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Treatment of stabilized landfill leachate using coupled Fenton-like and adsorption process onto Moroccan bentonite clay

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ABSTRACT

The present study aims to explore the feasibility to apply a sequential process combining Fenton-like and adsorption onto local Moroccan bentonite clay for the treatment of the stabilized landfill leachate of Fez City (Morocco). The stabilized landfill leachate was firstly treated using a homogenous Fenton-like (FL) process using $FeCl_3$ as a catalyst source. The pretreatment of landfill leachate using the FL process was performed under the optimal conditions: $[Fe^{3+}] = 250$ mg L^{-1}, $[H_2O_2] = 1,000$ mg L^{-1}, pH = 3, and contact time = 30 min, then the pretreated and neutralized leachate was treated by adsorption process on natural bentonite clay using the optimal mass 5 g L^{-1} and pH = 7. The experimental data of adsorption kinetic were well fitted to the pseudo-second-order model, while the isotherms data were in good correlation with the Langmuir model. The Fenton-like process reduced the chemical oxidation demand (COD) by 72% and the adsorption process enhanced further the COD removal efficiency to 85%. These findings represent a further contribution towards developing a promising technology for landfill leachate treatment.

Keywords: Landfill leachate; Fenton-like; Advanced oxidation processes; Chemical oxidation demand removal; Adsorption; Natural bentonite

1. Introduction

Leachate production is one of the greatest environmental challenges faced by many countries. Morocco one of the concerned countries considers the management of this dangerous effluent a matter of public concern. Therefore, many studies have been conducted on various landfills of Morocco, for several years to assess the different environmental aspects related to this issue. Asouam et al. [1] and El Mouine et al. [2] reported the geological and hydrogeological investigations of the controlled discharge of Tamelast (Agadir City) and the uncontrolled landfill of Tadla plain, respectively.

Moreover, many studies have been performed for the environmental impact assessment of landfill leachates, typically, on the quality of the groundwater: Oum Azza landfill Rabat [3], the uncontrolled dumping site of El Jadida City [4], Mediouna Site of Casablanca [5,6], the wild dump leachates of the region of El Hajeb [7], the landfill of Kenitra City [8], the uncontrolled landfill of Tadla plain [2]. On the other hand, Charkaoui et al. [9] studied the feasibility of composting the fermentable fraction of household and assimilated waste (Mohammedia landfill) and Arabi et al. [10] assessed the influence of solid waste typology and the seasonal variations on the leachate flow (landfill site of Oujda City).

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Besides, the physicochemical characterization of leachates produced in different landfills have been also surveyed: the controlled site of Oum Azza, Rabat City [11], landfills of Casablanca and Marrakech Cities [12], the uncontrolled landfill of Tangier [13], the controlled discharge of Berkane City [14], the landfill Ouled Berjal of Kenitra City [15].

In addition, many research works reported the application of the physical–chemical processes for the treatment of landfill leachates in the country. Mainly, the coagulation–flocculation process was widely applied using diverse types of coagulants: Mohammedia-Benslimane landfill [16–18], Mediouna landfill in Casablanca City [19] and Fquih Ben Salah City [20,21]. In other studies, Chaouki et al. [22,23] used the adsorption process as a secondary step after coagulation–flocculation pretreatment. While filtration on natural materials was used for the leachate treatment from the public landfill of Tangier City [24].

Moreover, a few researchers investigated the efficiency of biological treatment using aerobic and anaerobic processes: Kasba Tadla City [25], Mohammedia-Benslimane landfill site [26–29].

Overall, the majority of the studies reviewed here highlighted the complicated composition of the leachate and assessed its environmental impact on soil and groundwater, while other studies remain narrow in focus dealing only with leachate treatment with conventional processes. So far, however, none of the reviewed works has investigated the application of advanced oxidation processes (AOPs) for the treatment of any Moroccan landfill leachates. Hence, this type of process (single and combined with other processes) was assessed for the first time in our previous works for the treatment of leachate from the landfill of Fez City: Fenton and photo-Fenton [30], iron(II)/UV-activated persulfate oxidation [31], biological treatment followed by Fenton [32], and a sequence of Fenton and adsorption [33]. Besides, the adsorption process was not sufficiently studied for the removal of contaminants from landfill leachate.

Thus, the study reported in the present paper set out to further contribute to the assessment of the efficiency of other AOPs and adsorption processes for the treatment of landfill leachate by exploring the efficiency of the sequentially homogenous Fenton-like and adsorption process on natural bentonite clay.

The Fenton process is considered the first AOP and the most powerful oxidation used in the world around. The Fenton process can generate the hydroxyl radicals ($HO^{\bullet}$) a strong oxidant from the mixture of hydrogen peroxide (H_2O_2) and ferrous salts (Fe^{2+}) under acidic conditions [34] according to the reaction (1). The radicals produced during this mechanism can oxidize complex organic compounds into a series of less harmful or non-toxic compounds [Eq. (2)], which are mainly carbon dioxide, oxygen and water.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \tag{1}$$

$$\text{Organic pollutants} + HO^{\bullet} \rightarrow \text{Degraded pollutants} \tag{2}$$

During the Fenton-like process, the Fe^{2+} catalysts are substituted by Fe^{3+} species, which generates the hydroperoxyl radical ($HO_2^{\bullet}$) that decompose the organic matter following the reactions briefly described by Eqs. (3)–(5) [35,36].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \tag{3}$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \tag{4}$$

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \tag{5}$$

Indeed, Fenton-like is one of the most AOPs indicating high efficiency for pollutants degradation in aqueous solution. Homogenous Fenton-like is generally performed using metal ion ($FeCl_3$ and $Fe_2(SO_4)_3$ as a source of Fe^{3+}) [35–39], while heterogenous Fenton-like is carried out by iron-based solid catalysts [40–43].

