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Combined treatment of olive mill wastewater by multi-soil-layering ecotechnology and adsorption on activated carbon/lime

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ABSTRACT

The main objective of this work was to evaluate the ability of the multi-soil-layering (MSL) combined with adsorption, using two adsorbents: activated carbon and lime, for the treatment of olive mill wastewater (OMW). We have studied the influence of different physicochemical parameters, such as the type of adsorbents, the mass of the adsorbent, the dilution factor, the temperature, and the pH. This study has shown that the discoloration rate of OMW by activated carbon is more important in comparison to lime. Optimization of treatment parameters with activated carbon (pH = 2, T = 298 K, dilution factor = 5, mass (CA) = 5.5 g) allowed a 92% chemical oxygen demand reduction, 100% polyphenols reduction and almost a total discoloration of the effluent. Adsorption isotherm study shows that the adsorption on activated carbon is heterogeneous and in multilayer, and also that the adsorption sites have different interaction energies. Therefore, the process of MSL combined with adsorption on activated carbon could be a good option for the treatment of OMW

Keywords: Olive mill wastewater; Adsorption; Activated carbon; Lime; Multi-soil-layering

1. Introduction

Treatment of olive mill wastewater (OMW) is a serious environmental problem in many parts of the world, due to its high organic content and because of its resistance to biodegradation due to its high content of microbial growth-inhibiting compounds such as phenolic compound.

Several thermal, biological, and physicochemical processes have been examined for the treatment of OMW, resulting in considerable organic load and toxicity abatement: (1) thermal processes: natural evaporation [1], thermal concentration [2]; (2) biological processes: aerobic treatment [3], anaerobic treatment [4]; (3) physico-chemical processes: coagulation-flocculation [5–7], neutralization with lime [8], electro-coagulation [9], adsorption on activated carbon [10], adsorption on clay [11], ultrasound and advanced oxidation [12], and flocculation-sedimentation and microfiltration [13].

Conventional biological treatment (aerobic or anaerobic) has gained attention over recent years as it can achieve high removal efficiencies at a relatively low cost. However, due to the extremely high organic load of OMW, a post-treatment stage is imperative.

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Concerning thermal treatments, only a few processes using pomace as an energy source have been applied on an industrial scale. However, several physico-chemical technologies have proven to be more effective for the treatment of these effluents. Among these physico-chemical technologies, there is the technique of adsorption on different supports (activated carbon, clay, natural vase, lime, etc.).

According to the literature, the effective treatment of OMW typically requires the use of several technologies that combine chemical, biological, and physical processes [6,13].

Wakatsuki et al. [14] developed in Japan a low-cost technology of multi-soil-layering (MSL) for the treatment of domestic wastewater. The system combines physico-chemical and biological processes. It was then used successfully in Morocco for the treatment of domestic wastewater [15] and of OMW [16].

The current work aims at studying the efficiency of the combination of MSL technology and adsorption, using two adsorbents (activated carbon and lime), for the treatment of OMW. The objective was to determine if an effective treatment process that is capable of significantly increasing the degradations of OMW.

2. Materials and methods

2.1. OMW and adsorbent materials

OMW used in this experiment was collected from a modern triphasic unit located in the Marrakech region. This effluent was diluted to 50% by urban wastewater and was pretreated by MSL ecotechnology which is made up of layers of soil mix, sawdust, metallic iron, and of charcoal. The layers are arranged in a pattern similar to a layer of bricks surrounded by layers of gravel (Fig. 1) [16]. The filtrate is then subjected to a post-treatment by adsorption. The adsorbents used for the retention of organic matter are activated carbon and lime.

