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CHARACTERISTICS OF SOME PHYSIOCHEMICAL FACTORS FOR LIQUID WASTE WATER TREATMENTS

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ABSTRACT

Olive mill wastes exacerbate environmental problems in Mediterranean countries. These wastes are highly phytotoxic due to polyphenolic compounds, lipids and organic acids, they also contain high percentages of organic matter. For that importance the present study was designed in an attempt to study the effect of different chemical treatments (as pretreatments), aiming to minimize the level of organic load of Olive Mill Waste Water (OMW). The results of different tested parameters [color, pH, Total Dissolved Solids (T.D.S.) ,Chemical Oxygen Demand (C.O.D.) , Biological Oxygen Demand (B.O.D.) , Total Polyphenols & Trace elements of Cadmium (Cd^{+2}) , Copper (Cu^{+2}) , Zinc (Zn^{+2}) and Manganese (Mn^{+2}) which were recorded before and after each treatment & discussed .

Key words: olive mill waste water, physiochemical characteristics, chemical & biochemical characteristics, Total polyphenols & Trace elements content of olive mill waste water, clay soil filtration, sandy soil filtration.

INTRODUCTION

Olive production in the Meditrenean Sea area is presented approximately 90 % of the world olive production , according to that mentioned by **Kiritsakis *et al* (1990).**Outside the Meditrenean area , the main olive production countries area are Argentina and California State.Moreover, olive oil is one of the oldest known vegetable oils mainly produced in countries surrounding the Mediterranean Sea. Its importance increasd recently as a result of discovery many of its healthy benefit **(Kiritsakis *et al* 2002).**

Olive Mill Waste water (OMW) is generated in the production of olive oil. Its treatment is a major environmental problem in Mediterranean countries, where the generation rate is very high and concentrated in a short period of time (November- February). The high COD value and the presence of phytotoxic and anti bacterial polyphenols in OMW can be a serious pollution risk for superficial and underground waters. Moreover, the presence of phenolic compounds in OMW makes them highly toxic and ecologically noxious **(Capasso *et al* 1992; Aggelis *et al* 2003).**

MATERIALS AND METHODS

Samples collection:

Samples of olive mill waste water collected from one site location of North Sinai (El Arish Faculty of Environmental and Agricultural Sciences olive mill).

Water sample analysis :

Water samples analysis was carried out according to standard methods for examination of water and wastes (**APHA**). **APHA: 1998,** Standard Methods for the Examination of Water and Wastes, 20th ed., American Public Health Association (APHA), Washington, DC. All samples collected for chemical and biochemical analyses were stored in an ice box and delivered immediately to the desert central laboratory in cairo, all chemicals used were of analytical grade reagents obtained from British Drug Houses (BDH) or sigma Chemical Companies, Physical examination ,chemical and biochemical determinations of the tested trace elements, total polyphenols, chemical oxygen demand (C.O.D.) and biological oxygen demand (B.O.D.) were carried out according to those recommended by the standard methods (1998) for examination of water.

Table (1) :The effect of different treatments on some physiochemical characteristics of olive mill waste water:

Sample no.	PH ± SD	TDS ± SD	Color
A1	5.2 ± 0.05	147 ± 3.8	Red
B1	5.0 ± 0.01	147 ± 3.6	Red
A2	10.8 ± 0.2	112 ± 4.6	Dark yellow
B2	11.1 ± 0.15	102 ± 5.3	Pale brown
A3	7.8 ± 0. 1	92.6 ± 4.7	Yellow
B3	8.4 ± 0.2	83.4 ± 3.9	Yellow
A4	6.6 ± 0.12	94.3 ± 5.6	Pale brown
B4	7.8 ± 0.2	80.2 ± 8.3	Pale brown
A5	7.6 ± 0. 1	95.3 ± 4.8	Colerless
B5	8.4 ± 0.2	86.8 ± 3.9	Colerless
A6	7.7 ± 0. 1	96.4 ± 2.8	Colerless
B6	7.3 ± 0.2	89.5 ± 3.2	Colerless
AC	8.0 ± 0.14	114.0 ± 6.8	Dark brown
BC	8.0 ± 0.05	110.0 ± 5.4	Dark brown
AS	7.7 ± 0. 1	138.0 ± 5.6	V. pale Yellow
BS	7.3 ± 0.1	135 ± 6.3	V. pale Yellow
Raw Sample alone	4.4 ± 0.05	150.0 ± 6.7	Dark brown

A1=(aeration+shaking+sunlight) treatment. **B1**=(($NH_4(SO_4)_2$ (1%)+shaking) at anaerobic conditions treatment.