Similarly, the adsorption on based-clay materials was extensively investigated for the removal of pollutants from synthetic aqueous solutions and industrial effluents [44–49].

The present work reports the treatment of the raw landfill leachate from Fez City (Morocco) using in the first step the homogenous Fenton-like (FL) process where the effect of leachate pH, Fe^{3+} and H_2O_2 concentrations were studied. Thereafter, the adsorption process using natural bentonite clay as an adsorbent is applied as a secondary treatment to enhance the quality of this leachate by investigating the effect of the operational parameters, including the adsorbent mass, initial pH of leachate, kinetic and isotherms studies.

2. Experimental procedure

2.1. Landfill leachate sampling and characterization

The studied leachate was sampled from the public controlled landfill of Fez City. The physicochemical characteristics of this leachate were conducted according to the standard methods for the examination of water and wastewater [50].

Chemical oxidation demand (COD) measurement was conducted following the spectrophotometric method at 600 nm after the chemical digestion step based on the acidic oxidation using the reactor "ISCO RECOD". Biochemical oxidation demand (BOD_5) was determined using the manometric system "OxiTop IS 6 – WTW". Turbidity was measured by a turbidimeter "HI-88713 – ISO HANNA", a conductometer "inoLab – WTW" was used to obtain conductimetry and pH-meter "JENCO Electronics, Ltd" to determine pH values. The concentrations of nitrates, nitrites and sulfates were measured using the spectrophotometric method at 415, 435 and 650 nm, respectively. All the spectrophotometric analyses were performed using "UV-6300PC – VWR" UV-Visible spectrophotometry. The metals concentration was analyzed using ICP-AES "HORIBA Jobin Yvon – OVOU 1048 – ACTIVA". Noting that some analysis required the dilution of leachate samples.

The obtained results were reported in detail in our previous work showed that the leachate sample is mainly characterized by high values in terms of COD (5,198 mg L^{-1}), conductivity (34 mS cm^{-1}), turbidity (218 NTU), total suspended solids (14,000 mg L^{-1}), and color number (6.52). Moreover, the values of biodegradability ratio BOD_5/COD = 0.09 (<0.1) and pH = 8 indicate that the leachate sample is stabilized [31].

2.2. Fenton-like tests

FL tests were conducted in a batch system by introducing a volume of raw leachate, a volume of liquid $FeCl_3$ (40% w/w; Cadilhac, Casablanca, Morocco) and H_2O_2 (30% w/w; VWR Chemicals) allowing to obtain the desired dosages of Fe^{3+} and H_2O_2, respectively.

NaOH (99%; Fluka) and H_2SO_4 (96%; Sigma-Aldrich) solutions (2 M) were used to adjust the initial pH of leachate. Magnetic stirring (200 rpm) was used to assure the mixture homogeneity.

To begin this process, the pH effect was assessed in the range of 2–11 under $[H_2O_2]$ = 11,000 mg L^{-1} that was chosen based on the theoretical weight ratio $[H_2O_2]$/COD = 2.123 and $[Fe^{3+}]$ = 1,500 mg L^{-1} chosen after preliminary tests. Thereafter, the kinetic study was conducted under the optimal pH value and the same H_2O_2 and Fe^{3+} concentrations previously chosen, where samples were collected at 5, 15, 30, 45, 60 and 90 min.

The effect of Fe^{3+} and H_2O_2 concentrations was examined under the optimal pH and contact time by varying firstly $[Fe^{3+}]$ in the range of 0–3,000 mg L^{-1} then $[H_2O_2]$ between 0 and 15,000 mg L^{-1}.

At the end of each test, samples were recovered and sodium thiosulfate was added immediately for complete consumption of residual H_2O_2 to stop Fenton-like reaction [51] and centrifuged (2,000 rpm and 10 min), then the supernatant was analyzed for the residual COD and UV-Visible spectra measurements.

The treatment efficiency was assessed according to COD removal:

$$\text{COD Removal}\left(\%\right)=\frac{\text{COD}_i-\text{COD}_f}{\text{COD}_i}\times 100 \tag{6}$$

2.3. Bentonite characterization

The characterization of the natural bentonite was reported in our previous work: X-ray diffraction confirmed the presence of montmorillonite as the characteristic phase of this clay, N_2 adsorption–desorption analysis indicated its mesoporous nature and surface area $S_{\text{BET(Brunauer–Emmet–Teller)}}$ = 51.7 m^2 g^{-1}, Fourier-transform infrared spectroscopy showed the characteristic bands corresponding to Al–O–Si, Al–OH–Al, Si–O and –OH groups, and scanning electron microscopy (SEM-EDX) demonstrated that its surface is heterogeneous with irregular particle sizes and that is mainly composed of O (54.41%), Si (23.22%), and Al (11.19%) [33].

2.4. Adsorption tests

In order to investigate the adsorption efficiency of the bentonite clay, the experiments were carried out in a batch system. Where a volume of the pretreated leachate by FL process and a mass of natural bentonite were introduced in a flask and stirred at 200 rpm. The pH effect was investigated by varying the initial pH between 2 and 11 using NaOH and H_2SO_4 solutions (2M).

The kinetic studies were performed under fixed conditions of adsorbent mass, temperature and pH, where volumes were sampled regularly and centrifuged at 2,000 rpm for 10 min to separate the adsorbent and leachate for residual COD analysis. The corresponding experimental data were fitted with pseudo-first-order and pseudo-second-order models.

The temperature effect was studied at 25°C, 30°C and 35°C following the same previous procedure under the optimal parameters of adsorbent mass, initial leachate pH, and contact time. Noting that for each isotherm the initial COD values for different samples were obtained by diluting the pretreated leachate.

