



Treatment and valorization of olive mill wastewater by hydroxyapatite co-precipitation using experimental design

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ABSTRACT

In this study, the reduction of phenolic compounds content (PCC) and chemical oxygen demand (COD) from olive mill wastewater (OMW) by hydroxyapatite (HA) co-precipitation was investigated using experimental design. Six parameters namely reaction time (t), stirring rate (V), pH, HA/OMW ratio (S/L), reaction temperature (T) and CaCl_2 amount (m) were studied using Hadamard matrix in screening to identify the factors which have a significant influence on PCC and COD reduction. The selected factors in screening (t , pH, and S/L) were investigated in a quantitative study using full factorial design. Results obtained show that the main effects of t , pH, and S/L were significant for both responses. Only the first-order interaction effect pH- S/L was significant for the PCC. For the COD, the first-order interactions between t -pH, t - S/L , pH- S/L , and the second-order interaction t -pH- S/L were significant. Under the conditions minimizing the responses ($t = 30$ min, pH = 12 and $S/L = 10$ g/L), there was a substantial reduction of PCC and COD contents (87.30% and 76.30%, respectively). The regenerated HA after PCC extraction was reused for the OMW treatment using the selected optimal conditions. In this case, PCC and COD reductions obtained (72.40% and 71.90%, respectively) show that the proposed process could be a good alternative for OMW treatment.

Keywords: Olive mill wastewater (OMW); Chemical oxygen demand (COD); Hydroxyapatite (HA); Co-precipitation; Experimental design

1. Introduction

Algeria is one of the main Mediterranean countries producing olive oil. According to the international olive council [1] evaluations, Algerian olive oil production should reach 80,000 tons during the olive oil harvest of 2017/2018. In addition to its main product which is olive oil, olive oil extraction processes generate two wastes solid residue (olive pomace) which is rich in residual oil that can be recovered by solvent extraction [2–5] and aqueous liquor (olive mill wastewater (OMW)). For an Algerian olive oil

production of 30,000 tons, this industry rejects around 105,000 tons of OMW [6]. This important waste amount is often discharged into soil or watercourses without any prior treatment and leads generally to disastrous problems on the fauna and the flora [7]. In terms of pollution effect, it was reported that 1 m³ of OMW is equivalent to 200 m³ of domestic sewage [8].

The OMW is known for its acid pH (4.0–5.5) [9] and richness in organic constituents leading to high concentrations of chemical oxygen demand (COD) ranging from 70 to 150 g/L [10]. These organic matters include carbohydrates, proteins, lipids, mono and polyaromatic compounds such

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as polyphenols [11]. These phenolic compounds present in large quantities (2–15 g/L) [12] are responsible for the phytotoxicity effects and antimicrobial activity of OMW.

The wealth of OMW in mineral and organic matters captures the researchers' interest. The different methods of treatment for reducing pollution load of OMW are classified on physicochemical treatments, such as evaporation ponds [13], advanced oxidation processes [14–16], electrocoagulation [17], ultrafiltration [18], adsorption [19,20], and biological treatments with aerobic [21] or anaerobic [22] digestion. This effluent has been valorized as composting [23] and exploited in the extraction of phenolic compounds as antioxidants [24–26]. However, these treatment processes have drawbacks such as high cost and low efficiency.

Recently, the use of inexpensive minerals, such as bentonites, permeable clays [27–29], biosorbents [30], and natural zeolites [31] in the treatment processes of various effluents has shown an interesting reduction of the pollution. Calcium phosphates are also successfully used in hydroxyapatite (HA) form as adsorbent of trace metals [32] and soluble organic matters [33] in wastewaters. The satisfactory results obtained by these authors were prompted us to test the capacity of HA in the reduction of PCC and COD of OMW.

OMW treatment is currently considered as a value-added process to help reduce the environmental load and promote sustainable development [34]. Two objectives were assigned to this study:

- The first was to investigate the synthetic HA efficiency to reduce the PCC and COD from OMW by the co-precipitation process using experimental design (screening and full factorial design).
- The second objective was to valorize this effluent by extracting phenolic compounds from the recovered HA after the co-precipitation process and to reuse this HA after thermal treatment.

