purity was confirmed by infrared and NMR  $^{31}\text{P}$  spectroscopies. IR spectra were recorded on KBr pellets using a spectrophotometer Shimadzu FTIR-8400s.  $^{31}\text{P}$  NMR spectra were recorded on a Bruker 2000 apparatus operating at 110 MHz in the Fourier-transform mode. The  $^{31}\text{P}$  shifts were measured in a  $10^{-3}$  M solution of polyanions in a  $\text{D}_2\text{O}$  solution and were referenced to  $\text{H}_3\text{PO}_4$  85%.

Cyclic voltammetry experiments were performed on an EDAQ e-corder 401 potentiostat. All experiments were carried out using a three-electrode cell configuration with

a glassy carbon working electrode, a saturated calomel reference electrode (SCE), and a platinum auxiliary electrode.

All experimental solutions were de-aerated thoroughly by bubbling pure  $\text{N}_2$  into the solutions for 10 min. All cyclic voltammograms were recorded at a scan rate of  $50 \text{ mV s}^{-1}$ . All experiments were performed at room temperature.

**$\text{HFe}_{1.5}\text{P}_2\text{W}_{18}\text{O}_{61} \cdot 23\text{H}_2\text{O}$  (1):** 5 g (1.088 mmol) of  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  were dissolved in 20 ml of water at room temperature and 0.767 g of solid  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  (3.26 mmol) was then added. The mixture was then stirred for 10 min. A yellow powder of (1) was obtained after five days by slow evaporation. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1092(s), 1025(w), 960(s), 909(s). NMR of (1):  $^{31}\text{P}$   $\delta = -12.43$  ppm. Anal. calcd. (found): P 1.27 (1.20); W 68.10 (62.05); Fe 1.72 (2.01).

**$\text{HFe}_{1.5}\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{61} \cdot 22\text{H}_2\text{O}$  (2):** 5 g (1.2 mmol) of  $\text{H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$  were dissolved in 20 ml of water at room temperature and 0.541 g (3.56 mmol) of solid  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  was then added. The mixture was stirred for 10 min. A dark yellow powder of (2) was obtained after five days by slow evaporation. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1084(s), 1025(w), 953(s), 912(s). NMR of (2):  $^{31}\text{P}$   $\delta = -8.82$  ppm. Anal. calcd. (found): P 2.13(1.87); W 76.08(74.03); Mo 19.80(18.70); Fe 1.92(3.01).

### 2.2. Procedure for catalytic oxidations

#### 2.2.1. Reagents

Methyl violet (MV) was supplied by Merck.  $\text{H}_2\text{O}_2$  was purchased from Aldrich. All other reagents ( $\text{NaOH}$  or  $\text{H}_2\text{SO}_4$ ) used in this study were of analytical grade.

#### 2.2.2. Procedure – analysis

The initial concentration of the MV solution was 10 mg/L for all experiments, except for those carried out to examine the effect of the initial dye concentration. In all experiments, 100 mL of MV solution containing the appropriate quantity of catalyst and  $\text{H}_2\text{O}_2$  was magnetically stirred at room temperature.

The pH of the reaction was adjusted by using 0.1 N  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$  aqueous solutions.

The MV concentration was measured by a Jenway UV–vis spectrophotometer. The wavelength that corresponds to the maximum absorbance is  $\lambda_{\text{max}} = 585 \text{ nm}$ . The resolutions of the wavelength and the bandwidth were 1 nm and 0.5 nm. The cell used during the experiments was made of 1-cm-thick quartz.