2.4.1. Kinetic studies

The adsorption kinetics' modeling provides valuable information on the mechanisms controlling the rate of adsorption. The most commonly used kinetic models to determine experimental kinetic parameters are pseudo-first-order [52] and pseudo-second-order models [53].

The corresponding experimental data were fitted with two kinetic models, pseudo-first-order [Eq. (7)] and pseudo-second-order [Eq. (8)].

$$q_t=q_e\left(1-e^{-k_1t}\right) \tag{7}$$

where q_e and q_t correspond to the amount of the adsorbed compound (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant for the first-order adsorption process.

$$\frac{t}{q_t}=\left(\frac{1}{q_e}\right)t+\frac{1}{k_2q_e^2} \tag{8}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorbate amount at equilibrium and at time t (min), respectively; and k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order equation.

2.4.2. Isotherm studies

In order to effectively describe the mode of adsorbent–adsorbate interactions, several theoretical models have been developed and applied in the literature. However, the most commonly used models are those of Langmuir [54] and Freundlich [55]. Hence, the isotherms studies were investigated using Langmuir [Eq. (9)] and Freundlich [Eq. (10)] models.

$$q_e=\frac{q_{\max}+K_LC_e}{1+K_LC_e} \tag{9}$$

where $q_{\max}$ (mg g^{-1}) is the maximum adsorption capacity, C_e (mg L^{-1}) is the adsorbate concentration at equilibrium, q_e (mg g^{-1}) is the adsorption amount adsorbate at equilibrium and K_L (L mg^{-1}) is a constant linked to the affinity between an adsorbent and an adsorbate.

$$q_e=K_FC_e^n \tag{10}$$

where K_F (mg g^{-1})(mg L^{-1})$^{1/n}$ is the Freundlich constant, and n (dimensionless) is the Freundlich intensity parameter, which indicates the magnitude of the adsorption driving force or surface heterogeneity, where the more the $1/n$ value approaches zero, more heterogeneous the surface, while the interval $0 < 1/n < 1$ indicates the favorable adsorption condition.

3. Results and discussion

3.1. Leachate treatment by Fenton-like

3.1.1. Effect of pH

The effect of initial pH on the Fenton-like efficiency in terms of the COD removal was investigated by varying the pH of the leachate in the range from 2 to 11 using [Fe^{3+}] = 1,500 mg L^{-1} and [H_2O_2] = 11,000 mg L^{-1}. Therefore, Fig. 1 presents the effect of leachate initial pH on the evolution of COD removal, sludge volume percentage, and final pH. Fig. 1 shows that the higher COD removal values 68%, 75%, and 70% were noticed at the acidic range pH = 2, 3 and 5, respectively. The pH value at 3 depicted the maximum COD removal (75%). While the treatment efficiency decreased to 48%, 49% and 42% at alkaline pH range (pH = 7, 9 and 11). The pH value of 11 represented a low removal efficiency of 42%. Indeed, many studies have proven that the acidic pH is favorable for the generation of $HO^{\bullet}$, however, in alkaline pH the hydrolysis and precipitation of ferric ions Fe^{3+} as hydroxide becomes favorable, resulting in a decrease in the catalytic capacity of Fe^{3+} [56,57]. In addition, the deficiency of H^+ ions prevents the decomposition of H_2O_2 to generate $HO^{\bullet}$ radicals and the decomposition of H_2O_2 into water and oxygen is accelerated at pH > 5 [Eq. (11)] [58].

$$H^+ + HO^{\bullet} + e^- \rightarrow H_2O \tag{11}$$

On other hand, the reduction of the organic load is correlated with the color of the leachate [59,60]. This is noticed in the picture in the upper part of Fig. 1 showing that the samples' color turns from black to light brown with an obvious discoloration at the acidic pH range, which is probably due to the organic compounds' removal from the raw leachate by the Fenton-like process.

However, many researchers concluded different optimal pH values ranging between acidic and neutral [35,38,39,61,62]. In fact, the pH range varies depending on the types of Fenton-like process (homogeneous or heterogeneous), the nature of the catalysts, the type and concentration of organic pollutants [63,64].

The optimum initial pH value determined for the Fenton-like reaction was considered to be pH 3.0. Thus, in this work, the pH was carefully adjusted to a value of 3 for performing all the next experiments, which was similar to previous findings [35,37].

Moreover, the initial pH has also affected the percentage of sludge volume, where the highest percentage of 40% was obtained at pH 5, while the lowest values 16% and 11% at pH 9 and 11, respectively. The values of the final pH varied slightly at the end of the treatment.

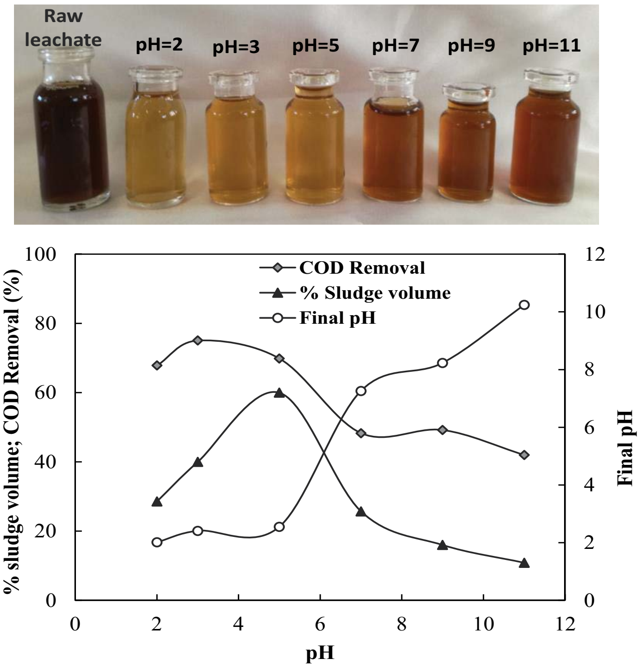

Fig. 1. Initial pH effect on COD removal, sludge volume percentage and final pH; experimental conditions: [Fe^{3+}] = 1,500 mg L^{-1}; [H_2O_2] = 11,000 mg L^{-1}.

