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Decolorization and Degradation of Ponceau 4R by the Super-Iron (VI) in an aqueous solution

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- ✓ COD removal;
- ✓ TOC removal

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ABSTRACT

The aim of the present work is to study the decolorization and degradation of the azo dye Ponceau 4R by the super-iron (VI) ($K_3(Fe_{0.748}Mn_{0.252})_2O_8$) – $K_3(Fe_{0.800}Mn_{0.200})_2O_8$). The azo dye ponceau 4R is generated in waste of food dyes industry in Casablanca (Morocco). The tests focused on the physico-chemical characterization (chemical oxygen demand, decolorization and total organic carbon) of the Ponceau 4R in aqueous solution (50 mg/L). The results are very interesting, using 2.5 g/L of $K_3(Fe_{0.800}Mn_{0.200})_2O_8$ leads to 90% of COD removal and 95% of COT removal.

1. Introduction

Many industries (textile, printing, cosmetic, food colorants…) are big consumers of water and they use organic dyes to provide color to their products in order to make them more currying. These organic dyes are not easily biodegradable due to the complexity of their chemical structure and the presence of aromatic cycles.

They are both toxic and responsible for the color present in the wastewater. The treatment of these effluents remains a major challenge especially for third world countries that have not yet all possibilities to integrate the concept of sustainable development [1].

The corresponding aqueous effluents then require specific treatment due to the singular impact they have on the environment. In order to stop this danger, we were interested in studying the degradation of an azo dye Ponceau 4R of the manufacturing food dyes industry located in Casablanca-Morocco.

The overdose (more than 4 mg/kg body weight) [2] of this azo dye causes carcinogenic and mutagenic effects [3-4].

We have carried out the specific degradation of this dye P4R by $K_3(Fe_xMn_y)_2O_8$.

The permanganoferrate (VI) of potassium known by its exceptional oxidizing power which is greater than the ferrates ($E°(FeO_4^{2-}/Fe^{3+}) = 2.2$ V and permanganates $E°(MnO_4^-/MnO_2) = 1.67$ V) [5]; its efficiency has been demonstrated in the treatment of organic and inorganic pollutants and inhibition of bacterial activity, which gives it a wide range of applications [6].

The results of this degradation will be later compared with those obtained by the application of iron sulfate in the presence of sodium hydroxide generally used in industries to treat waste waters.

2. Experimental details

2.1. *Pollutant agent*

The pollutant studied in this work, known by its resistance to the natural biodegradability, is a colorant used in agri-food field. Ponceau 4R is called "E124" or also 2-hydroxy-1- (4-sulfonate-1-naphthylazo) -6,8-naphthalene disulfonate trisodium ($C_{20}H_{11}N_2Na_3O_{10}S_3$) [7]. It can be natural (cochineal) or synthetic. Its macromolecular chemical structure is represented by figure 1.

Figure 1: Chemical structure of Ponceau 4R product ($C_{20}H_{11}N_2Na_3O_{10}S_3$) [8] **floue**

2.2. *Reagents of degradation*

The permanganoferrate (VI) of potassium $K_3(Fe_xMn_y)_2O_8$ (λ=510 nm) compound based on Fe(VI) and Mn(VII), is synthesized in a laboratory according to the protocol adopted by A. Tazi and al. [9]. It is obtained by the oxidation at ambient temperature of HFe_5O_8-5Mn(OH)$_2$ with calcium hypochlorite ($Ca(ClO)_2$) in a strongly alkaline medium [10]. The iron sulfate $FeSO_4,7H_2O$ is a byproduct of titanium and steel industry [11].

2.3. *Measuring pH*

The pH determination is carried out using pH-meter type cyber ion scan 510.

2.4. *UV-Visible Spectroscopy*

Monitoring the decolorization of P4R and optimizing the quantity of ferrate (VI) and iron sulfate was performed by measuring the absorbance using UV-Visible spectrophotometer type Heλios γ 091610 UVG series.

