Effective degradation and detoxification of landfill leachates using a new combination process of coagulation/flocculation-Fenton and powder zeolite adsorption

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ABSTRACT

The aim of this work was to examine the application of an integrated technique that consisted of coagulation/flocculation-Fenton-powder zeolite adsorption methods for the treatment of raw leachates from a landfill site of Bizerte (Northern Tunisia). The coagulation–flocculation process showed a moderate chemical oxygen demand (COD) removal efficiency (RE) (54%) and high turbidity RE (94%). The Fenton experiments suggested that the dosage of $1.2\,g\,L^{-1}$ of Fe^{2+} and $2.8\,g\,L^{-1}$ of H_2O_2 at pH 3 were the appropriate working conditions. Under these conditions, COD value was higher than the legal limits for discharge throughout the local municipal sewage. To achieve a satisfactory removal of pollutants, adsorption experiments were also carried out using $30\,g\,L^{-1}$ of powder zeolite. The removal efficiencies of COD, ammonia, iron, and aluminum were 97, 91, 99, and 97%, respectively. The phytotoxicity test showed that combined treatment process allowed a significant toxicity removal up to 90%.

Keywords: Adsorption; Coagulation; Fenton; Landfill leachates; Phytotoxicity

1. Introduction

In Tunisia, 1,700 tones of domestic garbage are collected daily. Landfilling is a fundamental step in any waste management strategy. Unfortunately, landfills generate a large amount of leachates containing heavy loads of ammonia nitrogen, heavy metals, chlorinated organic, and inorganic salts [1,2]. Landfill leachates have been identified as potential sources of ground water and surface water contamination, as they may percolate through soils and subsoils, causing extensive pollution. To achieve a satisfactory removal of refractory pollutants from the leachates, several types of physical–chemical and Biological treatments such as coagulation–flocculation, chemical precipitation, adsorption, anaerobic, and/or aerobic biological degradation have been employed worldwide.

The chemical oxidation using Fenton process makes possible the transformation of recalcitrant compounds into biodegradable products. This process is effective, simple, and inexpensive, and is based on the use of ferrous salts that activate H_2O_2 from highly

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oxidizing radicals. This system promotes the formation of the highly reactive hydroxyl radicals ·OH, able to oxidize a wide range of compounds [3,4]. High H_2O_2 doses lead to a higher amount of $HO^·$; however, when in excess, hydrogen peroxide reveals a radical scavenging capacity, decreasing the treatment efficiency and leading to production of hydroperoxyl radicals ($HO_2^·$) [5]. Generally, the Fenton reactant doses are determined as a function of the leachate organic content ($[Fe^{2+}]/[H_2O_2]$ and $[COD]/[H_2O_2]$), the oxidation time, and the pH [6].

One of the physicochemical processes is adsorption using activated carbon and zeolite. The combination of large amounts of organic and inorganic pollutants that exist in landfill leachates needs adsorbents which have the ability to remove a variety of pollutants. It is well known that activated carbons are the most effective adsorbents for the removal of organic pollutants from the aqueous or gaseous phase [7]. In contrast, granular and powder zeolite is widely used as a natural ion exchanger to reduce ammonia, chemical oxygen demand (COD), and other inorganic pollutants from leachates or other wastewaters [8]. Gao et al. [9] found new composite materials of zeolite-carbon [10,11], which combine the excellent properties of zeolite and carbon. The surface of zeolite is hydrophilic with regular aligned molecular-level pores and cationic exchange ability, which makes it a good adsorbent for metallic ions and ammonia from wastewater.

Biological processes are effective, when applied to relatively younger leachates, containing mainly volatile fatty acids and high BOD_5/COD ratio [10]. With time, the major presence of refractory compounds (mainly humic and fulvic acids) tends to limit process effectiveness. A high concentration of ammoniacal nitrogen is also known to inhibit the biological degradation by the micro-organism [11]. Thus, biological treatments of stabilized landfill leachates may be complex and expensive; therefore, several combinations of physicochemical treatments have been applied [12].

Coagulation/flocculation is a relatively simple technique that may be employed successfully for the treatment of stabilized leachates [13]. Nevertheless, this method may lead to moderate removal of COD or TOC content, presenting also certain drawbacks: excessive sludge may be produced, and in certain cases, when the conventional chemical coagulants are being used, an increase of aluminum or iron concentrations in the resulting effluent may be encountered [14,15].