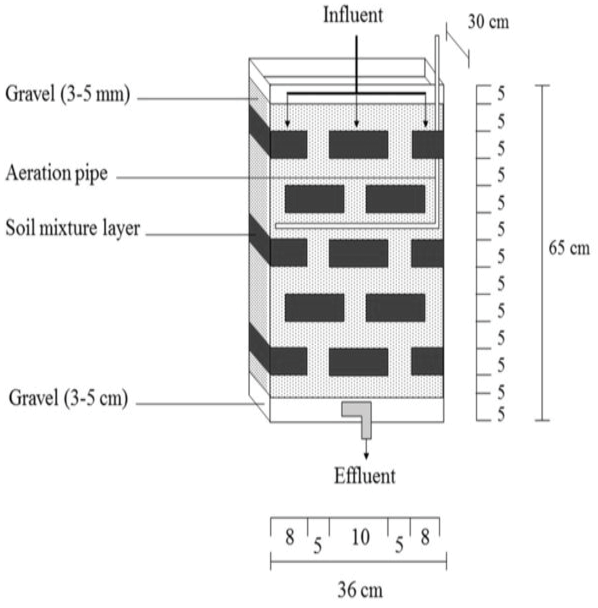

Fig. 1. Structure and components of the MSL pilot for OMW treatment.

Activated carbon is in a powder state, produced from selected qualities of carbon (Pulsorb 205 AP).

Lime is an odorless white powder with a molecular weight of 74.093 ± 0.005 g/mol.

2.2. Analytical methods

2.2.1. Physico-chemical analyzes of OMW

The hydrogen potential (pH), the electrical conductivity, and the dissolved oxygen of the OMW studies were determined by the methods of ANFOR [17].

The chemical oxygen demand (COD) was analyzed according to the standard method of potassium dichromate [18].

The biochemical oxygen demand and total nitrogen Kjeldahl were determined by the methods of AFNOR [17].

Total polyphenols were measured using the method developed by Macheix et al. [19].

2.2.2. Characterization methods for activated carbon and lime

- The morphology of the activated carbon and lime was observed using a scanning electron microscope (SEM) of the TESCAN VEGA3 brand. Images of the microstructure were obtained with a maximum voltage of 10 kV.
- The elementary composition of the study materials was determined using an energy dispersive X-rays spectroscopy (EDXS) type analyzer with a resolution of 0.1 mm.
- The point of zero charge (PZC) of each adsorbent (activated carbon and commercial lime) was determined by the solid addition method. Ten tubes containing pH solutions in the range of 2–12 (pH_0) and 0.10 g of the adsorbent are shaken using a rotator for 24 h at room temperature. Then the final pH is measured. The difference between the initial and final pH ($\Delta pH = pH_0 - pH_f$) is plotted as a function of the initial pH (pH_0). The point where $\Delta pH = 0$ is taken as the PZC.
- The determination of surface adsorbents was based on the method of Brunauer–Emmet and Teller (BET) [20] who designed a multi-layer adsorption model for nitrogen molecules. This area is estimated from the quantity of nitrogen adsorbed, in relation to its pressure at the boiling temperature of liquid nitrogen and under normal atmospheric pressure.

2.3. Experimental procedure

Different weights of adsorbent are added to the solution of OMW. Monitoring of OMW adsorption was carried out by determining the absorbance by a UV/Vis spectrophotometry of Jasco type V-630 series at a wavelength of 300 nm, and by measuring the COD.

The discoloration rate is calculated as follows:

$$Y(\%) = \frac{OD_i - OD_f}{OD_i} \times 100 \quad (1)$$

where Y is the discoloration rate (%); OD_i is the initial optical density; OD_f is the final optical density.

Once the adsorption process reaches a state of equilibrium, the adsorption isotherms were carried out for different initial concentrations (0–514 mg/L).