3.1.2. Effect of contact time

The evolution of the COD removal depending on contact time is presented in Fig. 2. With the dosages of 11,000 mg L^{-1} of H_2O_2 and 1,500 mg L^{-1} of Fe^{3+} at pH 3, the COD removal increased with contact time and reached 77% since the first 5 min. Then it is raised to its maximum value of 81% after 30 min. The slow rate of COD removal after the first minutes and its stabilization after 30 min could be due to the consumption of the generated $HO^{\bullet}$ through their reaction during the degradation of the pollutants or their inhibition by their reactions between themselves [Eq. (12)] or with $HO_2^{\bullet}$ [Eq. (13)], which decreases and limits the treatment efficiency.

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \tag{12}$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \tag{13}$$

3.1.3. Effect of Fe^{3+} dosage

The catalyst concentration has also a major effect on the efficiency of FL. Hence, the effect of Fe^{3+} concentration is shown in Fig. 3.

Under the experimental conditions of the initial pH = 3 and [H_2O_2] = 11,000 mg L^{-1} and variable Fe^{3+} dosage, the COD removal efficiency increased from 34% to 79% with increasing the Fe^{3+} dosage from 0 to 250 mg L^{-1}, simultaneously, it raised the volume sludge (v/v %) from 0% to 52%. Thereafter, the COD removal decreased slightly to 75% when Fe^{3+} concentration raised to 2,000 mg L^{-1}. Then, it dropped significantly to reach 49% at the highest concentration 3,000 mg Fe^{3+} L^{-1}. As it is known, the Fe^{3+} ions are used as catalysts to accelerate the generation of free hydroxyl radicals, which makes

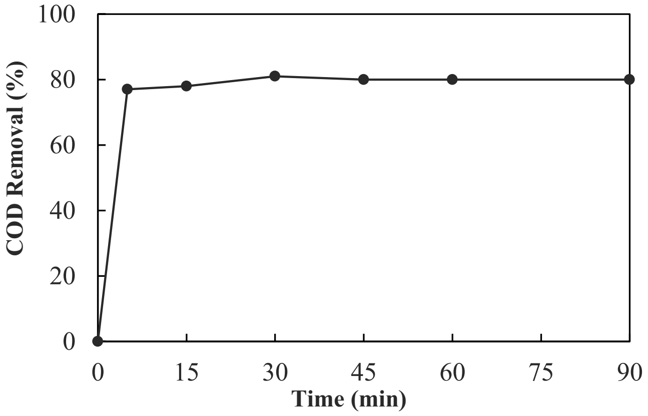

Fig. 2. COD removal evolution depending on contact time; experimental conditions: $[Fe^{3+}]$ = 1,500 mg L^{-1}; $[H_2O_2]$ = 11,000 mg L^{-1}; pH = 3.

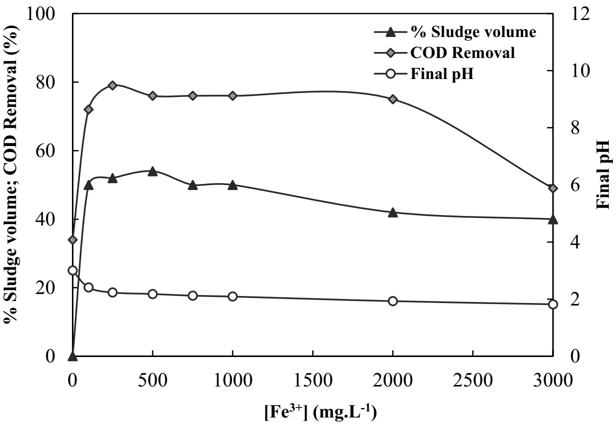

Fig. 3. Effect of Fe^{3+} dosage on COD removal, sludge volume (%) and final pH; experimental conditions: initial pH = 3; $[H_2O_2]$ = 11,000 mg L^{-1}; contact time = 30 min.

the degradation efficiency very low without catalysts' addition or at low dosages. Though, high dosages might produce an excess of radicals, thus decreasing the treatment efficiency due to the inhibition of radicals' effect following Eqs. (13) and (14). In addition, excessive concentration of Fe^{3+} could increase large volumes of the produced sludges which require their management increasing then the operational costs of the treatment [61,64].

Furthermore, the trend of final pH indicates that the addition of Fe^{3+} decreased progressively and slightly the pH values of the pretreated landfill leachate, which could be due to the acidic character of Fe^{3+} (Lewis acids).

The UV-Visible absorbance spectra in a wavelength range between 200 and 800 nm are widely used to characterize the presence of aromatic and organic matter (unsaturated double bonds characteristic of hydrocarbons, benzene and humic acids and polycyclic aromatic compounds) and monitor molecular degradation during leachate treatment [65–69].

Hence, Fig. 4 presents the UV-Visible spectra of leachate samples before and after treatment with FL process at 250, 500, 2,000 mg L^{-1} of Fe^{3+}.

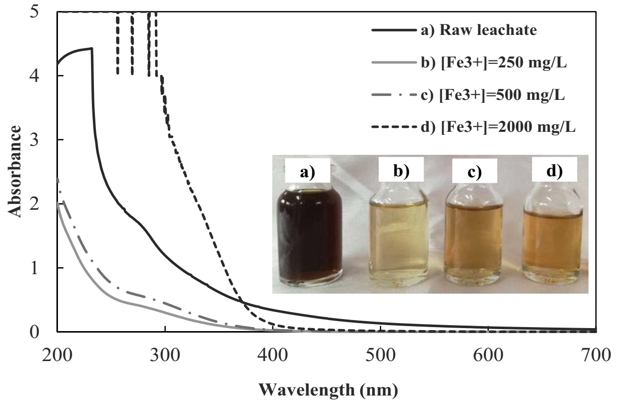

Fig. 4. UV-Visible spectra of leachate samples at different Fe^{3+} dosages (diluted 20X).