The combined processes including two or three physical/chemical methods were used in treating stabilized landfill leachates such coagulation–ozonation [16], and precipitation–prefiltration–reverse osmosis [17]. The number of papers on treatment methods used for landfill leachates is undergoing an exponential increase, as often occurs in the case of an explosively growing subject, a certain degree of confusion due to conflicting evidence and interpretations is present in the literature. The reasons for the confusion still present in the literature concerning leachates are essentially twofold. The former is due to the variety of treatment methods adopted for the removal of recalcitrant compounds from leachates, which span from the physical–chemical treatments of leachates to sophisticated biological methods. The second reason is due to chemical composition of leachates which can be influenced by the type of deposited wastes and mainly by the age of landfills.

To the best of our knowledge, there is no report on the combined process of coagulation/flocculation-Fenton-adsorption, as an efficient integrated technique for the treatment of landfill leachates, especially in terms of organic matter removal expressed by COD. More purposely, the aim of this work was the determination of most appropriate of the coagulant dosage, Fenton reagents, the influence of pH on removal capacity, and the COD absorption capacity of zeolite. Furthermore, the combined behavior of coagulation/flocculation-Fenton-adsorption processes was estimated under the optimized experimental conditions for the treatment of landfill leachates. Considering the potential effect of leachate on the ecosystem, a phytotoxicity test using tomato (*Lycopersicon esculentum*) and alfafa (*Medicago sativa*) seeds was successfully applied in ecological risk assessment of leachates-treated solution.

2. Materials and methods

2.1. Leachate characterization

2.1.1. Site description

The site used for this study was the sanitary landfill site of Bizerte, a city in the northeastern part of Tunisia (37˚16´N; 9˚52´E) (Fig. 1). A leachates management program has been applied, involving the collection of leachates through a drainage network and the continuous recirculation through the deposited landfill. At the lowest point of landfill, leachates exits to the surface, forming an evaporation pond. About $60\,m^3\,d^{-1}$ of leachates are transferred to the main wastewater treatment plant for further treatment.

2.1.2. Sampling campaign

Leachate samples were collected from the evaporation pond in 40 L plastic carboys. Samples were transported to the laboratory, stored at 4˚C and analyzed
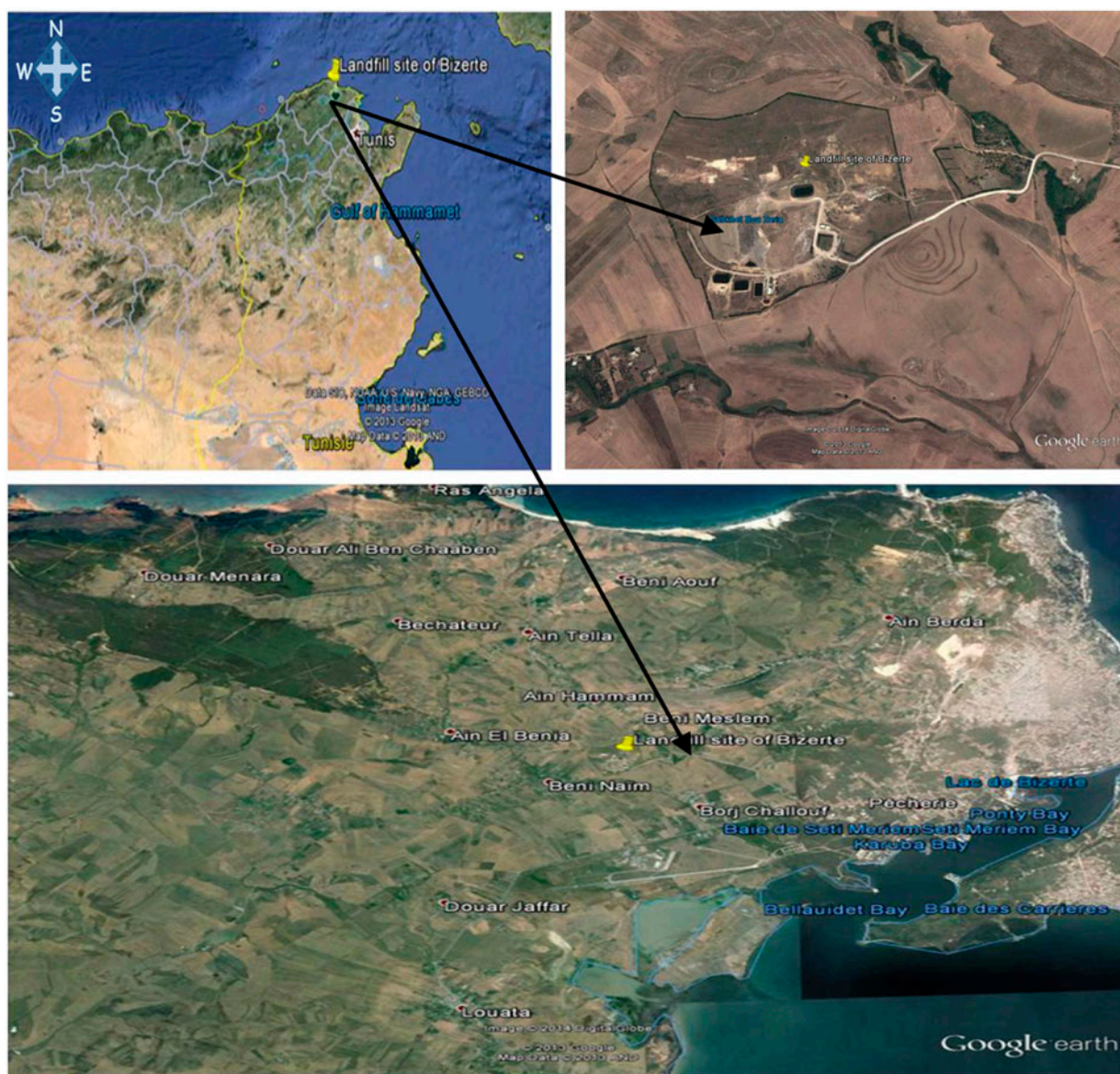
Fig. 1. Localization of site sampling.

