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REMOVAL OF VEGETABLE OIL FROM WASTEWATER BY PHOTO-FENTON PROCESS

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Abstract: The present work evaluated the use of photo-Fenton process ($UV/H_2O_2/Fe^{2+}$) for the treatment of oily aqueous solution using batch system. The photo-Fenton best operating conditions, such as time, pH, oil concentration, H_2O_2 dosage, $Fe_2SO_4.7H_2O$ concentration and temperature were evaluated. The efficiency of the treatment was measured by COD (chemical oxygen demand) removal. The results showed that the optimum pH for the photo-Fenton process was equal to 3. The increase in H_2O_2 application resulted in an efficiency increase of the photo-Fenton process at 800 mg/l, the optimum $Fe_2SO_4.7H_2O$ concentration found was 60 mg/l. It was found that the optimal temperature for the Photo-Fenton processes 30°C. Oil concentrations were varied and lower concentration was removed more efficient. Photo-Fenton process gave a maximum COD reduction of 80.59 % (COD from 2684 to 521 mg/l) after the total reaction time (180 min) at optimal operation conditions.

Keywords: *sunflower oil, advanced oxidation process, photo-fenton, industrial wastewater*

ازالة الزيوت النباتية من المياه الملوثة بواسطة الاكسدة المتقدمة (Photo-Fenton)

الخلاصة: تم دراسة عملية معالجة المياه الملوثة بالزيوت النباتية بطريقة الاكسدة المتقدمة (AOP). حيث استخدم طريقة الـ ($UV/H_2O_2/Fe^{2+}$).عدة عوامل تاثر على التفاعلات لذلك تم دراستها معظمها و لعله اهمها هي تركيز بيروكسيد الهيدروجين H_2O_2 وتركيزكبريتات الحديد الثنائي$Fe_2SO4.7H_2O$كعامل مساعد. لقد تم ايضا دراسة الوقت ودرجة الحموضة والحرارة وتركيز الزيوت في المياه الملوثة. تم احتساب نسبة الازالة بالاعتماد على المتطلب الاوكسجين الكيميائي COD. اظهرت النتائج ان افضل درجة حموضية تساوي 3 في افضل وقت وهو 180 دقيقة. كما ان زيادة تركيز بيروكسيد الهيدروجين ادى الى زيادة في نسبة الازالة عندا800 mg/l و افضل تركيز لكبيرتات الحديد الثنائي كانت 60 mg/l. كما وجد ان افضل درجة حرارة لاجراء التفاعل هي 30 درجة سيليزية و كانت نسبة ازالة % 80.59 (COD من 2684 mg/l الى 521 mg/l) في 180 دقيقة عند تركيز 1000 mg/l زيت. اظهرت النتائج بان هذه الطريقة قد تكون واعدة لازالة الزيوت النباتية في المصانع.

1. Introduction

Conventional water and wastewater treatment processes have been long established in removing many chemical and microbial contaminants of concern to public health and the environment. However, the effectiveness of these processes has become limited over the last two decades because of three new challenges. First, increased knowledge about

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the consequences from water pollution and the public desire for better quality water have promoted the implementation of much stricter regulations by expanding the scope of regulated contaminants and lowering their maximum contaminant levels (MCLs). Second, water resources are diminishing and populations are rapidly growing. The reuse of municipal and industrial wastewaters and the recovery potential pollutants used in industrial processes become more critical. This is especially true in arid or semi-arid areas where potable and irrigation water must be imported at great expense. Reclamation may be further justified in view of the growing concern over contamination of water resources and the release of more toxic compounds.

Last, advances in manufacturing and the growing market associated with advanced treatment processes have resulted in substantial improvements to the versatility and costs of these processes on an industrial scale.

To resolve these new challenges and better use economical resources, various advanced treatment technologies have been proposed, tested and applied to meet both current and anticipated treatment requirements. Among them, membrane filtration, advanced oxidation processes (AOPs) and UV irradiation have been proven to remove successfully a wide range of challenging contaminants and hold great promise in water and wastewater treatment. (Mohammadi & Esmaeelifar, 2004) [1].