It can be clearly seen from Fig. 4 that the treatment by FL process using 250 mg L^{-1} of Fe^{3+} reduced significantly the absorbance of UV-Visible spectra of leachate sample (diluted 20 times), especially in the wavelength range 200 and 400 nm, whereas 2,000 mg L^{-1} increased them, thus generating a spectrum higher than the one of raw leachate, which could be explained by the interference of the color resulted from the Fe^{3+} excess and the color related to the presence of residual pollutants. The attached picture in Fig. 4 shows also that the visual aspect of leachate color became clearer after the treatment and darker by increasing the Fe^{3+} amount. Consequently, it was well confirmed that 250 mg L^{-1} is the optimal concentration of Fe^{3+}.

3.1.4. Effect of H_2O_2 dosage

The effect of H_2O_2 concentration on COD removal, sludge volume percentage and final pH is displayed in Fig. 5. As shown, 32% of COD was removed without H_2O_2 addition, while, the addition of $[H_2O_2]$ = 500 mg L^{-1} removed 69% of COD. Thereafter, this efficiency increased slightly to 72% (+3%) by raising the H_2O_2 dosage to 1,000 mg L^{-1}. Then, a slight decrease in COD removal was noticed by further increasing the H_2O_2 amount beyond 1,000 mg L^{-1}.

These results could be explained by the direct impact of the H_2O_2 amount added to the effluent and the produced active radicals. Where low H_2O_2 dosage leads to a decrease in the degradation of organic pollutants due to a deficiency of $HO^{\bullet}$. However, an excessive quantity of H_2O_2 decreases the efficiency of the process by the self-decomposition of H_2O_2 [Eq. (14)], the scavenging of the $^{\bullet}OH$ radical by hydrogen peroxide which produces less reactive $HO_2^{\bullet}$ [Eq. (15)], the reaction between the radicals $HO^{\bullet}$ and $HO_2^{\bullet}$ to form water and oxygen [Eq. (13)], or by the consumption of radicals by their reaction between themselves [Eq. (12)], which considerably reduce the reaction rate [58,70,71].

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (14)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (15)$$

Moreover, the effect of H_2O_2 concentration was also assessed in terms of UV-Visible spectra evolution (Fig. 6). The corresponding trend indicates that the progressive addition of H_2O_2 reduced significantly the absorbance values especially in the range 250–300 nm. Furthermore, the attached picture in Fig. 6 illustrates obviously the significant discoloration of the treated samples compared to the raw leachate.

Following the effect's investigation of contact time, initial pH, and reagents' dosages on the Fenton-Like performance, it was concluded that the process was rapid (30 min), the initial pH was acid (3) which required the leachate sample neutralization at the end of the treatment, the concentration of reagents were $[Fe^{3+}] = 250$ mg L^{-1} and $[H_2O_2] = 1,000$ mg L^{-1} (mass ratio $[Fe^{3+}]/[H_2O_2] = 0.25$), and the mass ratio of the needed H_2O_2 to the removed COD (3,743 mg L^{-1}) ($[H_2O_2]$/COD = 0.27) was much lower than the theoretical mass ratio of 2.125. In fact, several studies have proven that the optimal $[H_2O_2]$/COD is generally different from the theoretical value which is explained by the variety of the applied AOP system and the effluent nature (Table 1) [42,74–80]. Moreover, this ratio widely varies among the same effluent category (landfill leachate) because of its heterogeneous composition influenced namely by the waste type (biodegradable, non-biodegradable, etc), dumping site (wild, controlled, etc), and climatic conditions (rainwater and temperature) [74–79].

Similarly, the optimal $[Fe^{3+}]/[H_2O_2]$ ratio differs significantly between studies depending on the model pollutant and the experimental conditions [61,72,73].

Hence, the determination of the optimal reagents' ratio is quite challenging because of the different controlling mechanisms which requires further investigations and analysis for each specific effluent and specific AOP system.

Finally, a stock volume of the pretreated leachate was prepared using the previously determined optimal parameters for the adsorption tests.

3.2. Adsorption of pretreated leachate on natural bentonite

3.2.1. Adsorbent mass effect

The effect of adsorbent mass on the COD removal and adsorption capacity was examined by introducing 15 mL of the leachate sample pretreated with FL process and with a fixed COD of 1,456 mg O_2 L^{-1} into flasks and adding various

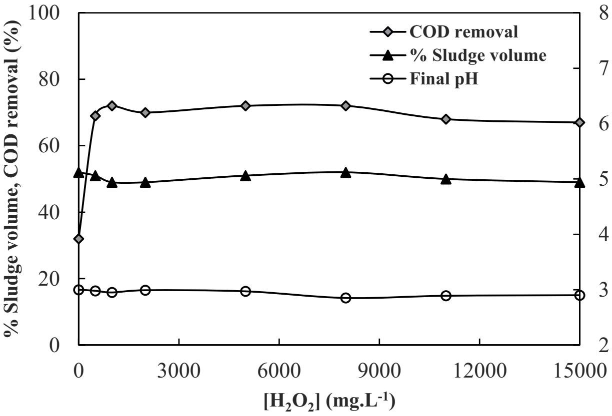

Fig. 5. H_2O_2 dosage effect on COD removal, % sludge volume and final pH; experimental conditions: initial pH = 3; $[Fe^{3+}] = 250$ mg L^{-1}; contact time = 30 min.