3. Results and discussion

3.1. Physico-chemical characterization of OMW studies

MSL-pretreated OMW samples have the following physicochemical characteristics (Table 1):

OMW studies are slightly alkaline (pH = 7.6). This alkalinity can be explained by the neutralization of organic acids (phenolic acids, fatty acids, and soil) [21] used during pretreatment by the MSL [16]. The content of polluting organic matter expressed in terms of COD is 3.97 g O_2/L. This value is very high compared to the standard value required by Moroccan standards relating to discharges into surface and groundwater (500 mg/L). In addition, we observe a low value of electrical conductivity (2,825 μS/cm 20°C).

The concentration of phenolic compounds is relatively high (0.055 g/L). In fact, the composition of phenolic compounds of OMW varies according to the oil extraction procedure and the variety of olive treated [22].

Moreover, the OMW studied is characterized by a dark black coloration (4.82). In fact, during the storage period, auto-oxidation and polymerization reactions transform phenolic alcohols into phenolic acids. These reactions are manifested by a change in the initial color of OMW from the brownish-red toward a very dark black [23].

3.2. Characterization of the adsorbents studied

3.2.1. Morphology, atomic composition, and specific surface of the adsorbents studied

The images of SEM of activated carbon were taken at different aggrandizements (Fig. 2). The study of the morphology of the activated carbon used shows aggregates made up of crystallites of different sizes perpendicular to the plane of the image. This study also shows irregular shapes typical of coal particles and an abundance of porous and microporous particles which constitute cavities in the form of suitable cages.

Regarding the lime studied (Fig. 2), it is made up of agglomerates of small particles and small grains.

The results of the EDX spectrum obtained for activated carbon and lime are shown in Table 2. This table shows the dominance of carbon with the presence in a small percentage of calcium, molybdate, silicon, and aluminum in activated carbon. While for lime, we note the presence of several elements in different quantities: oxygen, calcium, molybdate, magnesium, and silicon.

Moreno-Castilla et al. [24] have shown that the adsorption capacities of activated carbon depend on the degree of activation of the carbon, the hydrophobicity of the substituents of the phenols, and the solubility of the phenolic compound in water. In addition, the adsorption capacity increases with the development of the surface and the porosity of the carbon [25]. Consequently, the activated carbon studied has an appropriate morphology and a high capacity for the adsorption of OMW, compared to lime.

The specific surface of support has an essential role in the elimination of pollutants by retention. In the present work, the specific surface of activated carbon is 847 m^2/g while that of lime is 20 m^2/g.

Table 1
Physico-chemical characteristics of OMW studied

Parameters	Values
pH	7.66 ± 0.04
Conductivity (μS/cm 20°C)	2,825 ± 7.1
Total COD (g O_2/L)	3.97 ± 0.05
Coloration (Abs)	4.82
Polyphenols (g/L)	0.055 ± 0.008