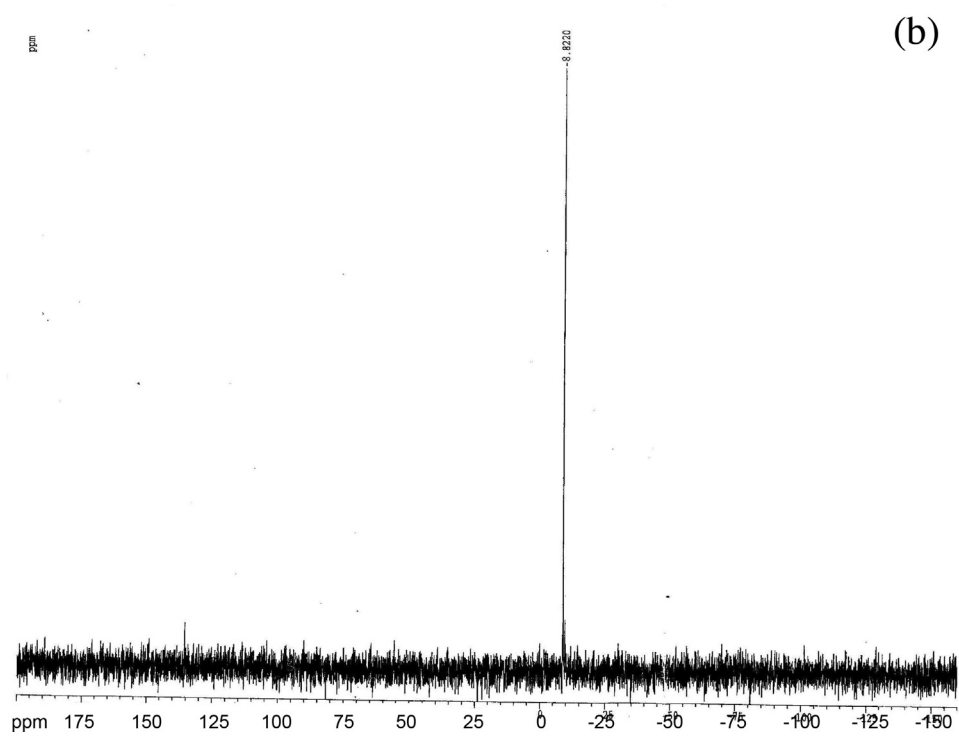
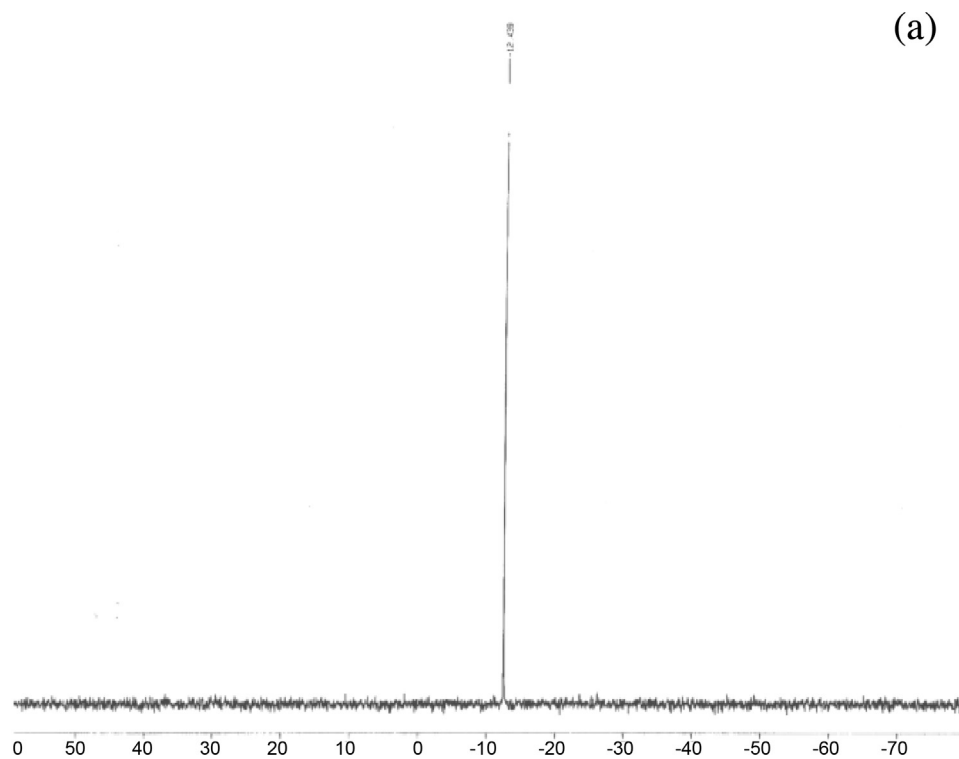


Fig. 3.  $^{31}\text{P}$  NMR spectra of a: compound (1); b: compound (2).