2.5. *Chemical oxygen demand*

The chemical oxygen demand (COD) is the quantity of oxygen consumed during oxidation matters in solution. It is evaluated by potassium dichromate under heating and in acid medium.

The COD-meter used is AL32 type heater and photometric reader MD 200 type.

2.6. *Total organic carbon*

The total organic carbon content is determined by sulfochromic oxidation of the recovered sludge and pre-dried at 105°C. The resulting product of this reaction is evaluated by a ferrous sulfate solution 0.5 N.

The percentage of TOC is given by the formula:

$$\mathbf{C} = \frac{(\mathbf{A} - \mathbf{B}) \times \mathbf{10} \times \mathbf{0.004} \times \mathbf{100}}{\mathbf{P} \times \mathbf{A}}$$

Where **C** is the organic carbon concentration (% C), **A** the volume of iron sulfate used for witness (mL), **B** the volume of iron ferrous used for the sample (mL), **10** is the volume of dichromate added initially, **0.004** the number of g of C per mL dichromate, **P** the weight of the assayed sample expressed on a dry basis (g), **100** is the percentage factor.

3. Results and Discussion

3.1. *Characterization of the dye Ponceau 4R*

The solution of 50 mg/L of P4R is prepared with demineralized water. Characterization results of this solution are presented on table 1.

The results of UV-visible spectroscopic measurements carried on the same solution are presented on figure 2. The figure 2 shows the existence of two bands at 292 nm and 333 nm, corresponding respectively to π→π* transition of benzene and naphthalene. The band observed at 508 nm is related to n→π* transition of the chromophore group (N=N) [12].

Table 1: Characteristics of 50 mg/L of P4R solution

Parameters	Values
Molecular weight (g/mol)	604.47
pH	7.3
COD (mg/L)	4320
BOD_5 (mg/L)	200
TOC (%)	48.80
Organic matter (%)	56.96
Mineral matter (%)	43.03

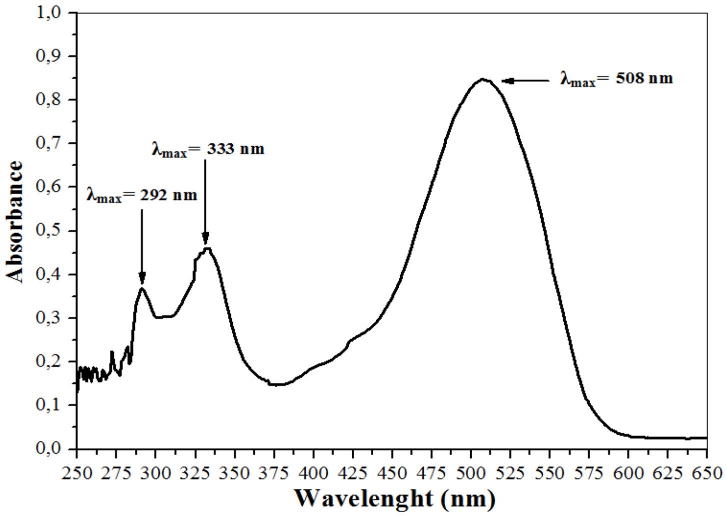


Figure 2: UV-Visible spectrum of Ponceau 4R

3.2. *Effect of $K_3(Fe_xMn_y)_2O_8$ on the dye P4R in aqueous solution*

3.2.1. *Optimization of the amount of $K_3(Fe_xMn_y)_2O_8$*

In an aqueous solution, Fe(VI) and Mn(VII) are reduced to ferric hydroxide ($Fe(OH)_3$) and manganese oxide (MnO_2) by releasing gaseous oxygen and hydroxyl groups as shown in the following reactions :

$$4\ FeO^{2-}_4 + 10\ H_2O \rightarrow 4\ Fe(OH)_3 + 3\ O_2 + 8\ OH^-$$
$$4\ MnO_4^- + 2\ H_2O \rightarrow 4\ MnO_2 + 3\ O_2 + 4\ OH^-$$

The oxygen released will then oxidizes the organic molecule P4R. The highly basic environment (pH ≈ 12) can only activate the degradation of the compound [13]. In order to optimize the needed quantities of the compounds A ($K_3(Fe_{0.748}Mn_{0.252})_2O_8$ and B ($K_3(Fe_{0.800}Mn_{0.200})_2O_8$), the UV-Visible spectrophotometry is used to monitor the degradation efficiency of red P4R (figure 3-4).