The demand for vegetable oils has increased rapidly in the past decade, catapulted by a combination of factors, including: i) increasing demand sparked off by higher consumption for edible oils, particularly in emerging countries such China and India caused by, among other things, population growth, improving living standards and changing diets; ii) the development of the biofuels industry (and more specifically biodiesel) around the world, particularly in the EU, USA, Brazil, Argentina, China and India, iii) price increases which have been due to varying factors e.g. increase in oil prices, low stock worldwide, droughts, and speculation, iv) changing weather patterns which can have major geographical impacts and can be, potentially, quite large (Rosillo-Calle et al, 2009) [2]

Vegetable oil refinery wastewater is a complex mixture composed of widely-distributed particle sizes influencing each unit operation of the treatment process. The elimination of the pollution load by physicochemical treatment is affected by many factors such as the characteristics of the organic matter, the nature and concentration of other components, and the design and operation of the treatment facility. As a result, the removal of pollution load may widely vary (Chipasa. 2001)[3] .

Vegetable oils and fats represent an important food market in Iraq, per capita consumption of cooking oil is in keeping with regional values at around 15 kg/year. Vegetable ghee – derived from palm oil – accounts for almost 50% of the market by volume while liquid oil – almost equally split among sunflower oil, palm oil, and soy oil – makes up the other 50%. Currently oil seed production in Iraq is negligible and limited to insignificant quantities of cotton seed and sunflower.

The objective of this study is to investigate the effectiveness of AOPs for the degradation of vegetable oil in wastewater and the different affective factors and have a general view of this process.

2. Experiments

Commercial sunflower oil was been used as the model pollutant and used to prepare an artificial vegetable wastewater sample. The commercial sunflower oil used was from BilBak, double refined sunflower oil and imported for Iraqi ministry of trade/ state company for foodstuff trading, for the purpose of ration card. It was analyzed at the Iraqi vegetable oil company laboratories (Table 1). Artificial sunflower oil-water emulsion was prepared as it is the critical level of oil wastewater. The samples were prepared by using 2.5 ml of 100 ppm sodium dodecyl sulphate (Biltrec, Spain) for every 100 ml of oil in 1 liter distilled water (Ebrahim et al,.2013) [4].

Table 1. Physical properties of sunflower oil sample

Test	Result	Standard
Relative Density	0.920	0.918- 0923
Refractive index (40 °C)	1.468	1.467 – 1.469
Cloud point	2	+ 6ºC
Peroxide value	1.6	Max. 2
F.F.A.	0.05	0.18 – 0.20
Fe	5	Max. 15 ppm
Color: R Y	R= 0.9 Y= 4.8	R= 3 Y= 30
Odor	Acceptable	Acceptable

2.1. Reagents

All the reagents used in the experiments was research grade without further purification whereby H_2O_2 (50%, w/w) from Solvochem, $FeSO_4{\cdot}7H_2O$ from Hopkin and Williams (England) and $Na_2S_2O_3$, NaOH and H_2SO_4 from Central Drug House (India).

2.2. Analytical Method

Chemical oxygen demand of the samples was analyzed by using Lovibond Checkit direct COD Photometer (Germany). The COD ranges used were from 0-15000 mg/l and 0-1500 mg/l.

2.3 Experimental work

Artificial sunflower oil-water emulsion are prepared as it is the critical level of oily wastewater. The emulsion is then filtered using a quantitative filter paper (Fushun, model 102) and the oil-water emulsion is considered as a stock sample. The desired concentration of oil in water used in the experiments is obtained by diluted the stock solution with distilled water, using the following equation:

$$V_1 \times C_1 = V_2 \times C_2 \qquad (1)$$

V_1, V_2 = Volume (l)
C_1, C_2 = Concentration (mg/l)

After adjusting the different factors, the removal efficiency is considered as the indicator for the best system which is calculated using the following formula:

$$\text{Removal Efficiency \%} = \frac{\text{COD}_{\text{initial}} - \text{COD}_{\text{final}}}{\text{COD}_{\text{initial}}} \times 100 \qquad (2)$$

$\text{COD}_{\text{initial}}$ = COD concentration before treatment (ppm)
$\text{COD}_{\text{final}}$ = COD concentration after treatment (ppm)

3. Result and Discussion

Different factors were studied in this study to discuss its effects on the AOP's. The performance of Photo-Fenton for COD removal from oily compounds aqueous solution using batch system was investigated. The following factors were studied: oil content, pH value, temperature, effect of H_2O_2 concentration, effect of $Fe_2SO_4.7H_2O$ concentration and irradiation time.