**Table 1**  
Selected IR data of heteropolyanions.

POM	$\nu_{as}(P-O_a)$	$\nu_{as}(W-O_d)$	M–Ob–M	M–OcM
H <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	1090	962	914	769
HFe <sub>2.5</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	1092	960	909	784
H <sub>6</sub> P <sub>2</sub> W <sub>12</sub> Mo <sub>6</sub> O <sub>62</sub>	1084	955	914	789
HFe <sub>2.5</sub> P <sub>2</sub> W <sub>12</sub> Mo <sub>6</sub> O <sub>62</sub>	1084	953	912	789

### 3. Results and discussion

#### 3.1. Preparation and characterization of catalysts

The addition of Fe<sup>3+</sup> ions to Dawson acid forms H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, 24H<sub>2</sub>O or H<sub>6</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>62</sub>, 24H<sub>2</sub>O in an aqueous medium, with a stoichiometric (3:1) amount, leads to a substitution of some protons by Fe<sup>3+</sup> ions yielding powder compounds HFe<sub>2.5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, 22 H<sub>2</sub>O (**1**) and HFe<sub>2.5</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>62</sub>, 23H<sub>2</sub>O (**2**).

The IR spectrum of the acid Wells–Dawson compound H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·24H<sub>2</sub>O is characterized by the elongation bands of P–O at 1090 cm<sup>-1</sup> and W–O terminal band, inter and intra W–O–W at 960, 914 and 769 cm<sup>-1</sup>, respectively [15]. However, the incorporation of transition ions in the structure of the two Dawson acids H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, 24H<sub>2</sub>O and H<sub>6</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>62</sub>, 24H<sub>2</sub>O generates a small displacement of these bands. The selected IR data are presented in Table 1.

It is well known that phosphorus NMR is an appropriate and powerful way to check the purity of the product. Phosphorous NMR spectra of (**1**) and (**2**) (Fig. 3) reveal a virtually pure product with a single resonance peak at  $\delta = -12.43$  ppm and  $\delta = -8.82$  ppm, respectively. This means that the two phosphorus atoms are equivalent.

According to the voltammogram of the compound HFe<sub>2.5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, 22 H<sub>2</sub>O, we observe five redox systems. The first peak is situated at +0.77 V/ECS; it appears in different voltammograms of heteropolyanionic complexes that contain Fe<sup>3+</sup>. Example: ( $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>Fe)<sup>7-</sup> and ( $\alpha_1$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>Fe)<sup>7-</sup> [16], (Fe<sub>3</sub>P<sub>2</sub>W<sub>15</sub>O<sub>59</sub>)<sup>9-</sup> [17]. It is attributed to the reduction of an electron iron (III) into Fe (II): (Fe<sup>3+</sup> + 1e<sup>-</sup> → Fe<sup>2+</sup>). The other peaks that appeared in 0,1, -0,07, -0,4, and 0,7 V/ECS are attributed to tungsten reduction.

According to the voltammogram of the compound HFe<sub>2.5</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>62</sub>, 23H<sub>2</sub>O, we can deduce that the introduction of iron in the compound H<sub>6</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>62</sub>, 24H<sub>2</sub>O makes the last stage of tungsten reduction disappear.

#### 3.2. Catalytic oxidation

Factors that influence the oxidation reaction of methyl violet are:

- the initial pH of the solution;
- the mass of the catalyst, Cat 1: (HFe<sub>2.5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>61</sub>, 23H<sub>2</sub>O) or Cat 2: (HFe<sub>2.5</sub>P<sub>2</sub>W<sub>12</sub>Mo<sub>6</sub>O<sub>61</sub>, 22H<sub>2</sub>O);

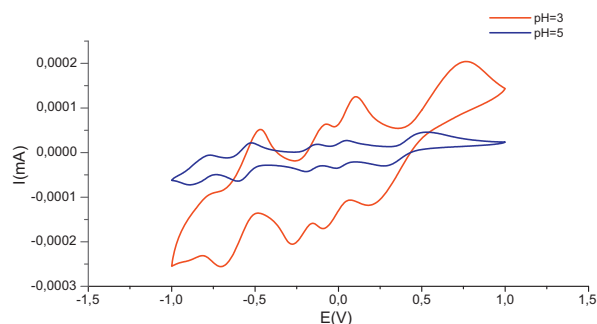


Fig. 4. Voltammograms of HFe<sub>2.5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, 22 H<sub>2</sub>O at pH = 3 and pH = 5.

- the concentration of H<sub>2</sub>O<sub>2</sub>;
- the initial concentration of the solution of MV.

The oxidation efficiency (discolouration), which was determined as shown below [18]:

$$DE = (C_i - C_f) / C_i \times 100 \quad (1)$$

DE: discolouration efficiency, C<sub>i</sub>: initial concentration of MV, C<sub>f</sub>: final concentration of MV.