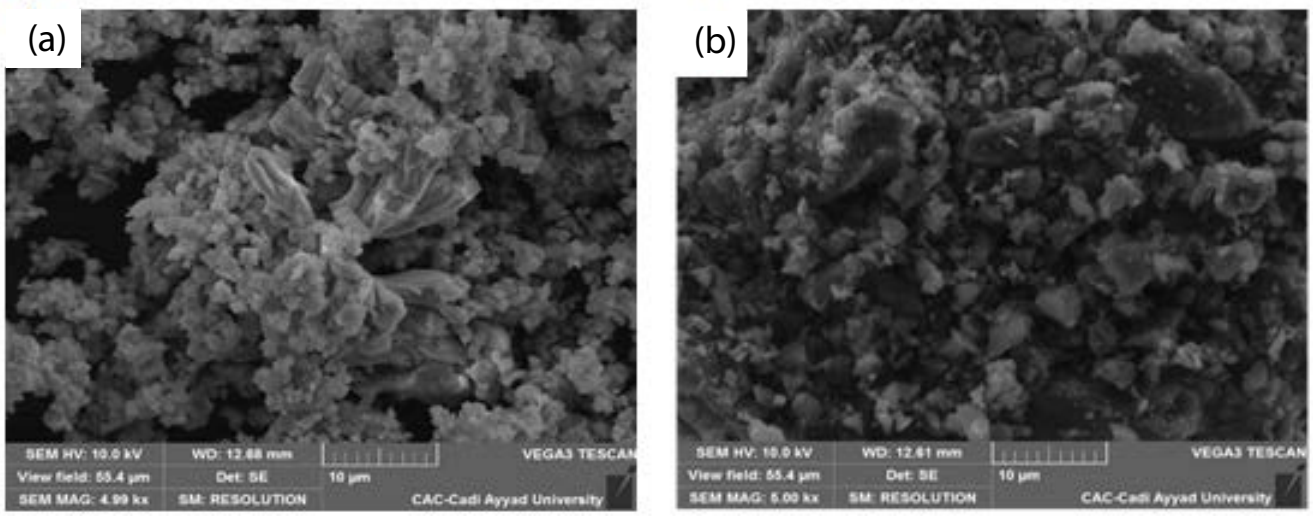

Fig. 2. Scanning electron microscope images of activated carbon and lime.

Table 2
Chemical composition of activated carbon and lime in % mass and atomic

Activated carbon			Lime		
Element	% Mass	% Atomic	Element	% Mass	% Atomic
C	92.77	97.75	C	5.67	10.24
Al	1.25	0.59	O	47.20	64.01
Si	1.21	0.55	Mg	0.61	0.54
Mo	2.13	0.28	Si	0.11	0.09
Ca	2.63	0.83	Ca	46.41	25.12

3.2.2. PZC of the adsorbents studied

Fig. 3 shows that the PZC of activated carbon and lime is successively 8,4 and 12.4. Below PZC, the surface carries a positive charge and above PZC, the charge is negative.

3.3. Effect of experimental parameters on the adsorption process of OMW

We have studied the influence of several parameters that can affect the adsorption process of OMW. These parameters are weight of activated carbon (*m*), dilution factor (DF), agitation speed, temperature (*T*), and the pH of the reaction medium.

3.3.1. Effect of the nature of adsorbent

The objective of this study is to compare the adsorption efficiency of the two adsorbents (activated carbon and lime). We have studied the evolution of the discoloration rates of pretreated OMW as a function of contact time (Fig. 4). The dose of each adsorbent introduced is 1 g/L.

Fig. 4 shows that the maximum discoloration rate of OMW is 30.68% after only 3 h of agitation using activated carbon. While for lime, the maximum discoloration is 16.5%. On the other hand, we have noticed that the kinetics of adsorption occurs in two stages. This can be explained, firstly, by the transfer of the adsorbate through the external liquid film of the two adsorbents, this is the external mass transfer step. Whereas, the second step may be due to the diffusion of the solute inside the particles of the adsorbents. Moreover, the results of Fig. 4 shows that OMW does not have the same affinity for the two absorbents and that the effectiveness of discoloration of OMW on activated carbon is much greater than that on lime.

Galiatsatou et al. [25] have indicated that the adsorption of total organic matter is mainly controlled by the microporosity of the adsorbent. This may explain the efficiency of adsorption of activated carbon which is rich in microporous particles compared to lime.

Given the adsorption efficiency of activated carbon (compared to lime), it was used as a model to test the other parameters (mass of adsorbent, dilution, temperature, and pH).

3.3.2. Effect of activated carbon weight

In order to optimize the quantity of activated carbon necessary to reach maximum discoloration of OMW, several experiments were carried out by adding different masses of activated carbon (from 1 to 6 g) to the effluent studied (Fig. 5).

The results of Fig. 5 show that the rate of discoloration increases with increasing of activated carbon mass. The best adsorption yield (89.07%) is obtained at 5.5 g/L, after a contact time of 120 min.