A2= aerobic [$Ca(OH)_2$(1%)] treatment. **B2**= anaerobic [$Ca(OH)_2$(1%)] treatment.

A3= aerobic [$FeCl_3$(1%)] treatment **B3**=anaerobic [$FeCl_3$(1%)] treatment.

A4= aerobic [P.A.C.(1%)] treatment. **B4**=anaerobic [P.A.C.(1%)] treatment

A5= aerobic mixture [$H_2O_2$7%+$FeCl_{3(50mg/l)}$] treatment.

B5= anaerobic mixture [$H_2O_2$7%+$FeCl_{3(50mg/l)}$] treatment.

A6= aerobic mixture [$Ca(OH)_2$+$Al_2(SO_4)_3$] in a ratio (1:3) treatment.

B6= anaerobic mixture [$Ca(OH)_2$+$Al_2(SO_4)_3$] in a ratio (1:3) treatment.

AC=(aerobic & clay soil filtration) treatment. **BC**=(anaerobic & clay soil filtration) treatment

AS= (aerobic & sandy soil filtration) treatment. **BS**= (anaerobic & sandy soil filtration) treatment

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RESULTS

Characteristics of O.M.W.

1. Effect of aerobic (A1) and anaerobic (B1) treatment on physiochemical

It was noticed that the color changed from dark brown to be a red color in both aerobic & anaerobic treatment, also the PH value changed from strong acidic (4.4) to be less in acidity (5.2 & 5.0) i.e; it increased with ≃ (18 & 14)% in both aerobic & anaerobic treatment respectively. In the same time the T.D.S value decreased with ≃ (2) % in both treatments.

2. Effect of $Ca(OH)_2$ (1%) in an aerobic (A2) and anaerobic (B2) treatment on physiochemical characteristics of O.M.W.

It was showed that the color changed from dark brown to be dark yellow& pale brown in both aerobic & anaerobic treatment respectively, also the PH value changed from strong acidic (4.4) to be strong alkaline (10.8 & 11.1) i.e; it increased with ≃ (145 & 152)% in both aerobic & anaerobic treatment respectively. In the same time the T.D.S value decreased with ≃ (25 & 32) % in both treatments respectively.

3. Effect of $FeCl_3$ (1%) on aerobic (A3) and anaerobic (B3) treatment on physiochemical characteristics of O.M.W.

It was arised that the color changed from dark brown to be yellow in both aerobic & anaerobic treatment, also the PH value changed from strong acidic (4.4) to be weak alkaline (7.8 & 8.4) i.e; it increased with ≃ (77 & 91)% in both aerobic & anaerobic treatment respectively. In the same time the T.D.S value decreased with ≃ (38 & 44) % in both treatments respectively.

4. Effect of P.A.C.(1%) on aerobic (A4) and anaerobic (B4) treatment on physiochemical characteristics of O.M.W.

It was declared that the color changed from dark brown to be Pale yellow in both aerobic & anaerobic treatment, also the PH value changed from strong acidic (4.4) to be weak alkaline (6.6 & 7.8) i.e; it increased with ≃ (50 & 77)% in both aerobic & anaerobic treatment respectively. In the same time the T.D.S value decreased with ≃ (37 & 47)% in both treatments respectively.

5. Effect of mixture $H_2O_2$7%+ $FeCl_{3(50mg/l)}$ on aerobic (A5) and anaerobic (B5) treatment on physiochemical characteristics of O.M.W.

It was noticed that the color changed from dark brown to be colorless in both aerobic & anaerobic treatments , also the PH value changed from strong acidic (4.4) to be weak alkaline (7.6 & 8.4) i.e; it increased with ≃ (73 & 91) % in both aerobic & anaerobic treatment respectively . In the same time the T.D.S value decreased with ≃ (36 & 42) % in both treatments respectively.

6.Effect of mixture [$Ca(OH)_2$+$Al_2(SO_4)_3$] in a ratio (1:3) on aerobic (A6) and anaerobic (B6) treatment on physiochemical characteristics of O.M.W.