within two days. Physicochemical characteristics of leachate samples were validated according to French standard NF XPT 90-210 [18]. Biochemical oxygen demand (BOD$_5$) was determined by the manometric method with a respirometer (BSB-Controlled Model OxiTop (WTW)) and the COD was estimated using the method described by Knechtel [19]. Total nitrogen contents (TN) were measured by the Kjeldhal method using an automated apparatus (Buchi, Switzerland). Phosphorus was determined colorimetrically at 430 nm using a Shimadzu U 1000 spectrophotometer. The phosphorus content (TP) was measured colorimet-

rically by atomic absorption (ICE, 3000 model). The pH was measured using pH meter (INOLAB WTW 720). Electrical conductivity was determined with an electronic conductivity meter (TACUSSEL, CD 6NG) equipped with an immersion measurement probe (cell constant Ks L^{-1} = 1 cm). Turbidity was measured using 2020 turbidimeter (LaMotte). The total suspending solid content was assessed by drying at 105°C for 12 h [20].

The total concentrations of Fe, Mn, Zn, Ni, and Cr were determined using atomic absorption flame emission spectroscopy AAS (Thermo scientific). Prior to

analysis, 20 mL of the sample was transferred into the Teflon flask and then completely dissolved in HCl–HNO$_3$ solution (30/70% in volume). After dissolution, the mixture was diluted with 100 mL of deionized water and analyzed by (AAS). The concentrations of heavy metals were also analyzed according to the standard methods for the examination of water and wastewater in order to validate/evaluate the produced results and they were found within accepted analytical error (±7%). All chemicals used for the analytical determinations were of analytical grade. The removal efficiency (RE) was determined as the percentage of decrease in influent with respect to effluent for each parameter measured.

2.2. Methods

2.2.1. Coagulation/flocculation

Coagulation/flocculation experiments were carried out in a conventional jar-test apparatus, equipped with six beakers of 1,000 mL volume at room temperature. Leachates sample was taken from the refrigerator and kept for about 2 h under ambient temperature. The sample temperature at the end of the 2 h period was measured and was around 17℃. Then, sample bottle was thoroughly shaken, for re-suspension of possibly settling solids and the appropriate volume of sample was transferred to the corresponding jar-test beakers. The experimental process consisted of three subsequent stages: the initial rapid-mixing stage took place for 6 min at 200 rpm, followed by a slow stage for 60 min at 60 rpm. Stirring was then discontinued and the sludge was left to settle for 2 h. After the settling period, the supernatant was withdrawn from the beakers using a plastic syringe (50 mL) from a point located about 2 cm below the liquid level at the beaker and used for chemical analysis. The produced wet sludge volume was estimated from the sludge level on the bottom of the glass beakers. Finally, the volume of sludge dehydrated by centrifugation at 3,000 rpm for 5 min was determined. The experiments were carried out with and without prior pH adjustments and for different dosages. Aluminum sulfate (Al$_2$(SO$_4$)$_3$·18H$_2$O, Merk) was used as coagulant. The treated sample is labeled according to its physical–chemical treatment. TL$_{CF}$ was the treatment of leachates by coagulation/flocculation.