3.1. The effect of irradiation time

The effect of time required for the Photo-Fenton process in order to get the best removal efficiency was studied under UV irradiation using UVM 9311 G lamp (6 watt 4P-SE, SO SAFE WATER TECHNOLOGIES, UAE). Fixed initial amount of H_2O_2, $Fe_2SO_4.7H_2O$, pH and temperature was set. Initial oil concentration (1000) mg/l with (COD = 2500 ± 500) was used in the experiments. The results for Photo-Fenton process plotted in Fig. (1)

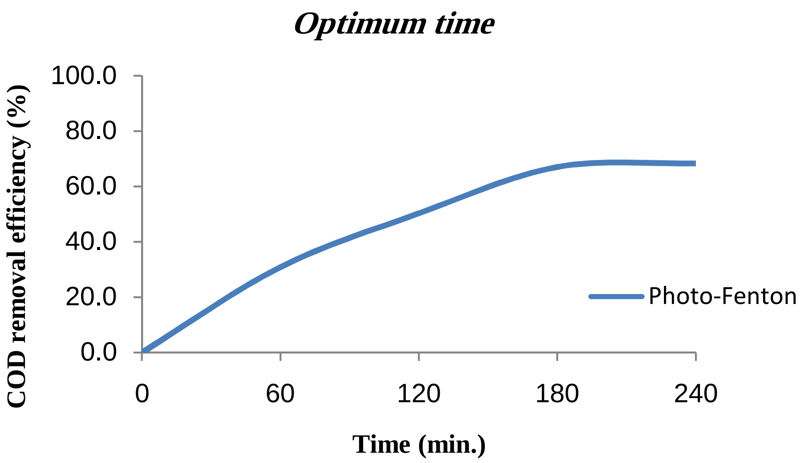

Figure 1. Effect of irradiation time on the COD removal by Photo-Fenton at H_2O_2conc. = 1000 mg/l, pH = 7, oil conc. = 1000 mg/l, temp. = 20°C and $Fe_2SO_4.7H_2O$ conc. = 100 mg/l

The optimum time that gave best removal efficiency was found after 180 min. It gave a total 67.07 % COD reduction for Photo-Fenton process.

Some intermediates are non-volatiles compounds, causing the lowness of COD reduction increase. Such intermediates (quinines, acetic acid etc.) require sufficient time to push reaction beyond CO2 (Nasr, 2004)[5].

3.2. The effect of H_2O_2 concentration

The effect of initial concentration of H_2O_2 on Photo-Fenton, process was tested to optimize the amount of H_2O_2 required to reduce the COD. The H_2O_2 concentration range for Photo-Fenton was (200,400,600,800 and 1000) mg/l. Fixed initial oil concentration, $Fe_2SO_4.7H_2O$ concentration, pH and temperature was used in all experiments. The results were plotted in Fig. (2).

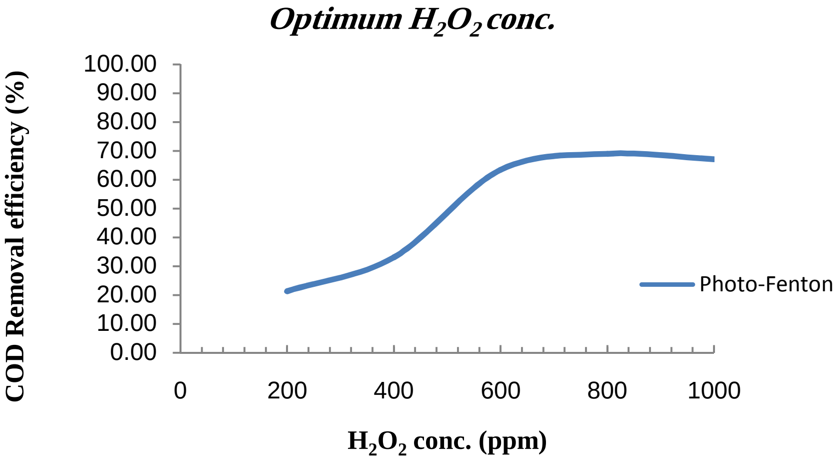

Figure 2.Effect of initial H_2O_2 concentration on the COD removal by Photo-Fenton system at pH = 7, oil conc. = 1000 mg/l and temp. = 20°C and $Fe_2SO_4.7H_2O$ conc. = 100 mg/l

From this figure it can be noticed that the COD removal increased as the concentration of H2O2 increased, reaching a maximum removal efficiency at H2O2 = 800 mg/l. At higher H2O2 dosage there was an increase or no change in COD removal efficiency. Hydrogen peroxide was the main responsible species of the degradation process by the generating of hydroxyl radicals from the direct photolysis. It can be observed that the degradation rate increased considerably when H2O2 increased (Esplugas, 2002)[6] .