Analysis of figures 3 and 4 shows a decrease of the three peaks intensity with oxidizing species. Probably, the oxidizing compounds A and B attack at first the azo bonds N=N (508 nm), and naphthalene groups (333 nm) and finally the benzene rings (292 nm). However the variation of the peak intensity is higher for compound B (x/y =4) than A (x/y =3). The possible organic products can be obtained after the degradation of the P4R by $K_3(Fe_xMn_y)_2O_8$ are summarized in the table 2.

The absence of the absorption band after attack the Ponceau 4R by optimal amounts of 3.75 g/L ($K_3(Fe_{0.748}Mn_{0.252})_2O_8$) and 2.5 g/L ($K_3(Fe_{0.800}Mn_{0.200})_2O_8$), probably means that the oxidation of the molecule P4R by the permanganoferrate (VI) of potassium conducts to the rupture and/or the opening of aromatic rings to give aliphatic compounds which may be also subsequently mineralized.

To study this hypothesis, the values of chemical oxygen demand (COD) and the total organic carbon (TOC) are monitored over time.

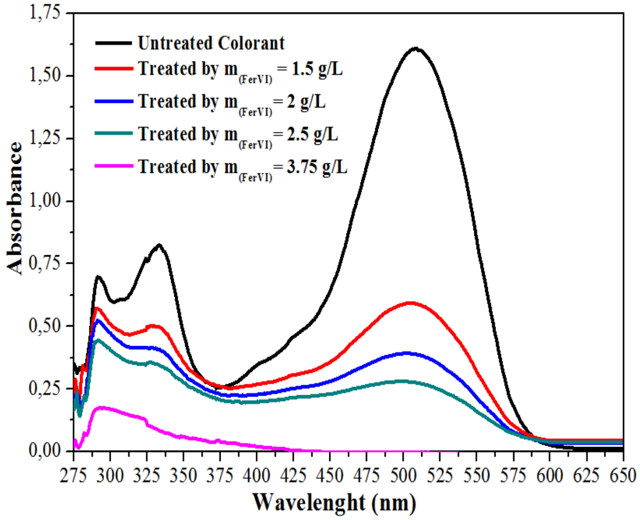


Figure 3: Evolution of the absorbance with the quantity of $K_3(Fe_{0.800}Mn_{0.200})_2O_8$

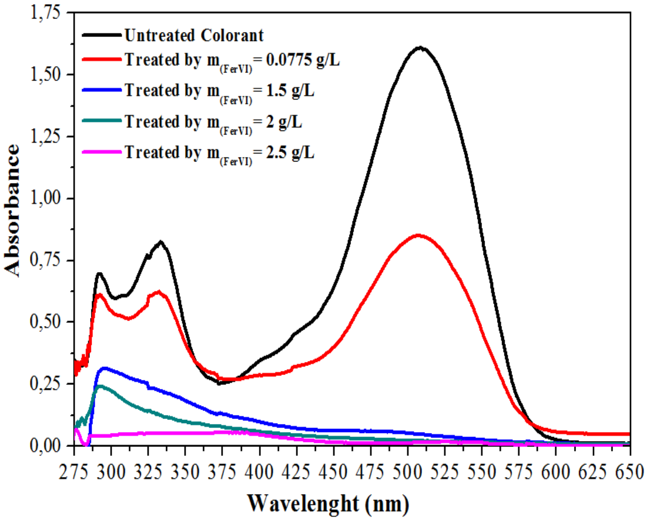
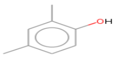
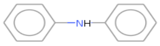
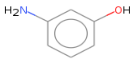
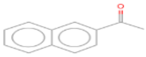
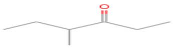
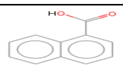
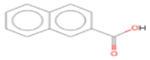
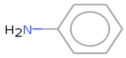
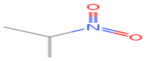
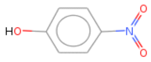