Azzam et al. [26] also found that the concentration of phenols decreased as the concentration of activated carbon

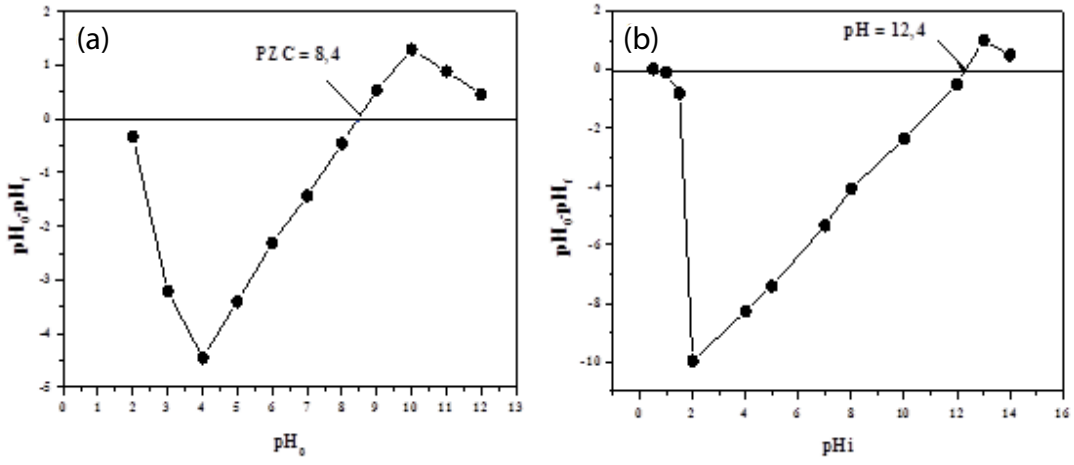

Fig. 3. Point of zero charge (PZC) of activated carbon (a) and lime (b).

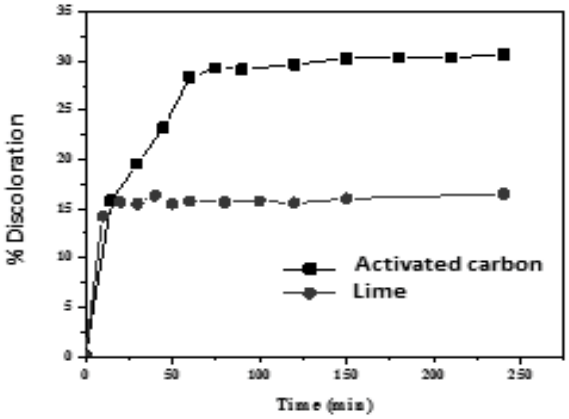

Fig. 4. Influence of the nature of adsorbent on the efficiency of OMW discoloration. (pH_i = 7.6, T = 298 K, m (Activated carbon and lime) = 1 g).

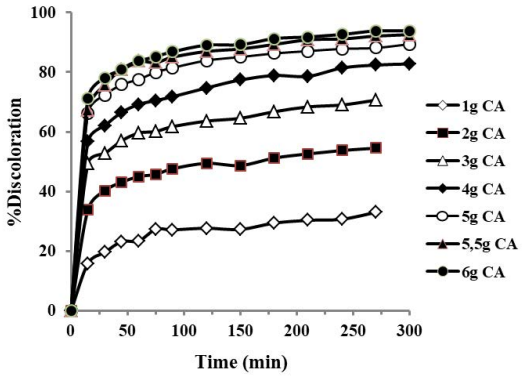

Fig. 5. Effect of activated carbon mass on the discoloration of OMW (pH_i = 7.6, T = 298 K).

increased. This behavior could be explained by the fact that the more the mass of activated carbon increases, the greater the surface offered.

3.3.3. Effect of dilution on activated carbon adsorption

Fig. 6 represents the effect of OMW concentration on the discoloration performance. The dilution factors (DF) studied (with distilled water) are 1, 1/2, 1/3, 1/4, and 1/5. According to this figure, we notice that the discoloration rate increases inversely with the concentration of OMW. The percentage of discoloration increases to 98.75% at a dilution factor of 5. This finding indicates that the lower the initial concentration of pollutants, the more effective the treatment.