It was found that further increase of H2O2 concentration retarded effluents COD. This inhibition of mineralization is probably due to both auto decomposition of H2O2 into oxygen and water and the scavenging of hydroxyl radicals by the excess of H2O2. Also hydroxyl radical may recombine and participate in radical-radical reactions to form H2O2. At higher H2O2 concentrations lower light intensity is available for oil degradation, since H2O2 also absorb slights in the system (Ebrahim, 2013)[4].

3.3. The effect of $Fe_2SO_4.7H_2O$ concentration

The effects of initial Iron salt ($Fe_2SO_4.7H_2O$) on Photo-Fenton process were tested by carrying out experiments with different concentration of $Fe_2SO_4.7H_2O$ (20, 40, 60, 80 and 100 mg/l). Initial oil concentration, pH and temperature were used in all experiments. The results were plotted in Fig. (3). By this figure it can be noticed that the degradation rate of oil increased with the increasing amounts of iron salt. It reached its maximum value (72.35 %) at 60 mg/l after about 180 min. of irradiation time. The addition of the iron salt above these values did not affect the degradation; it decreased or remained unchanged. This is explained as:

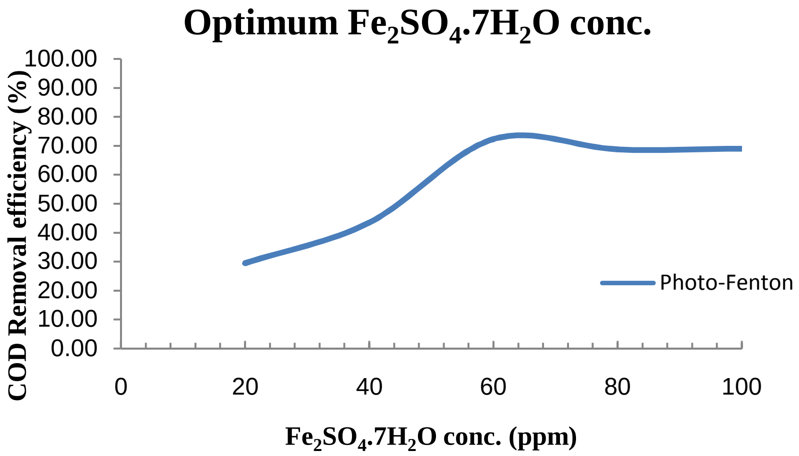

Figure 3.Effect of initial $Fe_2SO_4.7H_2O$ concentration on the COD removal by Photo-Fenton system at pH = 7, oil conc. = 1000 mg/l and temp. = 20°C, H_2O_2conc. = 800 mg/l

Addition of ferrous ions increases wastewater brown turbidity during the photo-treatment, which hinders the absorption of the UV light, required for the Photo-Fenton process (Dincer et al., 2008)[7] .Excessive formation of Fe^{+2} can compete with the organic carbon for OH radical. Also high Fe ions disposal will require another process to remove the iron residual so for an economical point of view, in this condition, it is not necessary to have high concentration of Fe ion (Galvao et al., 2006)[8]. Fixed H_2O_2 concentration can be the limiting factor (Rodriguez et al, 2002)[9].

3.4. The effect of pH value

The pH plays an important role in the AOP's and has a considerable effect on the reactions, because of the big influence to the oxidation potential of OH radical according to the eciprocal relation of the oxidation potential to the pH value (E_0=2.8 V and E_{14}=1.95 V) (Alalm et al, 2013) [10] . Different values of pH were examined in this study (3,7 and 11) keeping the other parameters and dosage constant. The results are plotted in (4).