2.2.2. Oxidation procedures

Fenton experiments were conducted in a 1,000 mL glass beaker. About 400 mL of treated TL$_{CF}$ was introduced into the reactors and agitated in an orbital shaker at 10 rpm. Fenton oxidation is initiated by the addition of Fenton reagents and hydrogen peroxide. Because low pH favors Fenton oxidation, the pH was adjusted initially and controlled continuously at the desired value using sulfuric acid and sodium hydroxide solution. The leachates was then filtered using a filter (Schleicher and Schuell of 25 μm pores) to remove precipitated solids. COD, BOD$_5$, heavy metals, and turbidity in the supernatant are measured to evaluate the overall treatment efficiency. The treated sample is also labeled according to its physical–chemical treatment TL$_{CF-F}$.

2.2.3. Adsorption

Adsorption experiments were performed in Erlenmeyer flasks where 200 mL of treated leachates TL$_{CF-F}$ was mixed with the appropriate amount of powdered zeolite PZ (zeolite 4A, aluminosilicate, [Na$_{12}$(Al$_{12}$Si$_{12}$O$_{48}$)] 27H$_2$O, CEC, 5.47 meq/g), in the range of 10–60 g L^{-1} and then shaken for a period of 12 h at 150 rpm. The resulting mixture was heated at 70℃ for 30 min in order to remove the excess hydrogen peroxide from the solution. The sample was then settled for 2 h and the supernatant was analyzed with respect to its COD content and heavy metal concentration. The treated sample was denoted as TL$_{CF-F-A}$. The physicochemical properties of the zeolite 4A adsorbent are listed in Table 1.

Table 1
Physicochemical characteristics of powder zeolite *4A*

Physicochemical properties of zeolite *4A*	
Molecular formula	Na$_{12}$(Al$_{12}$Si$_{12}$O$_{48}$)] 27H$_2$O
BET surface area (m^2 g^{-1})	725
Particle size (μm)	3
Cation-exchange capacity, CEC (meq g^{-1})	5.47
Thermal stability	High
Ratio Si/Al	1
Application	Adsorption, ion exchange, catalysis

2.2.4. Toxicity test

The phytotoxicity was assessed on seed germination of tomato (*L. esculentum*) and Alfafa (*M. sativa*) according to a modified Zucconi test [21] by measuring the seed germination. Ten undamaged seeds with identical size were placed uniformly in 90 cm petri dishes, in a filter. Five dilutions of the sample and one control were prepared with three replicates. Each dish contained 5 mL sample dilution or 5 mL of distilled water (control). Three replicates were carried out for each sample, including the control. Dishes were then covered and incubated in the dark at 20 ± 2°C for five days. A germination index (GI) was calculated by counting the number of germinated seeds and the average root length observed in each sample compared to control seeds. Seeds were considered to have germinated when the radical penetrates the seed coat [22]. The median effective concentration (EC_{50}) was calculated from the dose relationship between GI and leachates concentration by the Brian–Cousens model [23]. Results finally expressed according to the formula (Eq. (1)):

$$GI = \frac{\text{number of germination seeds in sample}}{\text{number of germination seeds in control}}$$
$$\times \frac{\text{average of root lengths in sample}}{\text{average of root lengths in control}} \times 100 \qquad (1)$$

A seed was considered germinated when the root length exceeded 5 mm. For root lengths below 5 mm,

it was considered equal to 0 and the seed was not considered germinated. The average sum of root lengths comprised the sum of the lengths of all germinated seeds in a Petri dish. The effect results obtained with each toxicity test were transformed into toxic units according to the formula (Eq. (2)):

$$TU = 1/EC_{50} \times 100 \qquad (2)$$

3. Results and discussion

3.1. Leachate characteristics

Table 2 shows the physicochemical characterization of the collected samples and Tunisian discharge standards in the sewer [24]. The main characteristics of these leachates are COD in the range of 25,000–26,000 mg L^{-1} and BOD_5 of 5,200 mg L^{-1}. In addition to organic compounds, the leachates were also characterized by high concentration of ammonium. Furthermore, the color of raw leachates was brown due to the presence of humic substances. These substances contain both aromatic and aliphatic compounds with primarily phenolic and carboxylic functional groups [25]. The chemical nature of these species and a reliable mechanism for their formation in leachates will not be proposed in the present work. Fer (Fe) was the predominant metal in leachate (6.87 mg L^{-1}). The high level of Fe indicates the dumping of steel scrap in the landfill. This explains the brown dark color of the leachate which is a

Table 2
Physicochemical characterization of raw and treated leachates and legal limits for Tunisian discharge standards in the sewer [24]