2. Materials and methods

2.1. Materials

2.1.1. Olive mill wastewater

The OMW was collected from a traditional olive oil mill located at Tizi-Ouzou (Northern Algeria) during the season of 2015/2016. The fresh effluent was obtained from the malaxation of Chemlal olive variety. In order to partially eliminate lipids and solids matters, this effluent was subjected to defat, filtration, and centrifugation processes and stored in closed and opaque plastic bottles at 5°C until use. The lipids extraction from OMW was carried out in a separation funnel where 50 ml of wastewater was mixed with 100 ml of hexane. After 10 min of stirring, the aqueous phase was separated from the organic phase containing the lipids.

2.1.2. Synthetic HA

The HA was synthesized in our laboratory by precipitation method [35]. It is a fine white powder with a chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and calcium-to-phosphorus molar ratio equal to 1.67.

2.2. OMW treatment

For each experiment, 50 mL of OMW was introduced in a glass beaker, the synthetic HA was dissolved completely in hydrochloric acid (2 M). The HA solution obtained was added to OMW to have a final concentration of 1 and 10 g/L. The suspension was then continuously stirred (100–400 rpm) at temperatures of 25°C and 40°C. The pH of the mixture was adjusted (6–12) by the addition of potash to co-precipitate HA with organic compounds of OMW. Once the pH value was reached, 0.2 g of calcium chloride (CaCl_2) was added to the mixture and stirred until total dissolution. The obtained suspension was decanted during 5 and 30 min and filtered through a filter paper under atmospheric pressure.

The recovered filtrates were analyzed. The PCC (g/L) was quantified by Folin–Ciocalteu colorimetric method using gallic acid as standard [36] and the COD (g/L) was determined by the dichromate method as described by LaPara et al. [37].

2.2.1. Extraction of phenolic compounds

The phenolic compounds were extracted from the recovered HA after the treatment of OMW using diethyl ether as a solvent. Briefly, the HA was mixed with diethyl ether under the conditions: liquid/solid ratio = 40 mL/g, contact time = 10 min, and stirring speed = 400 rpm. The obtained mixture was filtered under atmospheric pressure using a filter paper. The recovered filtrate was subjected to distillation at 35°C, using Rotavapor to eliminate the solvent. The obtained extract was dried in an oven at 40°C to constant weight. The total phenolic compounds level in the resulting extract was determined using the Folin–Ciocalteu colorimetric method [36].

2.2.2. Regeneration and reuse of HA

After phenolic compounds extractions, the collected HA was calcined at 800°C for a 60 min period inside a muffle furnace in open-air crucibles. The treated HA was then reused in the OMW treatment by the co-precipitation method using the selected optimal conditions ($t = 30$ min, $\text{pH} = 12$, and $S/L = 10$ g/L). The percentages of phenolic compounds and COD reductions in OMW were measured.

2.3. Experimental methodology

2.3.1. Screening study

This step was aimed to identify among a large number of factors those which have a significant influence on the considered responses (PCC and COD). The studied factors are mentioned in Table 1. To estimate the effect of each factor, the Hadamard matrix [38] was implemented by rotation from the bottom. Seen the factors number (6 factors), 8 experiments should be achieved. To estimate all main effects clear of any first-order interactions, another matrix of 8 experiments was added. This second matrix (fold-over) that allows the increase of the resolution is obtained by reversing the signs of the original matrix. So the used matrix which was the sum of two matrices (Hadamard

matrix + fold-over matrix) included 16 experiments to perform. This experimental design with real variables is given in Table 2.

2.3.2. Quantitative study

The detected factors as influential in the screening were investigated in the quantitative study using a full factorial design to highlight their main effects and their eventual interactions on the studied responses. This procedure required 2^k experiments.

3. Results and discussion

3.1. Physicochemical properties of crude OMW

Some of the physical and chemical properties of the crude OMW are listed in Table 3. The pH value of OMW before any treatment is 4.17. This acidity is attributed to the presence of phenolic acids and free fatty acids. The total dry matter content of crude OMW used was 48.85 g/L. This value is lower than those (92.40 and 56.75 g/L) reported

by other researchers [39–40]. The effluent electrical conductivity (10.05 mS/cm) was higher than that reported by Achak et al. [30] and Majbar et al. [41]. The values obtained by these authors were 6.85 and 5.42 mS/cm, respectively. The observed difference would be related to the olive variety, salting practices, and pedoclimatic conditions. The COD and PCC of crude OMW used were 86 g O₂/L and 4.50 g/L, respectively. These values are close to those given by other authors [14,30]. The COD value obtained was much higher than that reported by Khoufi et al. [42].