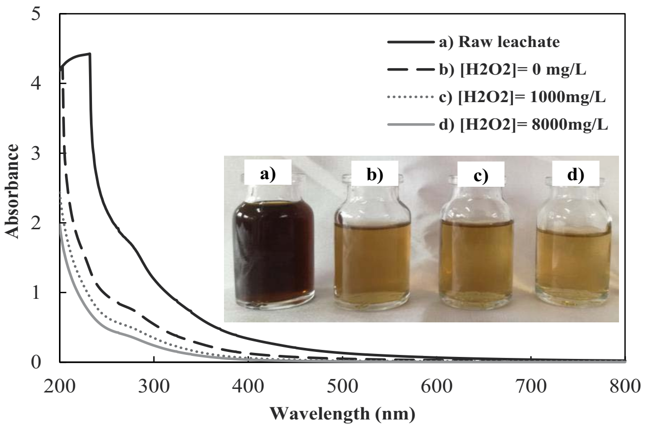

Fig. 6. UV-Visible spectra of leachate samples at different H_2O_2 dosages (diluted 20X).

Table 1
Literature review about the H_2O_2-based AOPs for COD removal

Effluent	AOP	Initial COD (mg L^{-1})	Mass ratio H_2O_2/COD	COD removal (%)	Reference
LL (Fez, Morocco)	Fe^{3+}/H_2O_2	5,198	0.27	72	This study
Synthetic melanoidin wastewater	ACC-CH-nZVI/H_2O_2	8,000	1.02	76.2	[42]
LL (Mumbai, India)	US/H_2O_2 US/Fe^{2+}/H_2O_2	8,600	0.8 0.6	72 90	[74]
LL (Winnipeg, MB, Canada)	O_3/H_2O_2	1,276	2.1	33	[75]
LL (Kuala Lumpur, Malaysia)	O_3/US/Fe^{2+}/H_2O_2	1,500	1.4	95	[76]
LL (North-eastern part of Poland)	UV/Fe^{2+}/H_2O_2	1,670	2.8	70.7	[77]
LL (Kömürcüoda Sanitary Landfill, Turkey)	PS/H_2O_2	5,575	2	56.9	[78]
LL (Kömürcüoda Sanitary Landfill, Turkey)	Electro-Fenton	5,250	1.42	67.1	[79]

LL: Landfill leachate

amounts of the bentonite adsorbent (0.05–10.6 g L^{-1}) to the flasks at 25°C.

Fig. 7 displays the effect of adsorbent mass on COD removal and COD adsorbed (q_e). It is well noticed that rising bentonite mass from 0.05 to 0.075 g enhanced COD removal from 6% to 22%, then a negligible enhancement was noticed by increasing the adsorbent mass up to 0.6 g. The COD removal enhancement noticed by raising the bentonite mass could be attributed to the increase of the number of active sites on the adsorbent surface [47,80]. Meanwhile, a progressive reduction of COD adsorbed (q_e) was noticed by increasing the adsorbent mass may be due to the particle interaction (aggregation).

Hence, the optimal dose of bentonite adsorbent was fixed at 5 g L^{-1} for other parameters' assessment.

3.2.2. Initial pH effect

The effect of initial pH on the COD removal and COD adsorbed was investigated by varying the pH of the pretreated leachate by FL process over 3–11 range using COD initial concentration of 1456 mg O_2 L^{-1} and bentonite dose of 5 g L^{-1}. The results obtained are presented in Fig. 8.

The initial pH effect of the pretreated leachate was investigated in terms of COD removal and q_e (Fig. 8). The initial pH values were ranged from 3 to 11, where the highest COD removal reached 32% at pH 3 and 30% at pH 7, while low removal values 24%, 19% and 22% were noticed at pH 5, 9 and 11. Therefore, the initial pH of all the occurred tests was fixed at 7.

Indeed, the determination of the optimal pH is highly related to the effluent composition. Many previous studies have examined the pH effect on the adsorption capacity of bentonite-based materials, where the optimum pH values widely varied between extremely acidic and neutral ranges depending on the nature and the complexity of the adsorbate (dyes, metal ions, industrial wastewater, landfill leachate, etc) [45,48,49,81–84].

3.2.3. Kinetic study

The adsorption kinetic of the pretreated leachate onto bentonite was studied by the assessment of COD adsorbed as a function of contact time and the fitting curve by pseudo-first and pseudo-second-order (Fig. 9). It is well noticed that the adsorbed COD (q_t) clearly increased in the first phase of contact time, where q_t reached 67.2 mg O_2 g^{-1} after 180 min, thereafter it raised slowly up to 77 mg O_2 g^{-1} at 480 min, then it almost stabilized despite increasing the contact time up to 1680 min. This trend of the adsorbed COD in terms of contact time could be explained by the high availability of accessible sites on the bentonite surface which enhance the adsorption capacity in the first minutes of the treatment [46,53,85], thereafter the adsorbed amount decreases due to the occupation of the adsorption sites by the previously adsorbed pollutants.

The obtained kinetic parameters for both kinetic models are summarized in Table 2. Based on correlation coefficient R^2, it is well noticed that that the experimental data is best correlated with pseudo-second-order than pseudo-first-order model, suggesting then that adsorption was mainly controlled by the chemisorption as the dominant mechanism

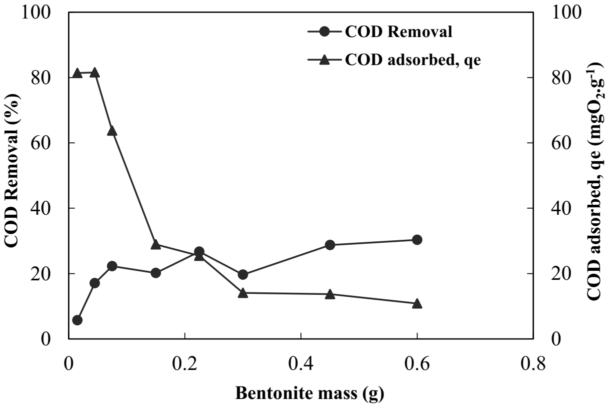

Fig. 7. Bentonite mass effect on COD removal and COD adsorbed (q_e); experimental conditions: bentonite mass = 0.05–06 g; COD = 1,456 mg O_2 L^{-1}; V = 15 mL; initial pH = 7; T = 25°C; contact time = 12 h.

