

Kinetic Study of the Degradation of Soap and Cosmetics Effluent by Potassium Permanganate: Case of a Soap and Cosmetics Industry in the Port Area of Abidjan-Sud, Ivory Coast

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Abstract This work is part of the context of wastewater management in developing countries. The objective is to set up a simple and less expensive treatment process for soap and cosmetic wastewater. The wastewater from a soap and cosmetics industry in the Abidjan-sud zone was studied. The chemical oxidation method using potassium permanganate is used for the degradation of this raw wastewater at room temperature and basic pH. Indirect volumetric dosage by manganometry and the linear regression method are used to determine the overall order and kinetic parameters of the degradation reaction of oxidizable materials in the wastewater. It appears from this study that permanganate oxidizes the wastewater from the soap and cosmetics unit. All of the materials oxidizable by potassium permanganate (MOPP) with a normality of $2.5 \cdot 10^{-3} \text{ eq} - \text{g} \cdot \text{L}^{-1}$ degrade after approximately 90 minutes. This MOPP degradation reaction follows kinetics of order 1 with a correlation coefficient. MOPPs behave like a single species and are essentially made up of organic pollutants. The oxidation reaction of MOPP by KMnO_4 at room temperature and basic pH is slow with an apparent rate constant $k_1' = 4.14 \cdot 10^{-2} \text{ eq} - \text{g} \cdot \text{L}^{-1} \text{ min}^{-1}$

Keywords: effluent, soap and cosmetics, indirect volumetric, manganometry

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1. Introduction

The recurrent problem of industrial wastewater management is one of the environmental concerns of the State of Ivory Coast. Despite the efforts made by the Ivorian authorities in terms of environmental protection, very few industries comply with the rules and recommendations [1,2]. As a result, effluents are a burden for the State of Ivory Coast, which is unable to treat its wastewater due to lack of technical facilities [3,4]. In Ivory Coast, as in other developing countries, wastewater is discharged into the environment without prior treatment [5,6]. The detergent and cosmetics industry represents an industry of prime importance for developing countries [7]. Because it makes it possible to satisfy an increasingly growing demand for detergent and cosmetic products [8]. In Ivory Coast, these industries are in continuous expansion, where several units are installed in the different industrial zones of the Abidjan District [9].

These industrial units contribute significantly to the growth of the Ivorian economy [9]. This strong contribution requires significant production activities, thus generating volumes of effluent linked to the use of water in the process [10]. Moreover, these industries use various formulation raw materials (surfactant, fatty acids, organic and inorganic dyes, adjuvants, etc.) whose toxicities on biodiversity have been proven [11,12]. Studies on industrial liquid effluents from soap factories in the Abidjan area have shown that these effluents present certain pollution indicators for aquatic biodiversity [13,14]. They are sources of organic, nutrient, and anionic surfactant pollution. Other studies have also revealed that these detergent and cosmetic effluents are sources of pollution from Trace Metal Elements (ETMs), including chromium [15]. These effluents, which are difficult to biodegrade, are unfortunately discharged into the Ebrié lagoon without prior treatment. In this context, the problem of degradation of detergent and cosmetic effluents is more than necessary.

Several processes (Fenton process, sonication

process, etc.) and oxidants (sodium persulfate, potassium dichromate, etc.) have been used for this purpose in order to effectively treat these micropollutants [16,17,18,19,20,21,22]. Unfortunately, these processes are very expensive and costly. Potassium permanganate, used as an oxidant, then appears as a palliative to these processes. It is a powerful oxidant, easily used in aqueous media because it is a colored self-indicator. It has been the subject of several studies [23,24,25,26,27]. This simple, rapid and less expensive process is used in this study. Indirect volumetric dosage by manganometry is used for this purpose. The general objective of this work is therefore to propose a simple and less expensive treatment mechanism for soap and cosmetic effluents. Specifically, it involves carrying out, at ambient temperature and pH of the effluent medium, a kinetic study by determining the overall order and the kinetic parameters of the degradation reaction of the oxidizable materials in the effluent by potassium permanganate. The content of these oxidizable

materials in the effluent must be determined.