3.2. Screening study

The experimental results obtained for PCC and COD (Table 4) were used in the calculation of the coefficients b_1 , b_2 , b_3 , b_4 , b_5 and b_6 which represent the weights associated to the variables t , V , pH, S/L , T , and m respectively (b_0 is the intercept). Their values and statistical analyses using the t -test for the responses PCC and COD are reported in Tables 5 and 6, respectively. However, only reaction time (t), pH, and HA-to-OMW ratio (S/L) influence the two responses. The other factors (stirring velocity, temperature, and CaCl₂ quantity) have no significant effect on the process treatment.

3.3. Quantitative study

The three selected factors (X_1 , X_3 , and X_4) in the screening step were investigated in order to evaluate their main effects and the eventual interactions between them. Eight experiments were carried out using a full factorial design 2^3 . The experimental matrix (in coded and real values) and the responses noted for experiments are given in Table 7.

Table 1
Experimental domain for the screening design

Factor	Symbol	Code	Level (-)	Level (+)
Reaction time, min	t	X_1	5	30
Stirring velocity, rpm	V	X_2	100	400
pH	pH	X_3	6	12
HA-to-OMW ratio, g/L	S/L	X_4	1	10
Temperature, °C	T	X_5	25	40
CaCl ₂ mass, g	m	X_6	0	0.2

Table 2
Design matrix of screening

Run	Real variables					
	t	V	pH	S/L	T	m
1	30	100	6	10	25	0.2
2	30	400	6	1	40	0
3	30	400	12	1	25	0.2
4	5	400	12	10	25	0
5	30	100	12	10	40	0
6	5	400	6	10	40	0.2
7	5	100	12	1	40	0.2
8	5	100	6	1	25	0
9	5	400	12	1	40	0
10	5	100	12	10	25	0.2
11	5	100	6	10	40	0
12	30	100	6	1	40	0.2
13	5	400	6	1	25	0.2
14	30	100	12	1	25	0
15	30	400	6	10	25	0
16	30	400	12	10	40	0.2

Table 3
Physico-chemical characteristics of the studied OMW

Parameters	Content
pH	4.17
Electrical conductivity (mS/cm at 22°C)	10.05
Dry matter (g/L)	48.85
Phenolic compounds content (g/L)	4.50
Chemical oxygen demand (COD) (g O ₂ /L)	86.00

Table 4
Results obtained for PCC and COD (screening design)

Run	PCC (g/L)	COD (g/L)	Run	PCC (g/L)	COD (g/L)
1	2.80	44.78	9	2.78	50.00
2	3.56	59.60	10	1.47	28.03
3	2.42	35.31	11	2.53	55.32
4	1.27	26.57	12	3.49	64.96
5	0.71	23.80	13	4.22	76.00
6	3.07	50.72	14	2.01	36.38
7	3.09	51.81	15	2.96	43.76
8	4.03	69.80	16	0.79	18.00

Table 5
Estimates and statistics of coefficients of the response PCC (screening design)

Name	Coefficient	Factor of inflation	Standard deviation	t-value	Significance %
b_0	2.58		0.07	–	–
b_1	–0.23	1.00	0.07	–3.20	1.09 ^a
b_2	0.06	1.00	0.07	0.83	42.62
b_3	–0.76	1.00	0.07	–10.56	<0.01 ^b
b_4	–0.63	1.00	0.07	–8.75	<0.01 ^b
b_5	–0.07	1.00	0.07	–0.97	35.64
b_6	0.09	1.00	0.07	1.25	24.28

^aSignificant at the 95% level.
^bSignificant at the 99.9% level.

Table 6
Estimates and statistics of coefficients of the response COD (screening design)

Name	Coefficient	Factor of inflation	Standard deviation	t-value	Significance %
b_0	45.93		0.74	–	–
b_1	–5.10	1.00	0.74	–6.89	<0.01 ^a
b_2	–0.93	1.00	0.74	–1.26	24.05
b_3	–12.19	1.00	0.74	–16.47	<0.01 ^a
b_4	–9.56	1.00	0.74	–12.92	<0.01 ^a
b_5	0.85	1.00	0.74	1.15	28.03
b_6	0.27	1.00	0.74	0.36	72.36

^aSignificant at the 99.9% level.