Figure 4: Evolution of the absorbance with the quantity of $K_3(Fe_{0.748}Mn_{0.252})_2O_8$

Table 2: The possible compounds may be formed after attack of the P4R by $K_3(Fe_xMn_y)_2O_8$

$290 \leq \lambda \leq 300$ nm	$325 \leq \lambda \leq 335$ nm
2,4-dimethyl- Phenol ($C_8H_{10}O$) [14] 	Diphenylamine ($C_{12}H_{11}N$) [22] 
3-aminophenol (C_6H_7NO) [15] 	2-naphthyl methyl ketone ($C_{12}H_{10}O$) [23] 
4-methyl-3-hexanone $C_7H_{14}O$ [16] 	1-naphthalenecarboxylic acid ($C_{11}H_8O_2$) [24] 
3,3-dimethyl-2, butanone ($C_6H_{12}O$) [17] 	2-naphthalenecarboxylic acid ($C_{11}H_8O_2$) [25] 
1,3-Butadiene (C_4H_6) [18] 	Aniline (C_6H_7N) [26] 
1-Propanol, 2-methyl-2-nitro- ($C_4H_9NO_3$) [19] 	Hydroquinone ($C_6H_6O_2$) [27] 
2-nitro-propane ($C_3H_7NO_2$) [20] 	4-nitro-Phenol ($C_6H_5NO_3$) [28] 
2-propenal (C_3H_4O) [21] 	2,4-Heptadiene (C_7H_{12}) [29] 

3.2.2. *Determination of chemical oxygen demand COD*

After adding the optimal weight of the super-iron in Ponceau 4R solution to 50 mg/L, the COD removal is followed according to time treatment (figure 5).

The figure 5 indicates that after 30 minutes, the COD removal reach 80 % for A and 90 % for B.

These results demonstrate that the COD of solution decreases more when iron (VI) is more present in the oxidizing matrix, allowing more effective degradation of the P4R molecule.

3.2.3. *Monitoring of decolorization efficiency*

The decolorization efficiency of the solution at λ_{max} = 508 nm (figure 6) is monitored over time.