2. Study Materials and Methodology

2.1. Study Materials

The effluent from a soap factory located in the port area of southern Abidjan is the study material. This coded unit (P16) is recognized for its manufacturing of detergent and cosmetic products (Figure 1).

The technical equipment consists of an opaque oxidation reactor and a volumetric dosing device. The commercial reagents used are Potassium permanganate ($KMnO_4$, purity 99%, Prolabo product), mohr salt ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, purity 99%, Prolabo product) and sulfuric acid H_2SO_4 (purity 95–98%, Panreac product).

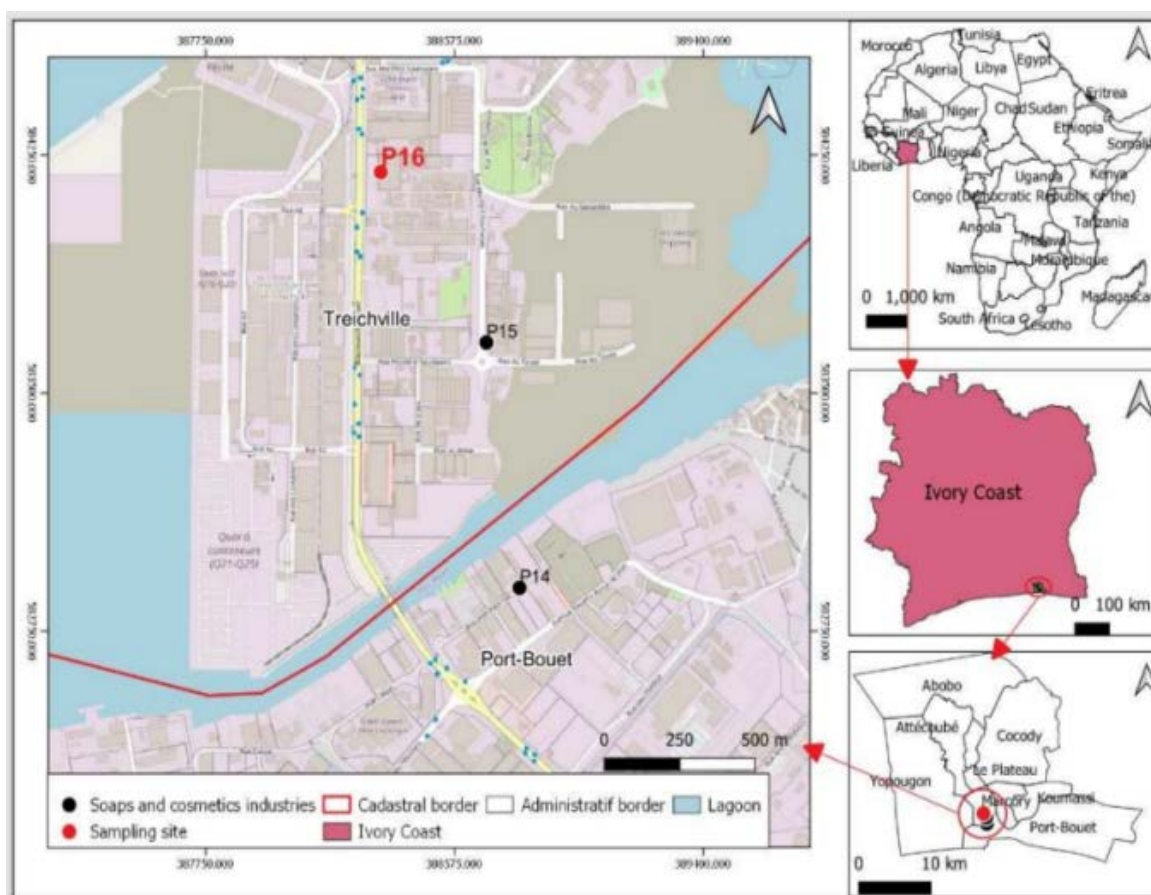


Figure 1. Soap and cosmetics units in the port industrial area: Study unit P16

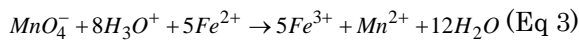
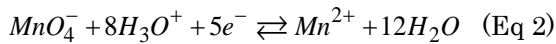
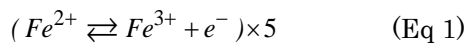
2.2. Study Methodology