The optimum pH found (3) can be explained by that the operational pH must be low (pH <4) to nullify the effect of sequestering radical species, specifically ionic species such as carbonate and bicarbonate ions, leading to a better degradation rate (Mota et al., 2008)[11] .

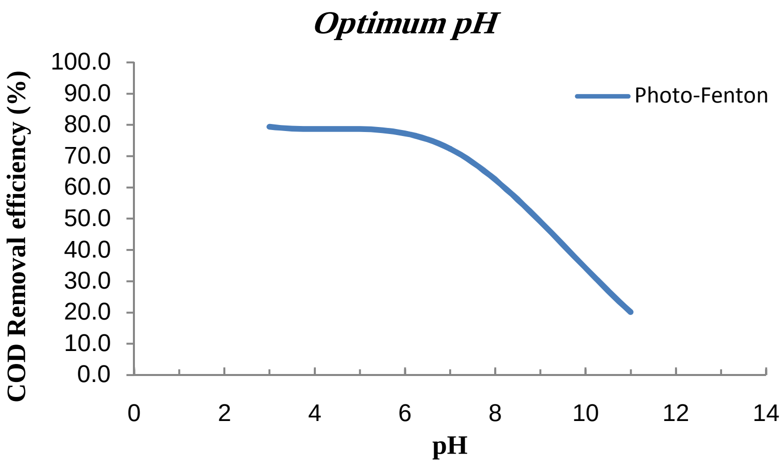

Figure 4. Effect of pH value initial concentration on the COD removal by Photo-Fenton system at oil conc. = 1000 mg/l and temp. = 20°C, H_2O_2conc. = 800 mg/l and $Fe_2SO_4.7H_2O$ conc. = 60 mg/l .

At high pH, iron reacts with the hydroxide ions (HO-), precipitating the iron hydroxide ($Fe(OH)_2$ or $Fe(OH)_3$, which does not react with H_2O_2, which will decrease the degradation rate (Mota et al., 2008)[11] .

The removal efficiency of COD was improved at the acidic conditions, raising the pH from 3 to 7 decreased the COD removal efficiency. A similar finding was reported by (Li et al.,2009)[12], who found that the decomposition rate of H_2O_2 is low at pH exceeding 4 resulting a drop in the hydroxyl radicals production.

In high pH condition, the reaction between Fe^{3+} and OH- will leads to the formationof $Fe(OH)_3$. This species will start to precipitate after pH 4.8 based on the calculation from its solubility constant value; K_{sp} ($Fe(OH)_3$ is 2.79 E^{-9}.

This precipitate will then act as coagulant. Therefore, it is expected that no dominance oxidation and OH radicals generation will occur at this stage (Fadzil et al., 2013) [13] .

3.5. *The effect of oil concentration*

Different concentrations of sunflower oil (1000, 2000 and 3000) mg/l were used at fixed pH, temperature, H_2O_2 and $Fe_2SO_4.7H_2O$ dosage for all experiments. The results are plotted in Fig.(5).

By these figures it can be observed that the removal efficiency decreases linearly in Photo-Fenton from 79.4 % to 38.2 % as the concentration of oil increases from 1000 to 3000 mg/l respectively.

This can be attributed to the increase in COD which leads to high turbidity of the solution. In Photo-Fenton the COD for 3000 mg/L oil solution was measured to be 5861, whereas for 1000 mg/L oil solution the COD was 2587 only. As turbidity in the solutions during the photo treatment hinders the absorption of the UV light for the photo

Fenton process(Rodriguez et al., 2002)[9] . (Dincer et al., 2008)[7] diluted wastewater with 21000 ppm COD (80%)in order to treat it with Photo-Fenton.