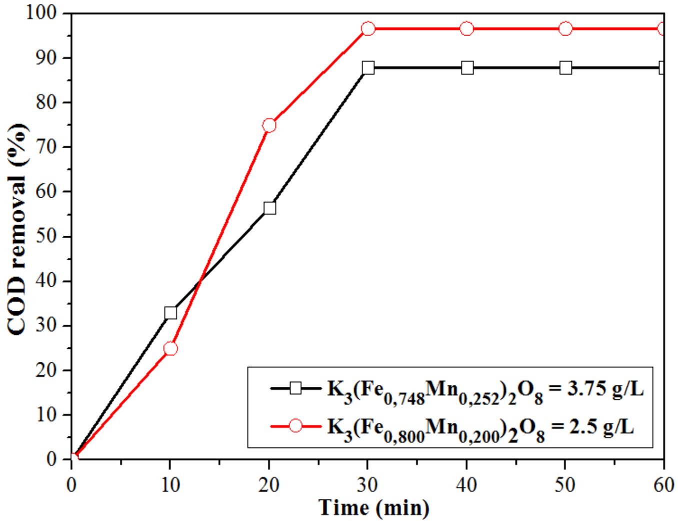


Figure 5: Evolution with time of COD removal

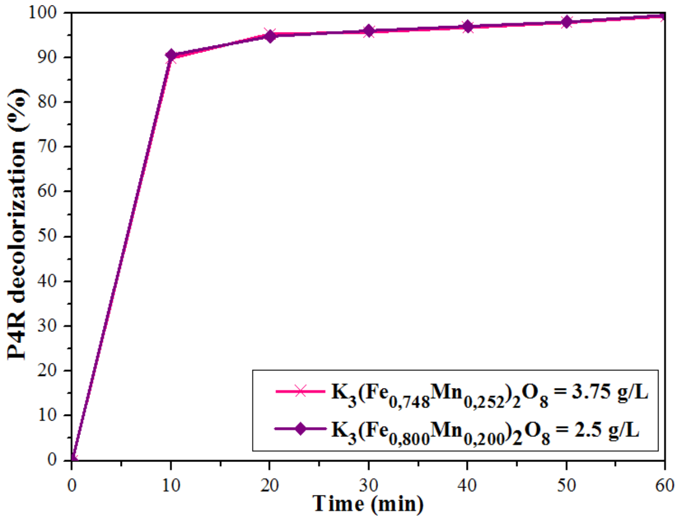


Figure 6: Evolution with time of color removal efficiency of Ponceau 4R

In less than 10 minutes, the decolorization efficiency of the solution P4R by the oxidizing products A and B is greater than 99 %. The complete decolorization was observed after 30 minutes.
The rapid discoloration (10 min) of the P4R solution is highlighted by the disappearance of the absorption peak at 508 nm. Discoloration confirms N=N bond degradation.

3.3. *Determination of the total organic carbon (TOC) in the flocs*

Figure 7 and table II are a representation of TOC removal evolution with time in the flocs recovered after oxidation of the Ponceau 4R by the optimal quantity of potassium permanganoferrates (VI).

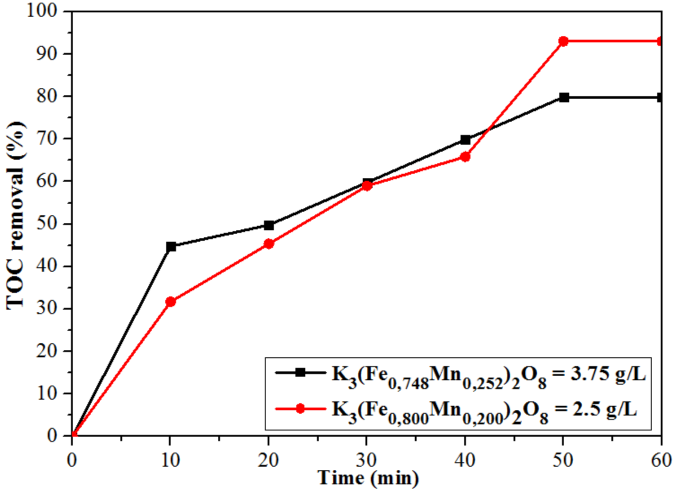


Figure 7: Evolution with time of TOC removal by iron (VI)

Table 3: Results of flocs analysis

	$m_{(opt)}$ (g/L)	**% TOC**	**$m_{(flocs)}$ (g/L)**
A ($K_3(Fe_{0.748}Mn_{0.252})_2O_8$)	3.75	80	0.6
B ($K_3(Fe_{0.800}Mn_{0.200})_2O_8$)	2.5	95	1.2

This study shows that the mineralization is improved by increasing the rate of iron (VI) in the oxidizing matrix.
The degradation of P4R and its derivatives is effective with 2.5 g/L of $K_3(Fe_{0.800}Mn_{0.200})_2O_8$; this mass is reduced by the half comparing to the floc generated after treatment. These results are in adequacy with previous studies by A. TAZI and al. [1-2-13] made on the resistant organic pollutants such as polyphenols.

However, the degradation efficiency of the P4R by the ferrate (VI), remains considerably higher than the result obtained by D.Oliveira and al [8] using TiO_2 photocatalysis; while the TOC rate doesn't exceed 50% during 120 minutes of treatment.