Table 7
Full factorial design (in coded and real variables) and the corresponding experimental responses

Run	Coded variables			Real variables			PCC (g/L)	COD (g/L)
	X_1	X_3	X_4	t	pH	S/L		
1	–1	–1	–1	5	6	1	4.02	67.50
2	1	–1	–1	30	6	1	3.22	59.95
3	–1	1	–1	5	12	1	2.80	51.70
4	1	1	–1	30	12	1	2.18	38.02
5	–1	–1	1	5	6	10	3.00	50.00
6	1	–1	1	30	6	10	2.62	43.50
7	–1	1	1	5	12	10	1.31	31.03
8	1	1	1	30	12	10	0.49	20.38

The mathematical model describing the responses values Y_i is as follows:

$$Y_i = c_0 + c_1X_{1i} + c_3X_{3i} + c_4X_{4i} + c_{13}X_{1i}X_{3i} + c_{14}X_{1i}X_{4i} + c_{34}X_{3i}X_{4i} + c_{134}X_{1i}X_{3i}X_{4i} \tag{1}$$

where X_1 , X_3 , and X_4 represent the coded variables of the system, c_0 intercept, c_1 , c_3 , and c_4 main effects of the factors, c_{13} , c_{14} , and c_{34} two-factor interactions effects and c_{134} represent three-factors interaction effect. In order to determine the experimental variance of the two responses, four experiments are performed in the center of the domain

($t = 17.5$ min, pH = 9, and S/L = 5.5 g/L). The variances found were 6.7×10^{-3} for PCC and 9.2×10^{-3} for COD with 3 *df*.

Estimates and statistics of coefficients using the *t*-test for the responses PCC and COD were reported in Tables 8 and 9, respectively. These results confirm those obtained in the screening step for the two responses, the main effects of the three factors are important and have negative values. Solely the effect of the first-order interaction pH-S/L is significant in the PCC case. For the COD response, all the first-order interactions (*t*-pH, *t*-S/L, and pH-S/L) are significant and the second-order interaction *t*-pH-S/L is also significant.

Table 8
Estimates and statistics of coefficients of the response PCC (full factorial design)

Name	Coefficient	Factor of inflation	Standard deviation	t-value	Significance %
c_0	2.46		0.03	–	–
c_1	-0.33	1.00	0.03	-11.38	0.15 ^a
c_3	-0.76	1.00	0.03	-26.21	0.01 ^b
c_4	-0.60	1.00	0.03	-20.69	0.02 ^b
c_{1-3}	-0.03	1.00	0.03	-1.03	37.70
c_{1-4}	0.03	1.00	0.03	1.03	37.70
c_{3-4}	-0.20	1.00	0.03	-6.90	0.62 ^a
c_{1-3-4}	-0.08	1.00	0.03	-2.76	7.02

^aSignificant at the 99% level.
^bSignificant at the 99.9% level.

Table 9
Estimates and statistics of coefficients of the response COD (full factorial design)

Name	Coefficient	Factor of inflation	Standard deviation	t-value	Significance %
c_0	45.26		0.03	–	–
c_1	-4.80	1.00	0.03	-141.18	<0.01 ^b
c_3	-9.98	1.00	0.03	-293.53	<0.01 ^b
c_4	-9.03	1.00	0.03	-265.59	<0.01 ^b
c_{1-3}	-1.29	1.00	0.03	-37.94	<0.01 ^b
c_{1-4}	0.51	1.00	0.03	15.00	0.06 ^b
c_{3-4}	-0.55	1.00	0.03	-16.18	0.05 ^b
c_{1-3-4}	0.25	1.00	0.03	7.35	0.52 ^a

^aSignificant at the 99% level.
^bSignificant at the 99.9% level.

3.4. Best PCC and COD removal conditions

To determine the operating conditions giving the smallest response value, the method to be used is as follows:

- when a factor is not involved in any interaction, we study its impact on the response when this factor passes from the low level ($x = -1$) to the high level ($x = +1$).
- when a factor interacts with another factor, its main effect cannot give any indication. The interaction must be studied to determine the values of these factors which lead to the smallest response value.