It was showed that the color changed from dark brown to be colorless in both aerobic & anaerobic treatments, also the PH value changed from strong acidic (4.4) to be very weak alkaline (7.7 & 7.3) i.e; it increased with ≃ (75 & 66)% in both aerobic & anaerobic treatment respectively . In the same time the T.D.S value decreased with ≃ (36 & 40) % in both treatments respectively.

7. Effect of Clay filtration on aerobic (AC) and anaerobic (BC) treatment on

physiochemical characteristics of O.M.W.

It was postulated that the color did not change i.e; still dark brown in both aerobic & anaerobic treatments, but the PH value changed from strong acidic (4.4) to be weak alkaline (8.0) i.e; it increased with ≃ (82)% in both aerobic & anaerobic treatment. In the same time the T.D.S value decreased with ≃ (24 & 27)% in both treatments respectively.

8. Effect of Sand filtration on aerobic (AS) and anaerobic (BS) treatment on physiochemical characteristics of O.M.W.

It was showed that the color changed from dark brown to be very pale yellow in both aerobic & anaerobic treatment , also the PH value changed from strong acidic (4.4) to be very weak alkaline (7.7 & 7.3) i.e; it increased with ≃ (75 & 66)% in both aerobic & anaerobic treatment respectively. In the same time the T.D.S value decreased with ≃ (8 & 10) % in both treatments respectively.

Biochemical characteristics of O.M.W.

1- Effect of aerobic (A1) and anaerobic (B1) treatment on chemical &

It was explained that the C.O.D. value decreased with ≃ (5 & 15)% in both aerobic & anaerobic treatment respectively. In the same time the B.O.D. value decreased with ≃ (12 & 22)% in both treatments respectively.

2. Effect of $Ca(OH)_2$ (1%) in an aerobic (A2) and anaerobic (B2) treatment on chemical & biochemical characteristics of O.M.W.

It was studied that the C.O.D. value decreased with ≃ (23 & 25)% in both aerobic & anaerobic treatment respectively. In the same time the B.O.D. value decreased with ≃ (16 & 19)% in both treatments respectively.

3. Effect of Fe Cl3 (1%) on aerobic (A3) and anaerobic (B3) treatment on chemical & biochemical characteristics of O.M.W. It was noticed that the C.O.D. value decreased with ≃ (34 & 31)% in both aerobic & anaerobic treatment respectively. In the same time the B.O.D. value decreased with ≃ (32 & 40)% in both treatments respectively.

4. Effect of P.A.C.(1%) on aerobic (A4) and anaerobic (B4) treatment on chemical & biochemical characteristics of O.M.W.

It was showed that the C.O.D. value decreased with ≃ (2 & 8)% in both aerobic & anaerobic treatment respectively. In the same time the B.O.D. value decreased with ≃ (11 & 14)% in both treatments respectively.

5.Effect of mixture $H_2O_2$7%+$FeCl_{3(50mg/l)}$ on aerobic (A5) and anaerobic (B5) treatment on chemical & biochemical characteristics of O.M.W.

It was postulated that the C.O.D. value decreased with ≃ (59 & 65)% in both aerobic & anaerobic treatment respectively. In the same time the B.O.D. value decreased with ≃ (28 & 40)% in both treatments respectively.

6.Effect of mixture [$Ca(OH)_2$+$Al_2(SO_4)_3$] in a ratio (1:3) on aerobic (A6) and anaerobic (B6) treatment on chemical & biochemical characteristics of O.M.W.

It was demonstrated that the C.O.D. value decreased with ≃ (69 & 77)% in both aerobic & anaerobic treatment respectively. In the same time the B.O.D. value decreased with ≃ (39 & 49)% in both treatments respectively.

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7. Effect of Clay filtration on aerobic (AC) and anaerobic (BC) treatment on chemical & biochemical characteristics of O.M.W.

It was noticed that the C.O.D. value decreased with ~ (12 & 19) % in both aerobic & anaerobic treatment respectively . In the same time the B.O.D. value decreased with ~ (13 & 23) % in both treatments respectively.

8. Effect of Sand filtration on aerobic (AS) and anaerobic (BS) treatment on chemical & biochemical characteristics of O.M.W.