The samples were taken over a period of four weeks in the month of October corresponding to periods of intense activity of the unit. These effluent samples collected are sent directly to the laboratory for dosage. The degradation of these effluent samples by permanganate (MOPP) is carried out in an opaque oxidation reactor coupled with a volumetric dosing device. The different solutions are prepared with distilled water and the aforementioned

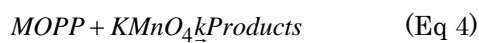
reagents, acidified with a 1 mol L^{-1} sulfuric acid solution. Potassium permanganate solutions are prepared in a volumetric flask by dissolving an appropriate mass of $KMnO_4$ in distilled water. Two solutions of $KMnO_4$ of different concentrations were prepared. This is a solution denoted S_1 of permanganate of normality $N_1 = 0.25 \text{ eq} \cdot \text{g} \cdot \text{L}^{-1}$ obtained by dissolving a mass $m_1 = 0.8 \text{ g}$ in a 100 mL volumetric flask and a solution denoted S_2 of permanganate of normality

$N_2 = 0.41 \text{ eq} - \text{g} \cdot \text{L}^{-1}$ obtained by dissolving a mass $m_2 = 1.3 \text{ g}$ in a **100 mL** volumetric flask. Finally the iron (II) solution with normality $N_{Fe} = 10^{-2} \text{ eq} - \text{g} \cdot \text{L}^{-1}$ is prepared by dissolving a mass $m = 3.9 \text{ g}$ of $(\text{NH}_4)_2 \text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (mohr salt) in a **1000 mL** volumetric flask. For each series of experiments, a volume $V = 190 \text{ mL}$ taken at raw effluent temperature and pH ($pH = 10.7; T = 33^\circ\text{C}$) is poured into the oxidation reactor. A volume $V_0 = 10 \text{ mL}$ of a permanganate solution with indicated normality (N_1 or N_2) taken using a pipette is added. A magnetic stirrer homogenizes the reaction medium continuously. Test samples of volume $V_p = 10 \text{ mL}$ are taken with a pipette in the reaction medium at different times (5, 15, 30, 45, 60, 75, 90 and 120 minutes). The test portion taken at time t is poured into an Erlenmeyer flask, initially containing ice to slow down the reaction and 5 mL of the prepared acid solution. This test portion is then dosed with the iron (II) titrant solution prepared for measuring the residual potassium permanganate content at time t . The end of the dosage, reflecting the total consumption of residual permanganate ions in the test portion at time t , is marked by the change from purple to colorless of the permanganate. The volume of the iron (II) titrating solution poured at the equivalence V_{eq} is marked and read on the burette. Each experiment linked to the initial concentration is repeated three times to check the reproducibility of the results. The effluent solution is diluted twice in order to have two different concentrations of MOPP. Knowing the remaining KMnO_4 content, the residual content of materials oxidizable by permanganate (MOPP) is determined.

The test portion having been acidified, the redox couples $\text{MnO}_4^- / \text{Mn}^{2+}$ and $\text{Fe}^{+3} / \text{Fe}^{+2}$ are used in the context of this study [28]. The redox half-equations of the two couples as well as the redox equation are:



The acronym MOPP (Materials Oxidizable by Potassium Permanganate) used throughout this work designates materials, which react in the presence of the oxidant KMnO_4 by oxidizing. This oxidation action therefore constitutes a degradation of all of these MOPPs whose balance equation is:



As MOPPs are complex and their identity is unknown, it is preferable to always reason in normality rather than molarity. At any time t in the reactor, we have:

Quantity of MOPP material consumed = Quantity of material KMnO_4 consumed.