3.5. Polyphenols compounds contents

Taking the significant coefficients into consideration (Table 5), the model explained PCC in the recovered filtrate is:

$$Y_{PCC} = 2.46 - 0.33X_1 - 0.76X_3 - 0.60X_4 - 0.20X_3X_4 \quad (2)$$

This model shows that contact time (X_1) does not interact with any other factor and his main effect is negative ($c_1 = -0.33$). So PCC decreases with increasing time contact and the smallest value is obtained when $X_1 = +1$, that is, $t = 30$ min.

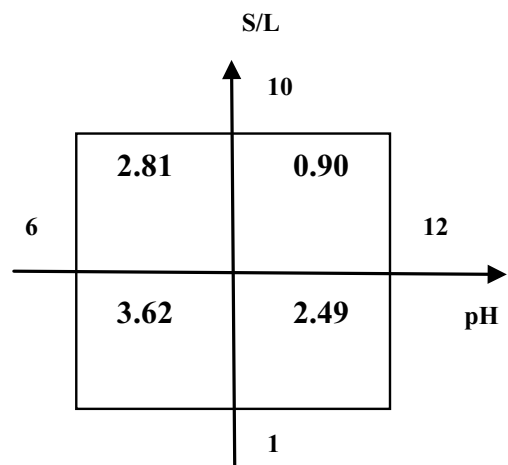


Fig. 1. First-order interaction pH-S/L (PCC).

Fig. 1 shows that whatever the value of S/L (X_4), a reduction in PCC is observed when the pH (X_3) increased. This reduction is greater at S/L = 10 ($\Delta PCC = 1.91$ g/L) than at S/L = 1 ($\Delta PCC = 1.13$ g/L). The minimum value (0.90 g/L) is reached at pH = 12 and S/L = 10 g/L.

Considering the 3 factors, the best conditions are $t = 30$ min, pH = 12, and S/L = 10.

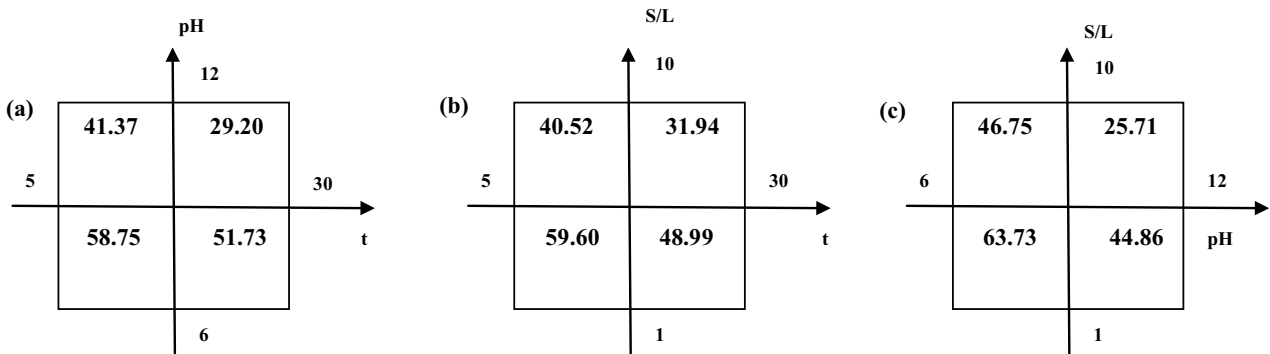


Fig. 2. First-order interactions (COD). (a) t -pH, (b) t - S/L , and (c) pH- S/L .

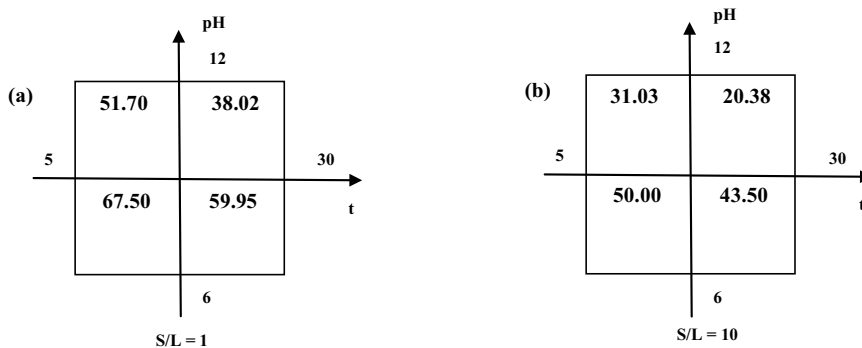


Fig. 3. Second-order interaction t -pH- S/L (COD), (a) $S/L = 1$ g/L and (b) $S/L = 10$ g/L.