Parameters	Raw leachates	[a]TL_{CF}	[b]TL_{CF-F}	[c]TL_{CF-F-A}	Discharge standards
pH	7.74 ± 0.4	5.5 ± 0.3	3 ± 0.11	6.5 ± 0.22	6.5 < pH < 9
Turbidity (NTU)	422 ± 15	48 ± 4.2	27 ± 1.7	9 ± 0.7	–
Conductivity (mS/cm)	34 ± 2.4	33 ± 1.2	17.2 ± 2.3	16.1 ± 1.3	–
COD (mg L^{-1})	26,200 ± 130	12,058 ± 75	4,990 ± 45	620 ± 22	1,000
DBO_5 (mg L^{-1})	5,200 ± 65	4,341 ± 55	1982 ± 23	391.3 ± 12	400
DBO_5/COD	0.19 ± 0.03	0.36 ± 0.02	0.4 ± 0.05	0.63 ± 0.02	–
TDS (g L^{-1})	28.56 ± 1.5	23.80 ± 1.8	16.80 ± 1.2	14.72 ± 1.1	–
TKN (mg L^{-1})	1,770 ± 19	1,503 ± 22	967 ± 23	127 ± 31	100
N-NH4$^+$ (mg L^{-1})	1,623 ± 21	1,406 ± 19	931 ± 25	107.3 ± 27	–
Total P (mg L^{-1})	13.64 ± 1.2	12.5 ± 1.7	11 ± 1.2	7.23 ± 1.4	10
Absorbance (nm)	1.192 ± 0.07	1.168 ± 0.04	0.053 ± 0.02	0.023 ± 0.015	–
Fe (mg L^{-1})	6.87 ± 1.2	5.418 ± 0.93	11.05 ± 3.1	0.085 ± 0.005	5
Al (mg L^{-1})	1.73 ± 0.05	8.27 ± 1.4	8.038 ± 1.3	0.05 ± 0.002	10
Cr (mg L^{-1})	1.64 ± 0.09	1.274 ± 0.06	1.263 ± 0.02	0.143 ± 0.03	2
Mn (mg L^{-1})	0.15 ± 0.03	0.1659 ± 0.01	0.102 ± 0.05	0.03 ± 0.001	1

[a]TL_{CF}: treated leachates by coagulation–flocculation: 1 g L^{-1} of Al^{3+}; pH5.5.
[b]TL_{CF-F}: treated leachates by coagulation–flocculation then Fenton process: 2.8 g L^{-1} of H_2O_2; 1.2 g L^{-1} of Fe^{2+}; pH3.
[c]TL_{CF-F-A}: treated leachates by coagulation–flocculation, Fenton then adsorption. Powder Zeolite PZ: 30 g L^{-1}.
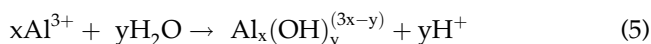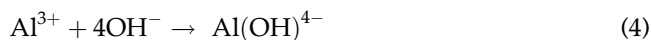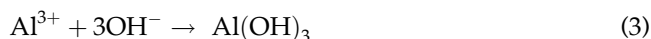
product of oxidation of ferrous to ferric form. This concentration is not tolerated by Tunisian discharge standards in the sewer. It should be also mentioned that leachates presented relatively high pH value (around 7.7), and rather low ratio of BOD_5/COD of about 0.19, low phosphorus content and high ammonia–nitrogen content. In our case, biological methods may be inappropriate for the direct treatment of this leachates type. First, as shown in Table 2, the leachates contain a high concentration of ammonia upto 1,743 mg L^{-1}, which may be toxic due to the biological processes for leachates treatment [26]. Second, the efficiency of subsequent (biological) treatment is dependent on the established BOD_5: N: $p = 100:5:1$ ratio, which is necessary for the efficient bacterial growth [27]. On account of that, they should be more susceptible to be treated by physical–chemical techniques, such as coagulation–flocculation, Fenton, and adsorption process. Diluted effluent up to 10 times remained toxic and inhibited seeds germination of selected plant indicators to the

complex leachates where inhibitory factors such as high salinity and toxicity coexist. As a consequence, detoxication of this effluent seems to be imperative prior to its rejection in the sewage or in the environmental body.

3.2. Coagulation/flocculation process

The experiments were performed again without prior adjustment of pH employing the same dosage 0.6 g L^{-1} of $Al_2(SO_4)_3$ with the aim of investigating the coagulation efficiency at raw pH and determining the optimum pH. It was found the optimum pH was 5.5 (Fig. 2(a) and (b)), obtaining reductions in turbidity and COD up to 84 and 45%, respectively. As observed in Fig. 2(a), pH played a vital role in removal of turbidity; the removal rate ranged between 55% at pH 4 and the optimal value 84% at pH 5.5. However, the COD RE only increased from 31% at pH 4.5–45% at pH 5.5, which can be explained by the hydrolysis of $Al_2(SO_4)_3$.