All the species being in the same volume V of solution,

we can write:

$$\begin{aligned} N_i(\text{MOPP})_{\text{Consumed}} &= N_{\text{MOPP}}(0) - N_{\text{MOPP}}(t) \\ &= N_{\text{KMnO}_4}(0) - N_{\text{KMnO}_4}(t) \end{aligned} \quad (1)$$

The residual normality $N_{\text{KMnO}_4}(t)$ of KMnO_4 is determined at the equivalence of the dosage:

$$N_{\text{KMnO}_4}(t) \cdot V_p = N_{Fe} \cdot V_{eq}$$

$$N_{\text{KMnO}_4}(t) = \left(\frac{N_{Fe}}{V_p} \right) \cdot V_{eq} = 10^{-3} \cdot V_{eq}$$

Relation (1) then becomes:

$$\begin{aligned} N_1(\text{MOPP})_{\text{Consumed}} &= N_{\text{MOPP}}(0) - N_{\text{MOPP}}(t) \\ &= N_{\text{KMnO}_4}(0) - 10^{-3} \cdot V_{eq} \end{aligned} \quad (2)$$

Thus for the solution S1 of KMnO_4 , we have

$$N_{\text{KMnO}_4}(0) = \frac{0.25 \times 10}{200} = 12.5 \cdot 10^{-3} \text{ eq} - \text{g} / \text{L}$$

Relation (2) then becomes:

$$\begin{aligned} N_1(\text{MOPP})_{\text{Consumed}} &= N_{\text{MOPP}}(0) - N_{\text{MOPP}}(t) \\ &= (12.5 - V_{eq}) \cdot 10^{-3} \end{aligned} \quad (3)$$

Furthermore, for solution S2 of KMnO_4 , we have:

$$N_{\text{KMnO}_4}(0) = \frac{0.41 \times 10}{200} = 20.5 \cdot 10^{-3} \text{ eq} - \text{g} / \text{L}$$

Relation (2) then becomes:

$$\begin{aligned} N_2(\text{MOPP})_{\text{Consumed}} &= N_{\text{MOPP}}(0) - N_{\text{MOPP}}(t) \\ &= (20.5 - V_{eq}) \cdot 10^{-3} \end{aligned} \quad (4)$$

Thus, although neither $N_{\text{MOPP}}(0)$ knows the initial MOPP concentration, nor $N_{\text{MOPP}}(t)$ the residual MOPP concentration; we can access the difference $N_{\text{MOPP}}(0) - N_{\text{MOPP}}(t)$. The reaction being assumed to be complete, when all the MOPP have been consumed, then we have $N_{\text{MOPP}}(t) = 0$. The graph $N_i(\text{MOPP})_{\text{Consumed}} = N_{\text{MOPP}}(0) - N_{\text{MOPP}}(t) = f(t)$ then reaches a bearing whose projection on the ordinate axis corresponds to $N_{\text{MOPP}}(0)$. Once $N_{\text{MOPP}}(0)$ is determined, the normality of the remaining MOPPs ($N_i(\text{MOPP})(t)_r$) at time (t), is deduced from the relation (5) below :

$$N_i(\text{MOPP})(t)_r = N_{\text{MOPP}}(0) - N_i(\text{MOPP})_{\text{Consumed}}(t) \quad (5)$$

The normality (N) and the molarity (C) of a species are linked by an integer corresponding to the number of particles (ε) brought into play by this species in a half-equation such as $N = \varepsilon \times C$. Therefore, the concentration

Table 2. Values $N_i(MOPP)_{consumed} = N_{MOPP}(0) - N_{MOPP}(t)$ of the normality of the MOPP consumed (Exp 1, 2 and 3)

Reaction time t (min)	0	5	15	30	45	60	75	90	120
$N_1(MOPP)_{consumed} (10^{-3} \text{ eq-g. L}^{-1})$	0	0.70	1.50	1.90	2.20	2.30	2.40	2.50	2.50
$N_2(MOPP)_{consumed} (10^{-3} \text{ eq-g. L}^{-1})$	0	1.40	2.00	2.30	2.40	2.50	2.50	2.50	2.50
$N_3(MOPP)_{consumed} (10^{-3} \text{ eq-g. L}^{-1})$	0	0.35	0.75	0.95	1.10	1.15	1.20	1.25	1.25