##### 3.2.1. Effect of solution pH

The effect of pH on the discolouration efficiency was investigated by varying the pH from 3 to 10. For more acidic pHs, there is a risk of dimerization of the catalyst, while for pHs above 10, the catalyst is likely to deteriorate. The obtained results are shown in Fig. 4.

The optimum results were found to be obtained at a pH of about 3 using the two catalysts. ED = 40% using catalyst Cat1 and ED = 49% using catalyst Cat2.

This result can be explained by the stability of the catalyst at this pH. Also, it has been shown that the catalytic efficiency of the Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> system towards the oxidation of organic dyes is better at pH = 3 than at other pH values [19]. H<sub>2</sub>O<sub>2</sub> molecules are unstable in alkaline solution, and therefore dye degradation decreases in alkaline solution [20]. The stability of heteropolyanions is also affected by a modification of the pH and they can decompose at alkaline pHs [21].

##### 3.2.2. Effect of the mass of the catalyst

The effect of the mass of the catalyst on MV oxidation by H<sub>2</sub>O<sub>2</sub>, using Cat1 or Cat2, was investigated. The results are displayed in Fig. 5.

These results show that the best discolouration efficiency (ED = 48%) is obtained for a mass of catalyst equal to 0.02 g using catalyst Cat1 and 0.01 g (ED = 61%) using catalyst Cat2. Beyond these masses, discolouration efficiency decreases.

This result is mentioned in the literature [22]. It can be explained by the presence of a secondary reaction consuming the hydroxyl radicals.

##### 3.2.3. Effect of H<sub>2</sub>O<sub>2</sub> concentration

Experiments were conducted to determine the effect of H<sub>2</sub>O<sub>2</sub> concentration on the MV oxidation using Dawson type heteropolyanions as catalysts; the obtained results are displayed in Figs. 6 and 7.

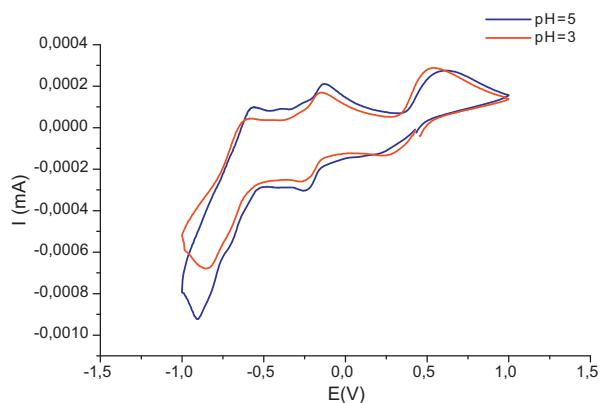


Fig. 5. Voltammograms of  $\text{HFe}_{2.5}\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$ ,  $23\text{H}_2\text{O}$  at pH = 3 and pH = 5.

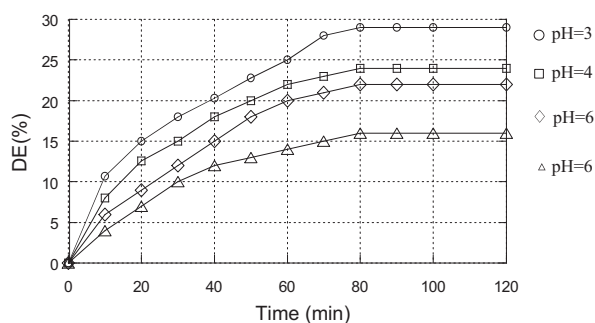


Fig. 6. Effect of the solution pH on MV oxidation using Cat1 as the catalyst ( $C_0 = 10 \text{ mg/L}$ ,  $m_{\text{cat}} = 0.05 \text{ g}$ ,  $[\text{H}_2\text{O}_2] = 0.25 \text{ mM}$ ,  $T = 25 \text{ }^\circ\text{C}$ ).