It was explored that the C.O.D. value decreased with ≃ (20 & 29)% in both aerobic & anaerobic treatment respectively. In the same time the B.O.D. value decreased with≃ (20 & 28)% in both treatments respectively.

Chemical & biochemical characteristics of O.M.W.

It was noticed that the C.O.D. value decreased with ≃ (12 & 19)% in both aerobic & anaerobic treatment respectively. In the same time the B.O.D. value decreased with ≃ (13 & 23)% in both treatments respectively.

1. Effect of aerobic (A1) and anaerobic (B1) treatment on Total polyphenols & Trace elements content of O.M.W.

It was noticed that the total polyphenols content decreased in ≃ (8 & 9)% in both aerobic & anaerobic treatment respectively In the same time the trace elements (Cd^{+2}, Cu^{+2}, Zn^{+2} & Mn^{+2}) concentrations decreased with ≃ (8, 4, 1 & 1) % & (15, 5, 1 & 2)% in both aerobic & anaerobic treatment respectively.

2. Effect of $Ca(OH)_2$ (1%) in an aerobic (A2) and anaerobic (B2) treatment on Total polyphenols & Trace elements content of O.M.W.

It was concluded that the total polyphenols content decreased in ≃ (40 & 41)% in both aerobic & anaerobic treatment respectively.

Table (2) :The effect of different treatments on chemical & biochemical characteristics of olive mill waste water:

Sample no.	COD g/L ± SD	BOD g/L ± SD
A1	81.78 ± 5.30	20.17 ± 3.08
B1	73.41 ± 4.51	17.82 ± 2.70
A2	66.21 ± 5.62	19.24 ± 3.12
B2	64.70 ± 4.18	18.38 ± 3.16
A3	57.23 ± 3.28	15.67 ± 2.23
B3	59.53 ± 4.36	13.68 ± 2.15
A4	84.76 ± 6.43	20.35 ± 2.33
B4	79.04 ± 5.81	19.52 ± 2.36
A5	35.62 ± 2.90	16.40 ± 2.27
B5	29.89 ± 3.17	13.60 ± 2.74
A6	26.33 ± 3.43	13.85 ± 2.26
B6	19.46 ± 2.92	11.62 ± 3.38
AC	75.80 ± 3.60	19.76 ± 3.21
BC	70.18 ± 4.39	17.48 ± 3.09
AS	69.43 ± 5.26	18.24 ± 2.65
BS	61.58 ± 4.72	16.39 ± 1.78
Raw Sample alone	86.30 ± 5.41	22.80 ± 3.16

Table (3): The effect of different treatments on Total polyphenols & Trace elements content of olive mill waste water:

Sample no.	T.poly phenols ± SD g/L	Trace Elements g/L			
		Cd^{+2} ± SD	Cu^{+2} ± SD	Zn^{+2} ± SD	Mn^{+2} ± SD
A1	5.39±0.13	0.048±0.003	0.246±0.07	0.430±0.06	1.06±0.02
B1	5.30±0.25	0.044±0.002	0.243±0.08	0.430±0.05	1.05±0.09
A2	3.51±0.06	0.018±0.005	0.093±0.002	0.155±0.004	0.656±0.007
B2	3.45±0.05	0.018±0.003	0.089±0.006	0.151±0.008	0.650±0.008
A3	2.34±0.004	0.029±0.004	0.145±0.009	0.246±0.007	0.805±0.005
B3	2.29±0.004	0.026±0.006	0.142±0.006	0.240±0.005	0.801±0.006
A4	2.925±0.007	0.016±0.007	0.080±0.003	0.133±0.006	0.329±0.004
B4	2.910±0.008	0.016±0.006	0.076±0.005	0.130±0.008	0.320±0.003
A5	1.765±0.009	0.015±0.005	0.070±0.008	0.131±0.003	0.865±0.002
B5	1.742±0.006	0.014±0.004	0.069±0.004	0.129±0.004	0.860±0.007
A6	1.185±0.007	0.011±0.008	0.055±0.003	0.092±0.005	0.223±0.007
B6	1.174±0.006	0.010±0.003	0.051±0.005	0.089±0.003	0.219±0.004
AC	3.62±0.003	0.038±0.002	0.180±0.005	0.311±0.002	0.972±0.005
BC	3.58±0.005	0.036±0.007	0.176±0.009	0.306±0.007	0.966±0.004
AS	4.08±0.007	0.049±0.006	0.250±0.006	0.428±0.008	1.06±0.005
BS	4.07±0.004	0.048±0.003	0.250±0.004	0.427±0.006	1.05±0.002
Raw Sample alone	5.85±0.31	0.052±0.003	0.255±0.05	0.435±0.03	1.07±0.08