3.3.4. Effect of temperature on activated carbon adsorption

Fig. 7 shows that the increase of temperature allows the increase of discoloration rate of the effluent studied. This result agrees with the findings of Dogan et al. [27] and Saleh et al. [28] and can be explained by the fact that the temperature increases the speed of diffusion of the adsorbate

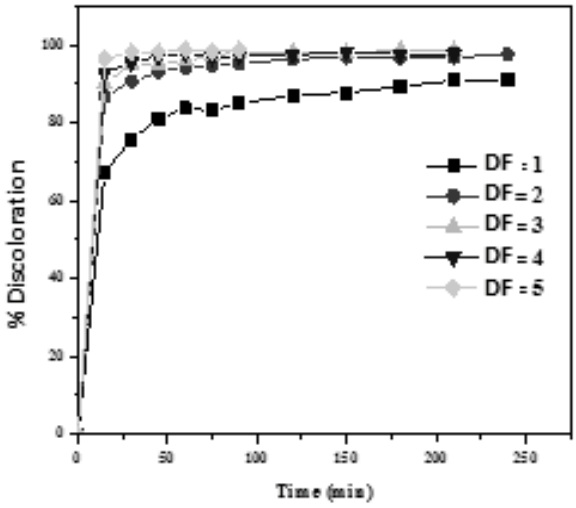

Fig. 6. Dilution effect of OMW on the discoloration kinetics by the adsorption process on activated carbon (pH_i = 7.6, T = 298 K, m (Activated carbon) = 5.5 g).

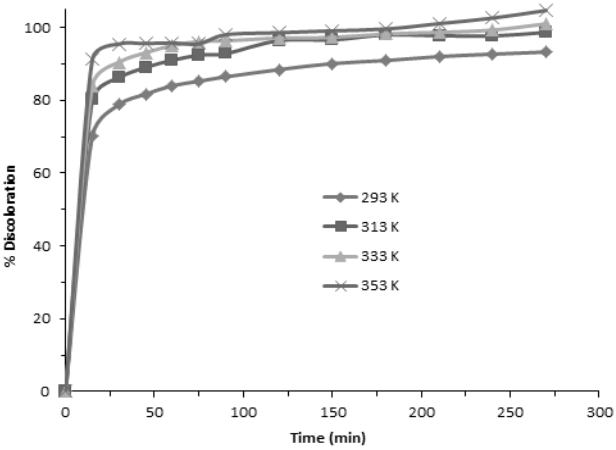

Fig. 7. Effect of temperature on the discoloration efficiency of OMW by adsorption on activated carbon (pH_i = 7.6, DF = 2, m (Activated carbon) = 5.5 g).

molecules through the outer boundary layer and inside the adsorbent particles, and this by the decrease in the viscosity of the solution.

3.3.5. Effect of pH on activated carbon adsorption

Fig. 8 shows the evolution of the OMW discoloration rate as a function of pH. Five pH values are tested (2, 4, 7.66, 9, and 11).

The results show that the discoloration rate of OMW on activated carbon is much greater at acid pH, with a maximum yield (99.57) at pH = 2. In fact, at low pH value, acidic media, an electrostatic attraction exists between the positively charged surface of the nanoparticles and the phenoxide molecules [29].

Since PZC of activated carbon studied is 8.4, so, at acidic pH less than 8.4 the surface of the absorbent carries

a positive charge which explains the increase of the adsorption efficiency.

3.4. Optimization of OMW treatment using adsorption

3.4.1. Evolution of COD reduction and discoloration of OMW

The optimal treatment conditions determined previously (pH = 2, T = 298 K, dilution factor = 5, m (activated carbon) = 5.5 g) were applied for the discoloration and for the mineralization of the OMW studied by adsorption on activated carbon.