Table 3. Values $N_i(MOPP)(t)_r = N_{MOPP}(0) - N_i(MOPP)_{consumed}(t)$ of the normality of the remaining MOPPs at the moment t (Experiments 1, 2 and 3)

Reaction time t (min)	0	5	15	30	45	60	75	90	120
$N_1(MOPP)_r (10^{-3} \text{ eq-g. L}^{-1})$	2.50	1.80	1.00	0.60	0.30	0.20	0.10	0.00	0.00
$N_2(MOPP)_r (10^{-3} \text{ eq-g. L}^{-1})$	2.50	1.10	0.50	0.20	0.10	0.00	0.00	0.00	0.00
$N_3(MOPP)_r (10^{-3} \text{ eq-g. L}^{-1})$	1.25	0.90	0.50	0.30	0.15	0.10	0.05	0.00	0.00

The graphs ($N_1(MOPP)$ et $N_2(MOPP)$) on the ordinate axis at $t=0$ give the content of MOPP in the soap effluent which is $2.510^{-3} \text{ eq-g. L}^{-1}$. In addition, the curve $N_3(MOPP)$ of experiment 3 gives the value $1.2510^{-3} \text{ eq-g. L}^{-1}$. This third experience consolidates the first two experiences. In fact, the normality of MOPP in soap factory waste water diluted twice is $1.2510^{-3} \text{ eq-g. L}^{-1}$. This value is equal to half of that obtained for experiments 1 and 2 (initial raw effluent) which is $2.510^{-3} \text{ eq-g. L}^{-1}$.

The kinetic quantities of degradation of oxidizable materials in soap and cosmetic effluent were determined. To do this, hypotheses of order 1 and 2 are formulated. Experiment 1 with raw effluent is retained for this study. The first order hypothesis leads to the kinetic law:

$$\ln\left(\frac{N_1(t)}{N_0}\right) = -k_1' t \quad (8)$$

In addition, the second-order hypothesis gives the relation (9):

$$\frac{1}{N_1(t)} - \frac{1}{N_0} = k_2' t \quad (9)$$

With k_1' and k_2' which are respectively the rate constants of reactions of order 1 and 2. They are expressed in $\text{eq.g.L}^{-1}.\text{min}^{-1}$.

The linear regression correlation graph of the MOPP degradation reaction of order 1 is illustrated in Figure 3 with a correlation coefficient ($R_1^2 = 0.9916$). Figure 4 gives that of the hypothesis of order 2 with a correlation coefficient ($R_2^2 = 0.8622$)

Analysis of the correlation coefficient values shows that $R_1^2 = 0.9916 > R_2^2 = 0.8622$. The degradation reaction of MOPP from soap and cosmetic effluent by potassium permanganate at room temperature and basic pH is of order 1 with an apparent rate constant $k_1' = 4.14.10^{-2} \text{ eq-g.L}^{-1} \text{ min}^{-1}$