According to Fig. 2, it can be seen that the RE was better in acid condition than that in basic condition and the optimum pH was 5.5. However, the reason for this phenomenon can be explained by the different hydrolyzed species of aluminum. In the basic condition, aluminum (Al^{3+}) can react with hydroxyl (OH^-) and form $Al(OH)_3$ or $Al(OH)^{4-}$ according to the following reactions (3) and (4). In the acid condition, aluminum can hydrolyze and form polynuclear cation as (Eq. (5)) showed. Obviously, polynuclear cations are preferable than $Al(OH)_3$ and/or $AL(OH)^{4-}$ in that nearly all colloidal impurities in water are negatively charged. Similar to the coagulation of $Al_2(SO_4)_3$, the treatment efficiency of $FeCl_3$ as coagulant increased with the dosage in a certain range and the reason was similar with that of $Al_2(SO_4)_3$ [28].

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \tag{3}$$

$$Al^{3+} + 4OH^- \rightarrow Al(OH)^{4-} \tag{4}$$

$$xAl^{3+} + yH_2O \rightarrow Al_x(OH)_y^{(3x-y)} + yH^+ \tag{5}$$

Once the optimal pH was determined, the next purpose was to determine the optimal dosage at pH 5.5. Dosage ranging between 0.2 and 1 g L^{-1} of Al^{3+} were tested, obtaining an optimum value of 0.6 g L^{-1} with reduction in COD and turbidity of 53 and 94%, respectively. The data obtained are shown in Fig. 2(b). The treatment efficiency of $Al_2(SO_4)_3$ increased with the dosage in a certain range. Wei et al. [29] simply reported the abatement of the pollutant character of
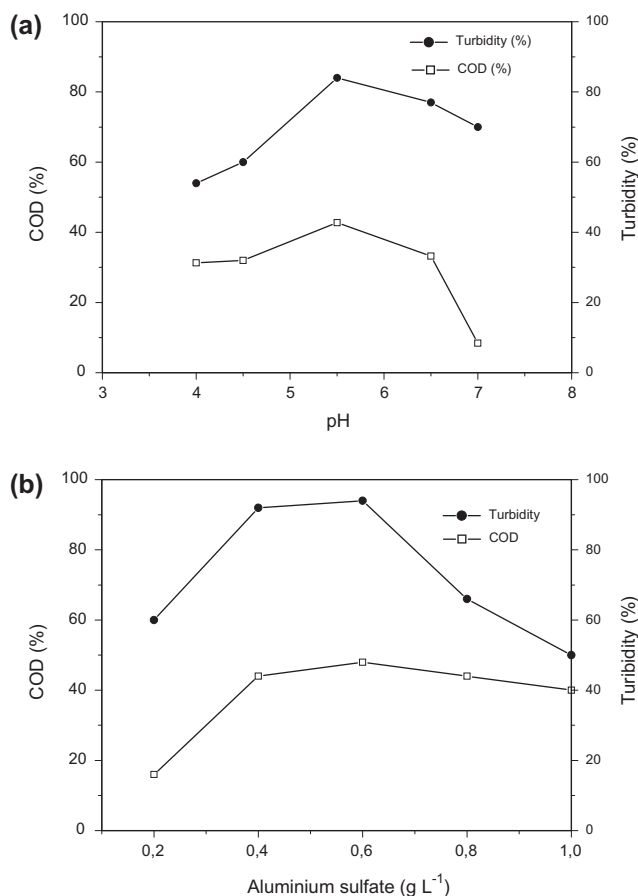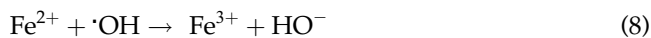
Fig. 2. (a) Removal of turbidity and COD vs. pH for a dosage of 0.6 g L^{-1} of Al^{3+}; and (b) removal of COD and turbidity for different doses of Al^{3+} at pH 5.5.

landfill leachates using $Al_2(SO_4)_3$ and $FeCl_3$ as coagulants. The authors demonstrated that the optimal removal (62%) of COD can be obtained at pH 6 and the RE of COD between two coagulants at different pHs was also not very different. However, when the dosage of $Al_2(SO_4)_3$ exceeded $0.6\,g\,L^{-1}$, the treatment efficiency significantly decreased, which can be explained by the charge neutralization theory. When $Al_2(SO_4)_3$ is added to the leachates, Al^{3+} and its hydrolyzed products interact with negative colloids and neutralize their charges, which destabilize the colloids. Over the appropriate dosage, the colloids can absorb the cations and become positively charged, hence, may be stable again as a result of electrical repulsion. Dosage played a vital role in the treatment efficiency of $Al_2(SO_4)_3$, because turbidity and COD RE increased sharply with the increase of the dosage in a certain range.