Fig. 9 shows the evolution of the COD reduction rate and the discoloration of OMW over time. The reduction rate of the COD of the solution increases regularly during treatment. After 6 h of treatment, 92% of the COD initially was removed and total discoloration was reached. Azzam et al. [26] found that the maximum decrease of COD was 83%, with an activated carbon concentration of 24 g/L. This reduction can be explained by the adsorption of a large part of the phenolic compounds and of the organic matter on the activated carbon.

Moreno-Castilla et al. [24] showed that adsorption capacities of the activated carbon depend on the degree of carbon activation, hydrophobicity of the substituents of the phenols, and the solubility of the phenol compound in water. Moreover, chemical heterogeneities [30,31] and microporosity [32] of activated carbon contribute to the sorption properties.

Therefore, in our study, the adsorption capacity grew with the development of carbon surface area and porosity, also with optimization of treatment conditions (pH, T, dilution factor, m).

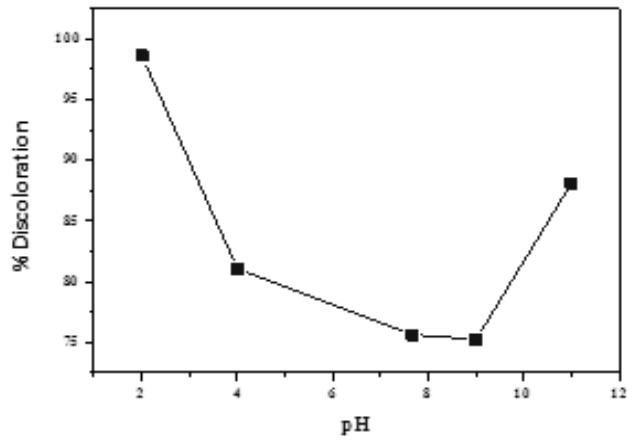

Fig. 8. Influence of pH on discoloration efficiency of OMW (pH_i = 7.6, dilution factor = 2, m (Activated carbon) = 5.5 g).

3.4.2. Adsorption isotherm

Several models are cited in the literature to describe the experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently used [33,34].

We have used these two models are used to describe the mode of organic matter adsorption on activated carbon (Fig. 10). The values of different parameters calculated from the Langmuir and Freundlich models are represented on Table 3.

The comparison of the correlation coefficients shows that the retention of organic matter in terms of COD follows the Freundlich isotherm, with a correlation coefficient R^2 = 0.9456, which indicates that adsorption is done in a heterogeneous way and multilayer, and that the adsorption sites have different interaction energies. This characterization is not the same for all types of activated carbon and the adsorption of organic matter follows different paths depending on the type [26].

3.4.3. Comparison between purifying yields before and after combined treatment of OMW by MSL ecotechnology and adsorption on activated carbon

Table 4 represents the values of the coloration, COD, and the polyphenols before and after each treatment used in this study.

Polyphenols are not detected (phenols removal: 100%) in all samples of OMW treated by MSL coupled with adsorption on activated carbon. Moreover, the final

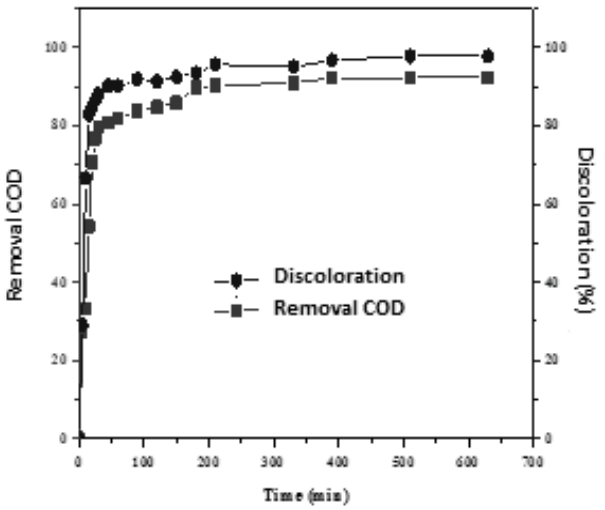

Fig. 9. Evolution of the COD reduction and of the discoloration rate of OMW as a function of time by adsorption on activated carbon (pH = 2, T = 298 K, DF = 5, m(CA) = 5.5 g).