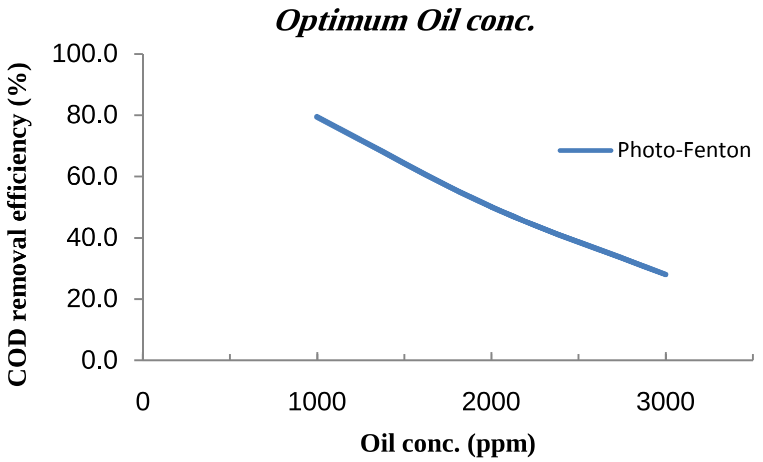

Figure 5. Effect of oil concentration on the COD removal at pH = 3, temp. = 20°C, H_2O_2conc. = 800 mg/l and $Fe_2SO_4.7H_2O$ conc. = 60 mg/l

3.6. *The effect of temperature*

Reaction temperature is another important process parameter that affects the degradation process. Different temperatures (20, 30 and 40)°C were used. The dosage of the reagents and other parameters were remained constant as obtained from previous sections.

The results were plotted in Fig. (6). this figure shows that the COD removal efficiency increases at 30°C and then decreased at 40°C. For Photo-Fenton the maximum removal efficiency was 80.59 % at 30°C.

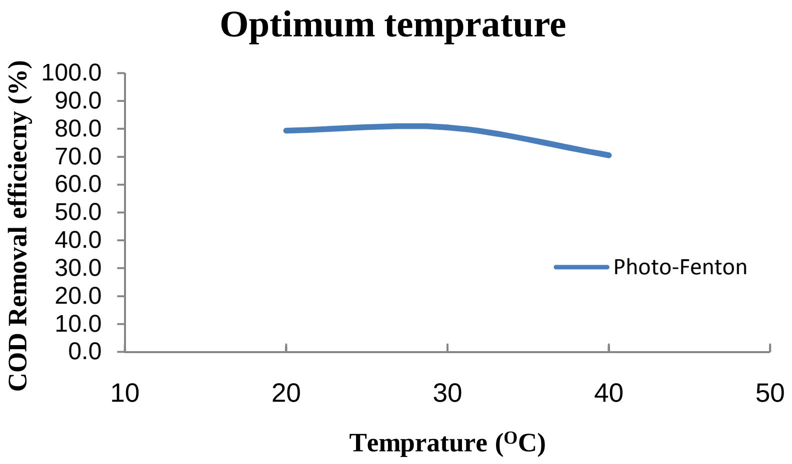

Figure 6. Effect of temperature on the COD removal at pH = 3, oil conc. = 1000 mg/l, H_2O_2 conc. = 800 mg/l and $Fe_2SO_4.7H_2O$ conc. = 60 mg/l

The increase in temperature accelerated the decomposition of H_2O_2 thus increasing the generation of OH radicals which enhances the degradation process slightly. There is no significant COD removal different with different temperatures; the range of the COD removal on predetermined time for these three different temperatures is less than 10%. This finding is in agreement with the previous observation of (Leong and Bashah, 2012)[14].

The optimal temperature is in the range of 30-40^{o}C and this result is similar to other researches findings (Lucas and Peres, 2009[15]; Nieto et al., 2011[16]; Leong and Bashah, 2012[14]).

4. Conclusions

The COD removal from synthetic vegetable oil wastewater was investigated by the Photo-Fenton process. The COD removal efficiency was strongly affected by many factors such as the concentration of H_2O_2, $Fe_2SO_4.7H_2O$, pH, temperature and the oily content amount.

It was found that the Photo-Fenton processes have the potential to partially reduce the COD of oily wastewater in different removal percentage. The overall results of this study indicate that the application of Photo-Fenton process is a feasible method to treat vegetable oily content wastewaters achieving a significant decrease of COD. Optimum initial pH was found 3 and temperature = 30^{o}C for the process studied. Optimum chemical reagents dosage for Photo-Fenton at H_2O_2 = 800 mg/l and $Fe_2SO_4.7H_2O$ = 60 mg/l, led to a COD reduction of 80.59 %.

5. Acknowledgements

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Appendix A

$$\mathrm{V_1 \times C_1 = V_2 \times C_2} \qquad \text{(A-1)}$$

$$\text{moval Efficiency \%} = \frac{\mathrm{COD_{initial} - COD_{final}}}{\mathrm{COD_{initial}}} \times 100 \qquad \text{(A-2)}$$