It is worth noting, however, that the volume of sludge generated had a similar tendency with turbidity and COD RE. The volume of the sludge generated increased from 180 mL for a dosage of $0.2\,g\,L^{-1}$ of Al^{3+} to 290 mL for a dosage of $0.6\,g\,L^{-1}$. Then the volume of the sludge generated decreased slowly with the increase of the dosage. This can be attributed to the repulsion between the positively charged colloids that can occur when the dosage was high. Thus, the colloids cannot settle down and form sludge. Therefore, the sludge produced in the optimal coagulation conditions represented 290 mL. After dehydration by centrifugation, the volume of the sludge reduced to 60 mL. The effect related to the presence of sludge is, however, complex and it will not be discussed further in this paper as it requires a detailed analysis. Obviously, lower removal efficiency was observed after coagulation–flocculation treatment (Table 2). To achieve a satisfactory removal of pollutants, the treated leachates were further treated by Fenton process.

3.3. Oxidation procedure: Fenton process

In the Fenton process, hydrogen peroxide (H_2O_2) is added to wastewater in the presence of ferrous species (Fe^{2+}), generating species that are strongly oxidative with respect to organic compounds present. Hydroxyl radicals ($\cdot OH$) are traditionally regarded as the key oxidizing species in the Fenton processes, though high valence ferric species have also been proposed [30,31]. Classical Fenton-free radical mechanism mainly involves the sequence of reactions below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + HO^- \qquad (6)$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \qquad (7)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + HO^- \qquad (8)$$

3.3.1. Effect of pH

An essential characteristic of the Fenton process is that pH in the acidic range strongly favors oxidation. In fact, optimal pH values reported for Fenton processes for landfill leachates treatment range between 2 and 8, using $0.8\,g\,L^{-1}$ of Fe^{2+} and $1.4\,g\,L^{-1}$ of H_2O_2 with a ratio $[Fe^{2+}]/[H_2O_2]$ of 0.6 according to result reported by Ramírez et al. [32]. The COD removal treated leachates TL_{CF-F} is depicted in Fig. 3(a)–(c). At optimum pH 3, the COD removal was 42% (Fig. 3(a)). A pH value below optimal can inhibit oxidation in two ways. First, at around pH 2, the $[Fe(H_2O)]^{2+}$ formed reacts relatively slowly with H_2O_2, producing less $\cdot OH$ radical [33]. Second, exceptionally low pH can inhibit reaction between Fe^{3+} and H_2O_2 [34]. A decreased efficiency is observed when pH rises, which is related with the diminution on the production of $\cdot OH$ radicals due to the formation of ferric-hydroxo complexes [35]. Moreover, hydrogen peroxide self-decomposition into oxygen and water is promoted at alkaline conditions leading to lower amounts of oxidant available for the organics oxidation [36]. The interpretation of these factors is often difficult due to the chemical complexity of leachates. Therefore, when considering these factors, pH 3 was selected to pursuit the research.