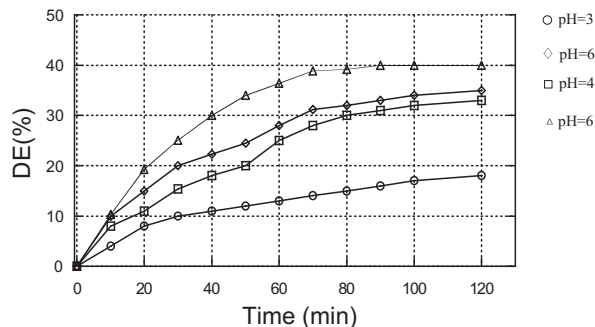


Fig. 7. Effect of the solution pH on MV oxidation using Cat2 as the catalyst ( $C_0 = 10 \text{ mg/L}$ ,  $m_{\text{cat}} = 0.05 \text{ g}$ ,  $[\text{H}_2\text{O}_2] = 0.25 \text{ mM}$ ,  $T = 25 \text{ }^\circ\text{C}$ ).

It was found that the best discoloration efficiency is obtained for a concentration of  $\text{H}_2\text{O}_2$  equal to  $0.25 \text{ mM}$  using catalyst Cat1 (ED = 48%) and  $0.4 \text{ mM}$  using catalyst Cat2 (ED = 63%).

Generally, the degradation rate of organic compounds increases as  $\text{H}_2\text{O}_2$  concentration increases until a critical  $\text{H}_2\text{O}_2$  concentration is achieved. However, when a concentration higher than the critical one is used, the degradation rate of organic compounds decreases; this result is called the scavenging effect [23,24]. The reaction

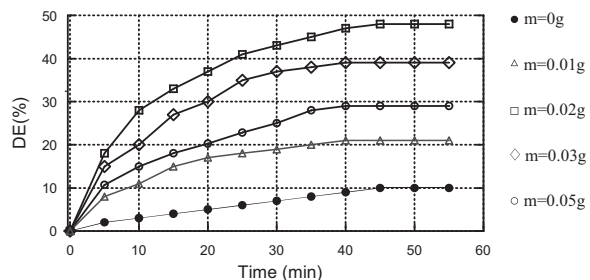


Fig. 8. Effect of the mass of the catalyst on MV oxidation using Cat1 as the catalyst ( $C_0 = 10 \text{ mg/L}$ ,  $[\text{H}_2\text{O}_2] = 0.25 \text{ mM}$ , pH = 3,  $T = 25 \text{ }^\circ\text{C}$ ).

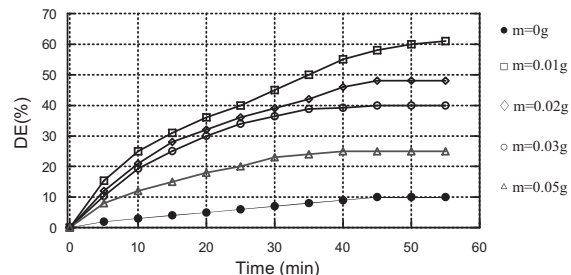


Fig. 9. Effect of the mass of the catalyst on MV oxidation using Cat2 as the catalyst ( $C_0 = 10 \text{ mg/L}$ ,  $[\text{H}_2\text{O}_2] = 0.25 \text{ mM}$ , pH = 3,  $T = 25 \text{ }^\circ\text{C}$ ).

of  $\text{H}_2\text{O}_2$  and  $\text{OH}^\bullet$  in aqueous solution can be expressed by the following equation [25]:



According to the above results, the critical  $\text{H}_2\text{O}_2$  concentration for the degradation of  $10 \text{ mg/L}$  of MV dye is about  $0.25 \text{ mM}$  using Cat1 as the catalyst and  $0.4 \text{ mM}$  using Cat2 as the catalyst.

### 3.2.4. Effect of methyl violet concentration

The study of the methyl violet dye initial concentration effect on discoloration efficiency was carried out for concentrations ranging from  $2 \text{ mg/L}$  to  $30 \text{ mg/L}$ . The results are presented in Figs. 8 and 9. The best result was found for a MV concentration equal to  $5 \text{ mg/L}$  using catalyst Cat1 (ED = 80%) and equal to  $2 \text{ mg/L}$  using catalyst Cat2 (ED = 91%) (Figs. 10–13).