Table 3
Parameters of Langmuir and Freundlich models of the adsorption of OMW studied

Parameters of Langmuir			Parameters of Freundlich		
Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F ((mg/g)(1/mg)$^{1/n}$)	1/n	R^2
46.51	0.0198	0.8435	0.70	0.9754	0.9456

Table 4
Purifying yields before and after combined treatment of OMW by Multi-Soil-Layering Ecotechnology and adsorption on activated carbon

Parameters	Treatment by MSL			Combined treatment by MSL and adsorption on activated carbon		
	Affluent	Effluent	Yield (%)	Affluent	Effluent	Yield (%)
Coloration	12.45	4.82	61.30	4.82	0.20	95.85
COD (g/L)	25.15	3.97	91	3.97	0.238	92
Polyphenols (g/L)	1.496	0.055	91.47	0.055	ND	100

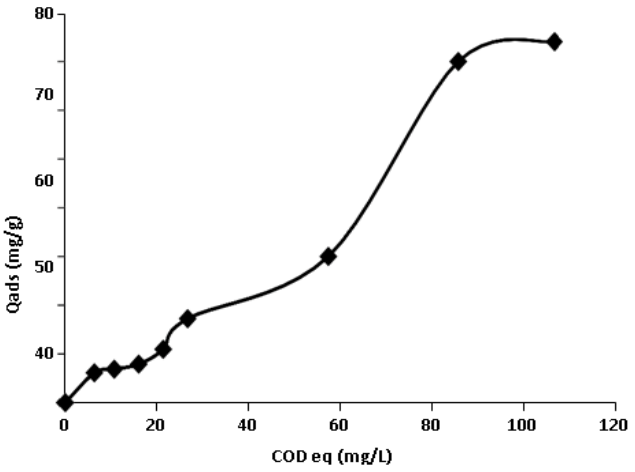

Fig. 10. OMW adsorption isotherms on activated carbon (Temps.: 24 h, R = 5.5 g/L, DF = 5, pH_i = 7.66; T = 25°C).

concentration of COD is 238 mg/L. This concentration meets the Moroccan standard for wastewater discharges which is 500 mg/L.

The maximum decrease of COD and coloration, with a coupling of the two processes, were successively 92% and 95.85%. These values are much higher than those found by Azzam et al. [26] and Khattabi Rifi et al. [35], which used respectively adsorption on activated carbon and natural flotation followed by an anaerobic–aerobic biodegradation.

These results show the effectiveness of using activated carbon (under the conditions used) as a finishing treatment after the treatment by the MSL.

4. Conclusion

The main characteristics of the process of MSL combined with adsorption can be summarized as follows:

- The rate of discoloration of OMW by activated carbon is more important in comparison to lime.
- The adsorption of OMW on activated carbon is more favored at acidic pHs. The maximum discoloration rate is obtained at pH = 2.
- The optimization of treatment parameters (pH = 2, T = 298 K, DF = 5, m (ativated carbon) = 5.5 g) increased the adsorption capacity of OMW on the activated carbon: 92% COD reduction, 100% polyphenols reduction and almost a total discoloration of the effluent.
- The study of the adsorption isotherm for activated carbon indicates that adsorption is done in a heterogeneous and multilayered way and that adsorption sites have different interaction energies.
- The process of MSL combined with adsorption on activated carbon showed high adaptability and could be considered as an effective solution to be adopted at an industrial scale for OMW treatment.

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