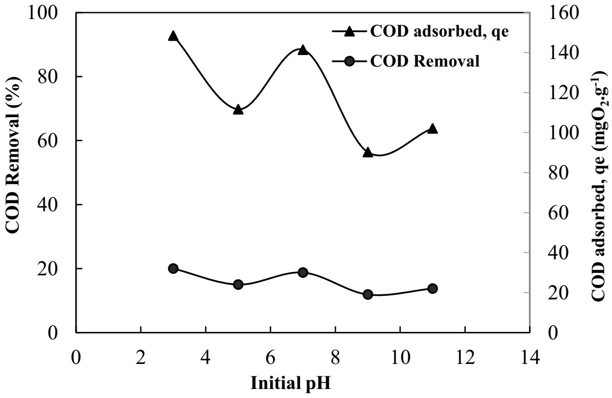

Fig. 8. Initial pH of L_{FL} effect on COD removal and COD adsorbed (q_e); experimental conditions: COD = 1,456 mg O_2 L^{-1}; bentonite mass = 5 g L^{-1}; T = 25°C, contact time = 12 h.

Table 2
Kinetic parameters of pseudo-first and pseudo-second-order for the adsorption of the pretreated leachate onto bentonite

Pseudo-first-order			Pseudo-second-order		
q_{max} (mg g^{-1})	k_1	R^2	q_{max} (mg g^{-1})	k_2	R^2
75.12	0.011	0.955	80.645	0.00029	0.9804

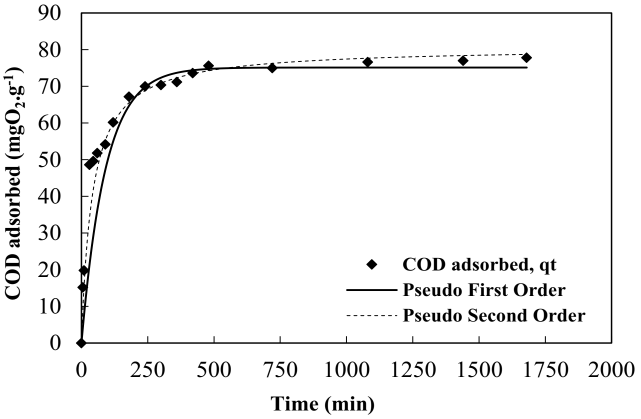

Fig. 9. Effect of contact time on the efficiency of L_{FL} adsorption onto the bentonite; experimental conditions: pH = 7; bentonite mass = 5 g L^{-1}; T = 25°C.

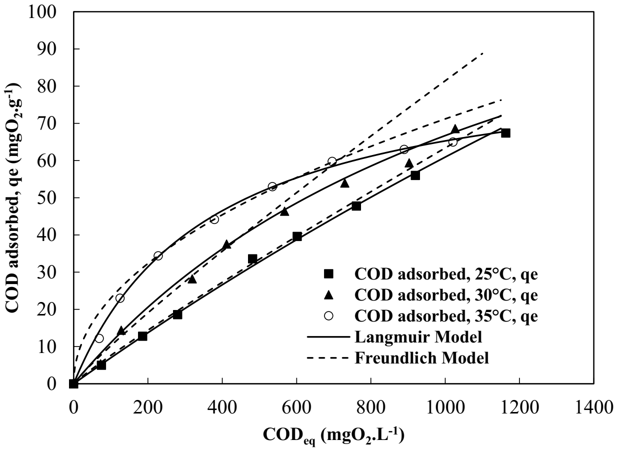

Fig. 10. Effect of temperature on the efficiency of L_{FL} adsorption onto the bentonite: equilibrium experimental (markers) and theoretical data (lines); initial pH = 7; bentonite mass = 5 g L^{-1}; contact time = 8 h.

which may suggest the chemical interactions between the leachate pollutants and the active sites on the bentonite surface [53,86,87].

3.2.4. Isotherms' study

Fig. 10 presents the experimental evolution of COD adsorbed onto bentonite clay (q_e) in terms of COD_{eq} at 25°C, 30°C and 35°C, and their correlation with Langmuir and Freundlich models. The results show that the amount of COD adsorbed increases slightly with temperature reflecting the endothermic nature of the adsorption.

The obtained parameters by the isotherms' modeling are presented in Table 3, where the highest values of correlation coefficient R^2 indicate that the Langmuir model describes the experimental results more than the Freundlich model, suggesting then the monolayer adsorption of landfill leachate on bentonite clay [86,87]. An increase in maximum adsorption capacity and in Langmuir constant values (K_L) was noticed by increasing temperature which indicates the endothermic nature of the adsorption process. Moreover, the Freundlich model provides $1/n < 1$ for the three temperatures indicating that the adsorption of leachate onto natural bentonite was feasible and favorable [86,87].

3.3. FL and adsorption efficiency

Fig. 11 shows the UV-Visible spectra corresponding to the raw landfill leachate, the pretreated sample with FL and the treated with FL followed by adsorption onto the bentonite clay. It is well shown that the absorbance values of the spectrum of the leachate treated with FL are significantly reduced compared to the absorbance values of the raw leachate sample, especially in the wavelength range of 200–400 nm. Thereafter, the secondary treatment with adsorption onto bentonite reduced further the UV-visible spectrum. This spectra evolution is well noticed on the attached image (Fig. 11), where the discoloration of samples treated with FL alone and FL/adsorption is highly significant compared to the dark color of raw leachate. These results are in line with the previous findings of COD removal where it reached 72% using FL then it was enhanced to 85% by adsorption, which is explained by the fact that COD and absorbance values are correlated positively [55,88].