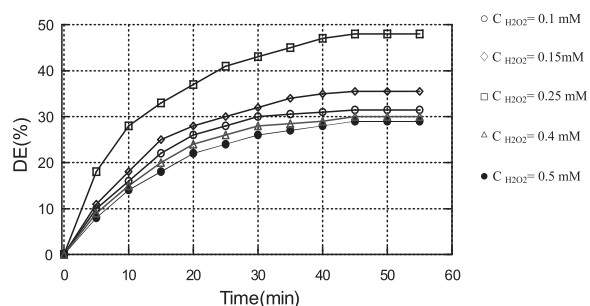


Fig. 10. Effect of the initial  $\text{H}_2\text{O}_2$  concentration on MV oxidation using Cat1 as the catalyst ( $C_0 = 10 \text{ mg/L}$ ,  $m_{\text{cat}1} = 0.02 \text{ g}$ , pH = 3,  $T = 25 \text{ }^\circ\text{C}$ ).

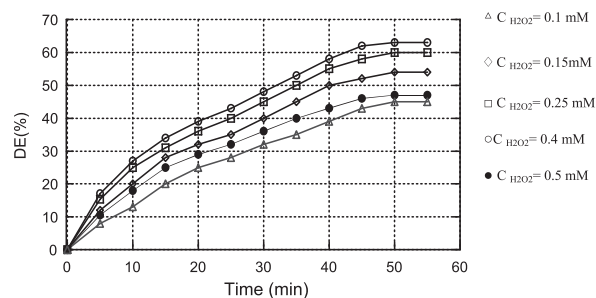


Fig. 11. Effect of the initial  $\text{H}_2\text{O}_2$  concentration on MV oxidation using Cat2 as the catalyst ( $C_0 = 10 \text{ mg/L}$ ,  $m_{\text{Cat}2} = 0.01 \text{ g}$ ,  $\text{pH} = 3$ ,  $T = 25^\circ \text{C}$ ).

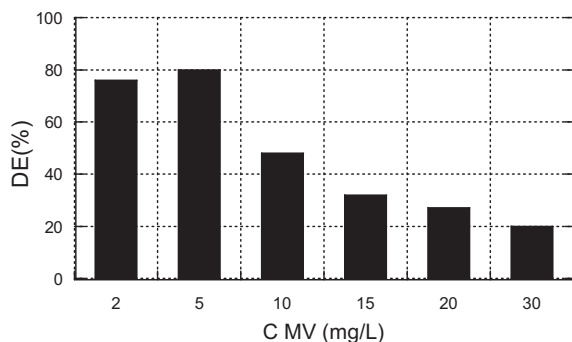


Fig. 12. Effect of the initial dye concentration on MV oxidation using Cat1 as the catalyst ( $m_{\text{Cat}1} = 0.02 \text{ g}$ ,  $\text{pH} = 3$ ,  $[\text{H}_2\text{O}_2] = 0.25 \text{ mM}$ ,  $T = 25^\circ \text{C}$ ).

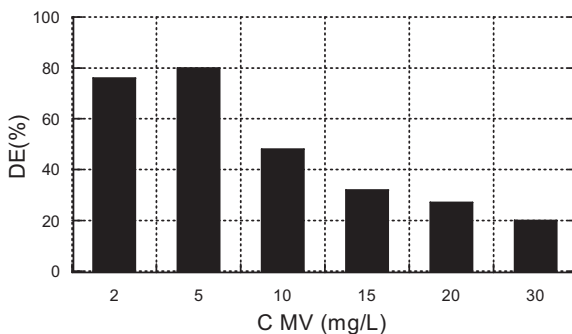


Fig. 13. Effect of the initial dye concentration on MV oxidation using Cat2 as the catalyst ( $m_{\text{Cat}2} = 0.01 \text{ g}$ ,  $\text{pH} = 3$ ,  $T = 25^\circ \text{C}$ ).

#### 4. Conclusion

A new iron substituted heteropolyanion with general formula  $[\text{HP}_2\text{W}_{18-n}\text{Mo}_n\text{O}_{62}]\text{Fe}_{2.5} \cdot x\text{H}_2\text{O}$ ,  $n = 0, 6$  have been synthesized and characterized by IR and  $^{31}\text{P}$  RMN spectroscopies.

Elementary analysis confirms the mentioned metals' insertion into the polytungstic and polymolybdotungstic matrix.

The Dawson entity was confirmed by IR spectroscopy for all synthesized heteropolyanions through the appearance of the characteristic peaks.

RMN confirms the synthesized compounds' purity.

Cyclic voltammetry shows that the iron is present in the Dawson structure.