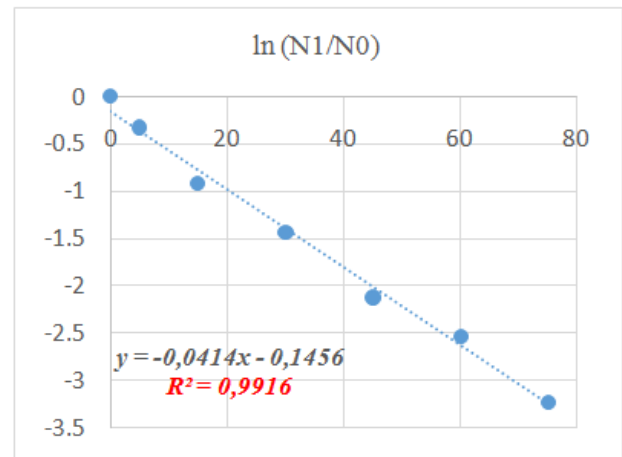


Figure 3. Linear regression curve of the MOPP degradation reaction of order 1

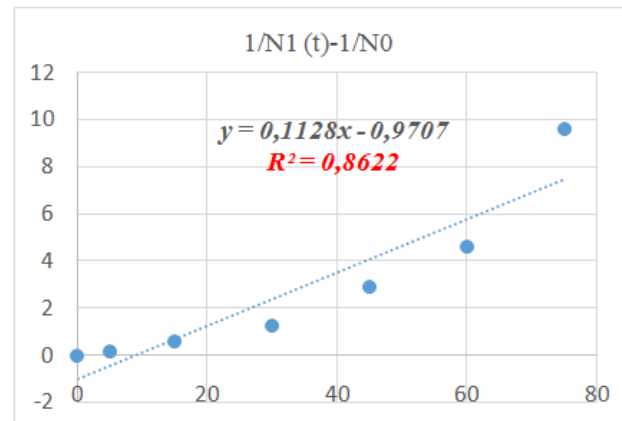


Figure 4. Linear regression curve of the MOPP degradation reaction of order 2

3.2. Discussion

The variation in the residual concentration of MOPP over time shows that permanganate has an oxidative action on the raw soapmaking effluent at the temperature and pH ($\text{pH} = 10.7; T = 33^\circ\text{C}$) studied. This oxidative action depends on the concentration of the oxidant. The more concentrated the permanganate, the faster the MOPP content consumed increases. In addition,

the action of permanganate on *MOPP* is slow (at least 1 hour reaction time). These results are in agreement with those obtained during the work of S. GUERGAZI, and S. ACHOUR [29,30]. Indeed, the study of the oxidative action of permanganate on surface water has shown that oxidation is favored for high levels of oxidant, a basic

pH and a fairly long time (approximately 1 hour) [29,30]. The *pH* could then strongly condition the oxidation mechanisms, depending on the nature of the redox couple present [30,31,32]. Moreover, the potassium permanganate solution being acidified, the redox couples with strong oxidizing power are MnO_4^- / Mn^{2+} and MnO_4^- / MnO_2 . These higher potential couples would react concurrently with the *MOPPs*. This last parallel reaction could slow down the main reaction considered with the redox couple MnO_4^- / Mn^{2+} . Also, the slow reactivity of permanganate would be due to the presence of free radicals in the reaction medium [32] generated by the different redox couples of permanganate [33,34,35]. These radicals would generate parasitic reactions thus blocking the main reaction of degradation of the effluent by potassium permanganate [33,34,35]. However, the degradation kinetics of *MOPP* follows a reaction of order 1 with a rate constant $k_1' = 4.14.10^{-2} \text{ eq-g.L}^{-1} \text{ min}^{-1}$ and a correlation coefficient *R*² greater than that of order 2. This shows proportionality with the concentration of the effluent, because the higher the concentration of the latter, the higher the rate of degradation of *MOPP*. The first order kinetics of the degradation reaction of *MOPPs* in soap and cosmetics effluent by potassium permanganate confirms that these *MOPPs* contain mainly organic pollutants [36,37,38]. This result is in agreement with several kinetic studies carried out on the kinetics of degradation of organic pollutants [36,37,38]. It is important to indicate that despite the slow nature of this process, it turns out to be faster than other processes which have remained at the laboratory stage, because they are very complex and their implementation turns out to be expensive [39,40]. This process has the advantage of being simpler, being able to be carried out in situ, with a less expensive reagent.

4. Conclusion

The degradation of Oxidizable Materials by Potassium Permanganate (*MOPP*) is part of the depollution of industrial effluents. The chemical oxidation process using potassium permanganate and the indirect volumetric dosage by manganometry used in this work provided interesting and consistent results. The degradation reaction of *MOPP* by $KMnO_4$ follows kinetics of global order 1 with a rate constant $k_1' = 4.14.10^{-2} \text{ eq-g.L}^{-1} \text{ min}^{-1}$ at room temperature and basic *pH*. It is remarkable that *MOPPs*, although made up of several oxidizable compounds, behave according to the kinetic law, as a single, predominantly organic species. However, the oxidation reaction of *MOPP* by $KMnO_4$ at room

temperature and at basic *pH* is slow, because all of the *MOPP* degrade after approximately 90 minutes. An improvement of this work is possible by taking into account other kinetic parameters such as *pH*, temperature, etc. Modeling this degradation reaction is possible for in situ treatment of soap and cosmetic effluents.

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