3.6. Chemical oxygen demand

In this case, all first-order interaction effects and second-order interaction effects are significant. The fitted model expressed in coded values is given by the following equation:

$$Y_{\text{COD}} = 45.26 - 4.80X_1 - 9.98X_3 - 9.03X_4 - 1.29X_1X_3 + 0.51X_1X_4 - 0.55X_3X_4 + 0.25X_1X_3X_4 \quad (3)$$

All the factors are involved in significant interactions. Therefore, to determine the best operating conditions, only the interactions are to be studied.

- Interaction t -pH (Fig. 2a): $t = 30$ min and pH = 12;
- Interaction t - S/L (Fig. 2b): $t = 30$ min and $S/L = 10$;
- Interaction pH- S/L (Fig. 2c): pH = 12 and $S/L = 10$;
- Interaction t -pH- S/L (Fig. 3): the analysis of Fig. 3a ($S/L = 1$) shows that COD decreases with increasing pH at $t = 5$ min as at $t = 30$ min. The best value (38.02 g/L) is reached at $t = 30$ min and pH = 12. In Fig. 3b ($S/L = 10$), the same COD evolution is observed whatever the value of the contact time. The best COD value (20.38 g/L) is also obtained at $t = 30$ min and pH = 12.

It is clear that the smallest COD value is obtained with $S/L = 10$. Therefore, the best operating conditions are $t = 30$ min, pH = 12, and $S/L = 10$ g/L.

Then the best experimental conditions that maximize the elimination of phenolic compounds and COD in OMW by

the studied process are $t = 30$ min, pH = 12, and $S/L = 10$ g/L. At these conditions, the average experimental value after five replicate analyses was 0.57 ± 0.06 g/L and 20.36 ± 0.70 g/L for PCC and COD, respectively. These values are very close to those given by the model (PCC = 0.57 g/L and COD = 20.37 g/L). Interestingly, the co-precipitation process using HA as a sorbent allowed removing 87.30% of PCC and 76.30% of COD from OMW.

The reduction of the OMW pollutants (PCC and COD) in our study was higher than that shown by other authors [28,40,43]. Indeed, the best results obtained by Achak et al. [40] during flocculation-coagulation treatment using lime were only 75% for PCC and 43% for COD. It's also worthwhile to note that the results given by Santi et al. [28] (PCC = 75% and COD = 43%) were lower than ours, although the OMW was subjected to a double treatment: the absorption on zeolite was followed by a second treatment with this same zeolite regenerated by the technique of low-temperature ash. Removal COD obtained in our study was also greater than that reported (35%) by Duarte et al. [43]. This author has used silica-alginate as a substrate for olive mill treatment.

3.7. Recovery of phenolic compounds

The content of phenolic compounds extracted was $25.50\% \pm 1.50\%$. This content was much smaller than that retained by the HA during the co-precipitation process. This phenomenon could be explained by phenolic compounds transformation by reactions with HA [44].

3.8. Reuse of HA in OMW treatment

The regenerated HA was reused in the OMW treatment by the co-precipitation process using the optimal conditions determined by the experimental design methodology ($t = 30$ min, $\text{pH} = 12$, and $S/L = 10$ g/L). The reduction percentages of PCC and COD obtained were 72.40% and 71.90%, respectively. These values had slightly decreased compared to those found by using a fresh HA. This decrease could be attributed to the reduction of specific surface area after the calcination step.

4. Conclusion

This study has shown that the co-precipitation process using HA as sorbent had an important potential for reducing PCC and COD in OMW. This reduction using the best-operating conditions ($t = 30$ min, $\text{pH} = 12$, and $S/L = 10$) determined using full factorial design reached 87.30% of PCC and 76.30% of COD in OMW.

Before regenerating HA for further use, phenolic compounds, known for their antioxidant properties, are recovered by solvent extraction up to 25.50% of the total amount precipitated with HA.

The regenerated and reused HA for a new treatment of OMW has given a good reduction of PCC and COD in OMW (72.40% and 71.90%, respectively).

Apatite is inexpensive and presents the ability to be regenerated without producing any new pollution. So this process is an eco-friendly method and offers a promising technology for OMW treatment.

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