Approximately 80% of the dye has been eliminated after 40 minutes under the following operating conditions:  $\text{pH} = 3$ ,  $[\text{MV}]_0 = 5 \text{ mg/L}$ , catalyst (Cat 1) mass:  $0.02 \text{ g}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.25 \text{ mM}$ . And approximately 91% of the dye has been eliminated after 80 min with the following operating conditions:  $\text{pH} = 3$ ,  $[\text{MV}]_0 = 2 \text{ mg/L}$ , catalyst (Cat 2) mass:  $0.01 \text{ g}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.4 \text{ mM}$ .

This system constitutes a simple and effective method compared to those previously reported for the oxidation of methyl violet using a commercial catalyst [26].

#### References

- [1] M.T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, New York, 1983.
- [2] J.F. Keggin, *Proc. Roy. Soc. Lond.* 131 (1933) 908–909.
- [3] B. Dawson, *Acta Crystallogr.* 6 (1953) 113–126.
- [4] M.N. Timofeeva, *Appl. Catal. B Chem.* 256 (2003) 19–35.
- [5] N.I. Kuznetsova, N.V. Kirillova, L.I. Kuznetsova, Y.M. Smirnova, V.A. Likhonobov, *J. Hazard. Mater* 146 (2007) 569–576.
- [6] C. Lee, D.L. Sedlak, *J. Mol. Catal. A Chem.* 311 (2009) 1–6.
- [7] O. Bechiri, M. Abbessi, L. Ouaheb, *Res. Chem. Intermed.* 38 (2012) 1839–1907.
- [8] R. Belghiche, R. Contant, Y.W. Lu, B. Keita, M. Abbessi, L. Nadjo, J. Mahuteau, *Eur. J. Chem.* 6 (2002) 1410–1414.
- [9] K. Ellass, A. Laachach, A. Alaoui, M. Azzi, *Appl. Clay Sci.* 54 (2011) 90–96.
- [10] P. Li, Y. Su, Y. Wang, B. Liu, L. Sun, *J. Hazard. Mater* 179 (2010) 43–48.
- [11] M. Hamza, R. Abdelhedi, E. Brillas, I. Sirés, *J. Electroanal. Chem.* 627 (2009) 41–50.
- [12] A. Mittal, V. Gajbe, J. Mittal, *J. Hazard. Mater* 150 (2008) 364–375.
- [13] R. Contant, J.-P. Ciabrini, *J. Org. Nucl. Chem.* 43 (1981) 1525–1528.
- [14] J.-P. Ciabrini, R. Contant, J.-M. Fruchart, *Polyhedron* 11 (1983) 1229–1233.
- [15] C. Rocchioccioli-Deltchev, R. Thouvenot, *Spectrosc. Lett.* 12 (1979) 127–138.
- [16] R. Contant, M. Abbessi, J. Canny, A. Belhouari, B. Keita, L. Nadjo, *J. Inorg. Chem.* 36 (1997) 4961–4967.
- [17] C. Zhang, C. Yan Sun, S. Xia Liu, H. Mei Ji, Z. Min Su, *Inorg. Chim. Acta* 363 (2010) 718–722.
- [18] S. Şaşmaz, S. Gedikli, P. Aytar, G. Güngörmedi, A.C. Evrim, H.A. Ünal, N. Kolankaya, *Appl. Biochem. Biotechnol.* 163 (2011) 346–361.
- [19] S. Tangestaninejad, M. Moghadam, V. Mirkhani, I.M. poor-Baltork, H. Salavati, *Ultrason. Sonochem.* 15 (2008) 815–822.
- [20] F. Ji, C. Li, J. Zhang, *Desalination* 269 (2011) 284–290.
- [21] Y.Y. Zhang, C. He, J. Deng, Y.-T. Tu, J.K. Liu, Y. Xiong, *Res. Chem. Intermed.* 35 (2009) 727–737.
- [22] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, *Chemosphere* 58 (2005) 1409–1414.
- [23] N.I. Kuznetsova, N.V. Kirillova, L.I. Kuznetsova, M.Yu. Smirnova, V.A. Likhonobov, *J. Hazard. Mater* 146 (2007) 569–576.
- [24] J. Fernandez, J. Bandara, A. Lopez, P. Buffar, J. Kiwi, *Langmuir* 15 (1999) 185.
- [25] G. Strukul (Ed.), *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic, Dordrecht, The Netherlands, 1992.
- [26] K. Tennakone, S. PUNCHIHewa, S. Wickremnayaka, R.U. Tantrigoda, *J. Photochem. Photobiol. A Chem.* 46 (1989) 247–252.