Table 4 presents further analysis of the physical–chemical characteristics for the treated leachate under the optimal conditions of FL and adsorption compared to those of the raw sample. The results, as shown in Table 4, indicate that turbidity, color number, nitrates and nitrites removal reached >95%. Cr, Cu, Mn and Zn were totally removed, while Fe and Cl^- concentrations highly increased after FL treatment because of $FeCl_3$ addition, then they significantly decreased after adsorption. Similarly, sulfate concentration increased after the FL step due to the pH adjustment using H_2SO_4 and reduced after the adsorption treatment. The results show also a remarkable enhancement of the

Table 3
Parameters of Langmuir and Freundlich models for the adsorption of the pretreated leachate onto bentonite at 25°C, 30°C and 35°C

Temperature (°C)	Langmuir model			Freundlich model		
	q_{max} (mg g^{-1})	K_L (L g^{-1})	R^2	$1/n$	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	R^2
25	67	0.00016	0.9996	0.92	0.11014	0.9876
30	68	0.000786	0.9845	0.902	0.15991	0.9691
35	70	0.002717	0.9923	0.490	2.40367	0.9747

Table 4
Landfill leachate characteristics before and after the application of the FL and adsorption process

Parameters	Raw leachate	Pretreated leachate (FL)	Treated leachate (Adsorption)	Cumulative removal (%)
Turbidity, NTU	218	21	6	97
Color number	6.48	0.35	0.16	98
COD, mg L^{-1}	5198	1456	780	85
BOD_5, mg L^{-1}	500	190	100	80
BOD_5/COD	0.09	0.13	0.13	–
Chlorides, mg L^{-1}	6845	15,300	8,000	–
N-nitrates, mg L^{-1}	8.13	0.7	0.22	97
N-nitrites, mg L^{-1}	7.15	0.61	0.35	95
Sulfates, mg L^{-1}	140	213	85	39
Cr, mg L^{-1}	1.74	<0.01	<0.01	100
Cu, mg L^{-1}	0.05	0.02	<0.01	100
Fe, mg L^{-1}	1.83	10.23	0.98	46
Mn, mg L^{-1}	0.043	<0.01	<0.01	100
Zn, mg L^{-1}	0.2	<0.01	<0.01	100

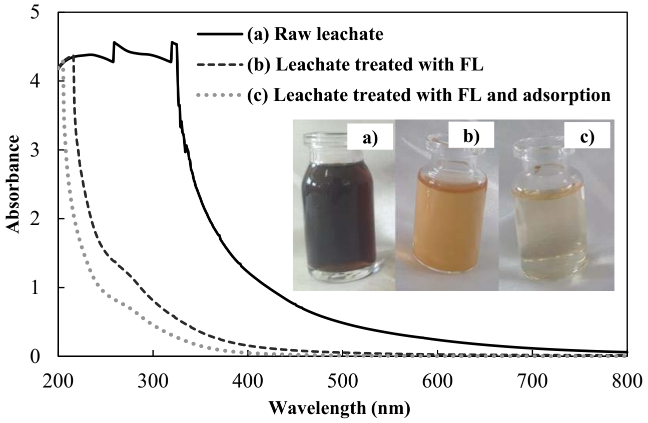

Fig. 11. UV-Visible spectra of (a) raw leachate, (b) L_{FL} and (c) L_{FL} adsorbed onto bentonite (diluted 10X).

leachate biodegradability in terms of BOD_5/COD ratio that raised from 0.09 to 0.13 after the FL and adsorption process.

4. Conclusion

The findings reported in this study indicate that the Fenton-like process was successfully applied for the pretreatment of raw landfill leachate highly loaded with organic matter.

The efficiency of this process is closely affected by the initial pH of leachate and the dosages of H_2O_2 and Fe^{3+}. Therefore, the optimization of these parameters should be considered in order to achieve maximum removal of organic pollutants.

Furthermore, the efficiency of FL is limited with the presence of refractory and complex organic molecules in landfill leachate that could be oxidized to small intermediate molecules, making then the reduction of the residual COD difficult. This suggested thereby the application of a second treatment to improve more the pollutants' removal and ensure compliance with liquid discharge standards. Indeed, the adsorption process onto local natural bentonite was applied for enhancing COD removal from the pretreated leachate by FL. Consequently, the obtained results showed an increase of COD removal using 5 g L^{-1} of mass adsorbent, pH = 7, contact time = 8 h and T = 35°C. The experimental data modeling indicated that they were well described by pseudo-second-order kinetic model and have been well fitted to Langmuir isotherm model.

Finally, it could be concluded that the application of the sequential Fenton-like and adsorption onto natural bentonite has proved a high treatment efficiency, especially for the treatment of a harmful and complex effluent such as landfill leachate. Despite these promising results, more research on this sequential treatment needs to be undertaken to further investigate the mechanisms controlling the processes and overcome their limitations. Hence, some recommendations would be the subject of future publications and would mainly focus on:

- Using of the response surface methodology to assess the interaction effect between the variables;
- Applying heterogenous Fenton-Like by using solid-state catalysts (i.e., clays and zeolites-based catalysts) as sources of Fe^{3+} instead of salt sources for reuse applications and to avoid sludges generation.
- Enhancing the Fenton-like performance by using ultrasonic waves and ultraviolet radiations for a further generation of hydroxyl radicals;
- Toxicity assessment of the landfill leachate after treatment for potential specific reuse or direct discharge.

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