3.4. *Effect of the iron sulfate $FeSO_4$, $7H_2O$*

3.4.1. *Optimizing the amount of $FeSO_4$, $7H_2O$*

The addition of $FeSO_4,7H_2O$ makes the medium acidic (pH = 3.42) and no elimination of the P4R molecule could be observed and no coagulation phenomenon happened. So basification of the solution by adding NaOH (10^{-1} M) is necessary. From figure 8, it can be noticed that the optimal elimination of P4R is obtained at 2 g/L concentration of iron sulfate.

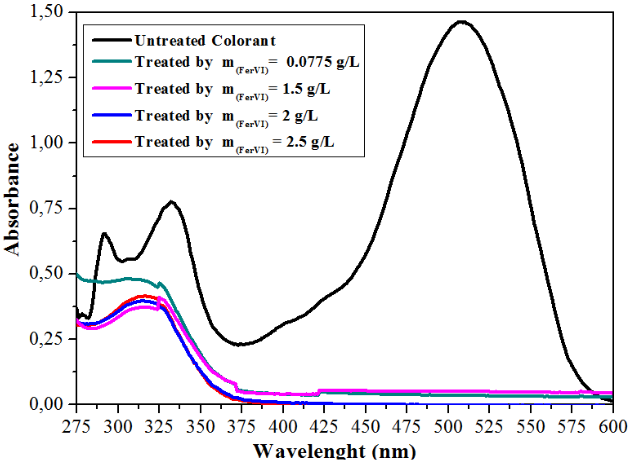


Figure 8: Followed by the absorbance of Ponceau 4R before and after attack by $FeSO_4,7H_2O$ (pH = 7)

It is o 33 nm) and benzene (292 nm) have created a new absorbing aromatic compound at $\lambda = 323$ nm. It can be attributed to 4 nitro-phenol or aniline (table 2).

3.4.2. *Monitoring of the chemical oxygen demand and decolorization*

The decolorization of the solution to 50 mg/L of P4R by iron sulfate (2 g/L) at pH=7 showed 60 % of COD removal after 20 minutes (figure 9). For the same conditions, solution became colorless at only 10 min (figure 10); this can be explained by total the elimination of the P4R molecule.

In this case, the decolorization observed is attributed to the coagulation process and adsorption on iron hydroxide flocs.