In the same time the trace elements (Cd^{+2}, Cu^{+2}, Zn^{+2}& Mn^{+2}) concentrations decreased with ≃ (65, 64, 64 & 39)% & (65, 65, 65 & 39)% in both aerobic & anaerobic treatment respectively.

3. Effect of $FeCl_3$ (1%) on aerobic (A3) and anaerobic (B3) treatment on Total polyphenols & Trace elements content of O.M.W.

It was showed that the total polyphenols content decreased in ≃ (60 & 61)% in both aerobic & anaerobic treatment respectively . In the same time the trace elements (Cd^{+2} , Cu^{+2}, Zn^{+2} & Mn^{+2}) concentrations decreased with ≃ (44, 43, 43 & 25)% & (50, 44, 45 & 25)% in both aerobic & anaerobic treatment respectively .

4. Effect of P.A.C. (1%) on aerobic (A4) and anaerobic (B4) treatment on Total polyphenols & Trace elements content of O.M.W.

It was noticed that the total polyphenols content decreased in ≃ (50)% in both aerobic & anaerobic treatment.

In the same time the trace elements (Cd^{+2}, Cu^{+2}, Zn^{+2} & Mn^{+2}) concentrations decreased with ≃ (69, 69, 69 & 69)% & (69, 70, 70 & 70)% in both aerobic & anaerobic treatment respectively.

5.Effect of mixture $H_2O_2$7%+$FeCl_{3(50mg/l)}$ on aerobic (A5) and anaerobic (B5) treatment on Total polyphenols & Trace elements content of O.M.W.

It was explored that the total polyphenols content decreased in ≃ (70) % in both aerobic & anaerobic treatment . In the same time the trace elements (Cd^{+2}, Cu^{+2}, Zn^{+2} & Mn^{+2} concentrations decreased with ≃ (71, 73, 70 & 19) % &

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(73, 73, 70 & 20) % in both aerobic & anaerobic treatment respectively.

6. Effect of mixture [$Ca(OH)_2$+$Al_2(SO_4)_3$] in a ratio (1:3) on aerobic (A6) and anaerobic (B6) treatment on Total polyphenols & Trace elements content of O.M.W.

It was studied that the total polyphenols content decreased in ≃ (80)% in both aerobic & anaerobic treatment . In the same time the trace elements (Cd^{+2} , Cu^{+2}, Zn^{+2} & Mn^{+2}) concentrations decreased with ≃ (79, 78, 79 & 79)% & (81, 80, 80 & 80)% in both aerobic & anaerobic treatment respectively.

7. Effect of Clay filtration on aerobic (AC) and anaerobic (BC) treatment on Total polyphenols & Trace elements content of O.M.W.

It was indicated that the total polyphenols content decreased in ≃ (38 & 39)% in both aerobic & anaerobic treatment respectively . In the same time the trace elements (Cd^{+2}, Cu^{+2}, Zn^{+2} & Mn^{+2}) concentrations decreased with ≃ (27, 29, 29 & 9) % & (31, 31, 30 & 10)% in both aerobic & anaerobic treatment respectively.

8. Effect of Sand filtration on aerobic (AS) and anaerobic (BS) treatment on Total polyphenols & Trace elements content of O.M.W. It was illustrated that the total polyphenols content decreased in ≃ (30) % in both aerobic & anaerobic treatment. In the same time the trace elements (Cd^{+2}, Cu^{+2}, Zn^{+2} & Mn^{+2}) concentrations decreased with ≃ (6, 2, 2 & 1)% & (8, 2, 2 & 2)% in both aerobic & anaerobic treatment respectively.

DISCUSSION

And now let us discuss and show from the beginning of the study (I) i.e, in case of applying aerobic & anaerobic treatments (A1 & B1) were generally in a similar agreement with the results obtained by **Tunay *et al* 1992, Sabbah *et al* 2004,** and very recently by **Mekki *et al* 2013**.