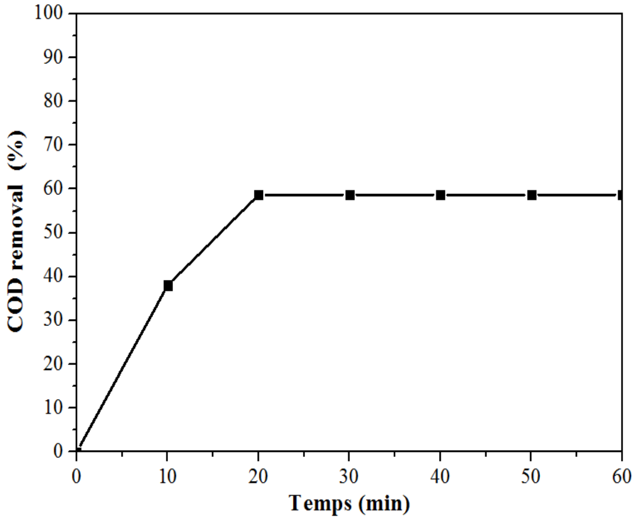


Figure 9: Evolution with time of COD removal

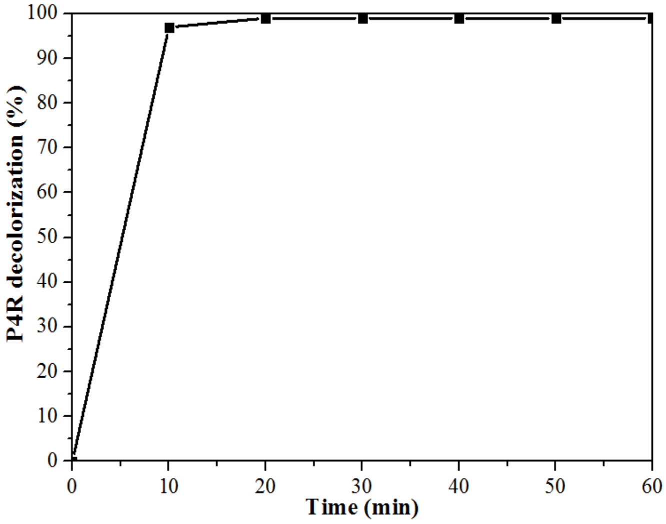


Figure 10: Evolution with time of decolorization efficiency

3.5. *Total organic carbon determination in the flocs*

Figure 11 shows the evolution with time of organic carbon in the flocs after treatment of the P4R solution by the iron sulphate.

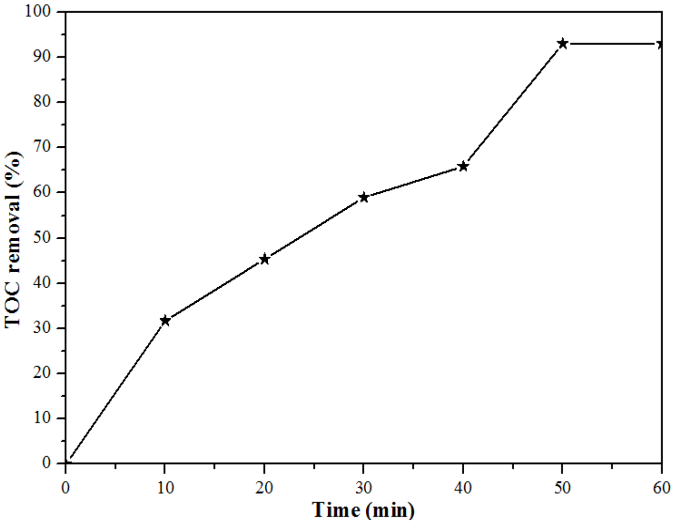


Figure 11: TOC in the flocs after treatment of P4R solution by $FeSO_4,7H_2O$ at pH=7 (pH = 7)

Table 4: The following table shows the results of this analysis

	$m_{(opt)}$ (g/L)	**%TOC**	**$m_{(flocs)}$ (g/L)**
$FeSO_4$, $7H_2O$	2	68	1.33

In the flocs, TOC increases in the first 20 minutes and remains stable subsequently. It can be explained by the fact that the aromatic or aliphatic derivatives resist to the elimination by the iron sulfate (pH=7).

Conclusions

After analyzing the results, we can conclude that permanganoferrate (VI) of potassium $K_3(Fe_xMn_y)_2O_8$ have a strong oxidizing potential. The effectiveness of the products increases with the rate of Fe(VI) present in the oxidizing matrix; this is demonstrated by a sharp deterioration of P4R solution.

Indeed, in terms of COD and TOC, the reduction rates achieved are respectively 80% - 80% for $K_3(Fe_{0.748}Mn_{0.252})_2O_8$ and 90% - 95% for $K_3(Fe_{0.800}Mn_{0.200})_2O_8$.

While these rates do not exceed 60% of COD and 68% of TOC for $FeSO_4,7H_2O$ (pH = 7).

Furthermore, following treatment by permanganoferrate (VI) of potassium $K_3(Fe_xMn_y)_2O_8$, decolorization and degradation of the P4R solution 50 mg/L were observed at after only 30 minutes of attack.

The permanganoferrates (VI) of potassium are the choice compounds for water treatment; especially when the products used for their synthesis are not expensive. Iron sulfate ($FeSO_4,7H_2O$) is a by-product of titanium oxide and steel industry.

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