Also via statistical analysis of data by **Duncan 1955** and Sndecor & Cochran 1990 by **(professor assistant Eman Ismail El-Sarag)** there was a significancy between raw sample and treatments .(II) i.e., in case of using the $Ca(OH)_2$ as a reference coagulant, where the results achieved in that study were in an approval with the results obtained by **Zouari 1998 and Aktas *et al* 2001** & recently proved by **Sarika *et al* 2005** and **El-Hajjouji *et al* 2008** and very recently by **Kılıç & Solmaz 2013 & Barbera *et al* 2013**.

Also via the same statistical analysis used before, there was a significancy between raw sample and treatments. (III) in case of using the $FeCl_3$ as another reference coagulant, the results exhibited in the study were in an agreement with that obtained by **Sarika *et al* 2005** and very recently by **Kılıç & Solmaz, 2013**.

Also via the same statistical analysis used before , there was a significancy between raw sample and treatments .(IV) i.e., in case of using P.A.C. treatment as an adsorbent agent where the results were in a correspondence with the results elucidated early by **Mohan & Singh 2002** also in a similar way with the results explained by **Mavros *et al* 2008 & Shabana *et al* 2010** supporting that concept and very recently by results of **Chouchene *et al* 2012, Kılıç & Solmaz, 2013** and **Barbera *et al* 2013.**

Also via the same statistical analysis used before , there was a significancy between raw sample and treatments. (V) in case of using the mixture of H_2O_2 & $FeCL_3$ as an oxidizing agent the results obtained were in an accordance with the results demonstrated very early by **Zouari**

1998 and recently with the results obtained by **Shabana *et al* 2010** and very recently by **Ochando-Pulido *et al* 2012**, **Kılıç & Solmaz, 2013 & Kılıç *et al* 2013.**Also via the same statistical analysis used before , there was a significancy between raw sample and treatments .(VI) in case of mixture $Ca(OH)_2$ & $Al_2(SO_4)_3$ as a flocculant agent , the results were in an agreement with the results achieved by **Mavros *et al* 2008, Shabana *et al* 2010** and very recently by **Kılıç & Solmaz, 2013.**

Also via the same statistical analysis used before , there was a significancy between raw sample and treatments. (VII) in case of using the clay as an infiltrate agent, the results were in an agreement with the results proved very early by **Proietti *et al* 1995**, **Al-Malah *et al* 2000** and recently by **Jarboui *et al* 2008.**

Also via the same statistical analysis used before, there was a significancy between raw sample and treatments. (VIII) finally in case of using the sand as a filtration agent, the obtained results were in a similar agreement with that obtained by **Sabbah *et al* 2004** and recently by **Achak *et al* 2009.** Also via the same statistical analysis used before, there was a significancy between raw sample and treatments.

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الملخص العربى

بعض الخصائص للعوامل الفيزوكيميائية لمعالجة مخلفات المياه السائلة

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إن مخلفات معاصر الزيتون سببت في تفاقم المشاكل البيئية في بلدان منطقة البحر الأبيض المتوسط، حيث تكون هذه المخلفات ذات سمية نباتية عالية بسبب احتوائها علي المركبات البولي فينولات والدهون والأحماض العضوية بالإضافة إلي احتوائها أيضا علي نسب عالية من المادة العضوية، لذلك صممت هذه الدراسة كمحاولة لدراسة تأثير عدة معالجات كيميائية مختلفة (كمعالجات أولية) بهدف تقليل مستوي الحمل العضوي من مخلفات مياه معاصر الزيتون، حيث تم تسجيل ومناقشة نسبة معاملات مختلفة مثل: اللون، الأس الهيدروجيني، المواد الصلبة الذائبة الكلية، متطلب الأكسجين الكيميائي، متطلب الأكسجين الحيوي، البولي فينولات الكلية وبعض العناصر الثقيلة مثل: الكادميوم، النحاس، الزنك، المنجنيز.

الكلمات الاسترشادية: المخلفات، المياه السائلة، المعالجة الاولية، الأس الهيدروجيني، المواد الصلبة الذائبة الكلية، متطلب الأكسجين الكيميائي، متطلب الأكسجين الحيوي.

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