3.3.2. Effect of Fe^{2+} concentration

The effect of Fe^{2+} concentration on the Fenton process for the depuration of treated effluent was tested within the range of $0.4–3\,g\,L^{-1}$ of Fe^{2+} at pH 3 using $1.4\,g\,L^{-1}$ of H_2O_2. Preliminary tests were performed by adding hydrogen peroxide without the presence of iron and up to 16% of COD removal was achieved after one hour of reaction. However, according to Fig. 3(b), the introduction of iron enhances to some extent the process efficiency. The removal COD efficiency (up to 45%) by oxidation linearly increased with increasing Fe^{2+} concentration from 0.4 to $3\,g\,L^{-1}$. However, this increase in COD RE would reach saturation for a dosage of $1.2\,g\,L^{-1}$ of Fe^{2+}. No changes in COD abatement can be noted when higher catalyst loads were applied. A possible reason is that some of the $\cdot OH$ produced is scavenged by excess Fe^{2+} ($>1.2\,g\,L^{-1}$) through Eqs. (8) and (6). An optimal molar ratio of H_2O_2 to iron salt required to maximize production of $\cdot OH$ has been theoretically calculated for some
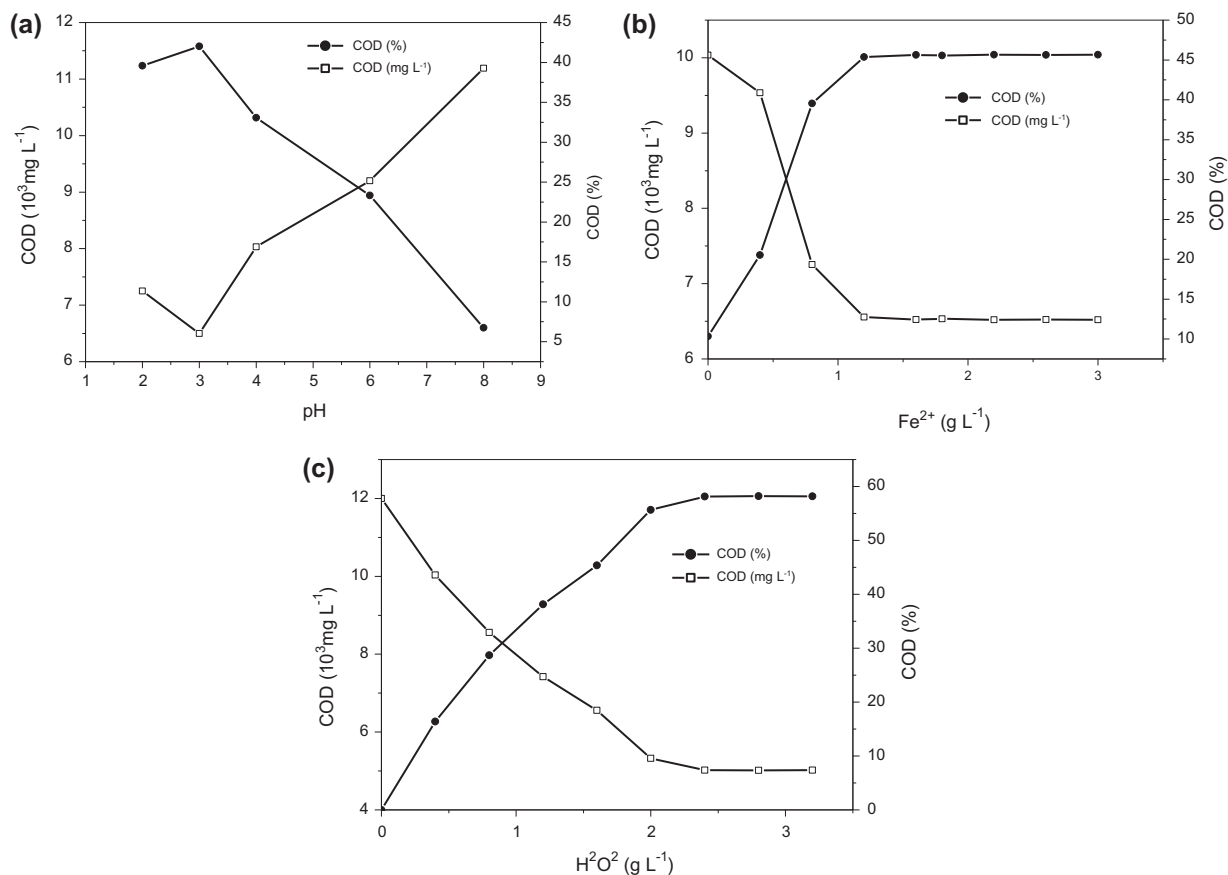
Fig. 3. (a) Removal of COD for a dose of $0.8 \, g \, L^{-1}$ of Fe^{2+}, $1.4 \, g \, L^{-1}$ of H_2O_2 at various pH values; (b) removal of COD for different doses of Fe^{2+} for a dosage of $1.4 \, g \, L^{-1}$ of H_2O_2 at pH 3; and (c) removal of COD for a dose of $1.4 \, g \, L^{-1}$ of Fe^{2+} and different doses of H_2O_2 at pH 3.

individual organic compounds. In our case, it seems that the molar ratio of Fe^{2+} to H_2O_2 is 0.85 which can be successfully used to refine the effluent before the adsorption process.

3.3.3. Effect of hydrogen peroxide concentration

Hydrogen peroxide is the source of hydroxyl radicals which are referred as the moieties responsible for the degradation of organic matter in the Fenton process. In this context, the increase in the H_2O_2 dose should lead to a higher amount of ·OH; however, when in excess, hydrogen peroxide reveals a radical-scavenging capacity as (Eq. (7)). Once the hydroperoxyl radicals ($HO_2^·$) become less prone to the reaction, the efficiency of the treatment decreases[36]. Thus, the impact of this reactant concentration has to be carefully studied.

Experiments involving H_2O_2 dose within the range of $0.4–3.2 \, g \, L^{-1}$ were carried out at pH 3 using $1.2 \, g \, L^{-1}$
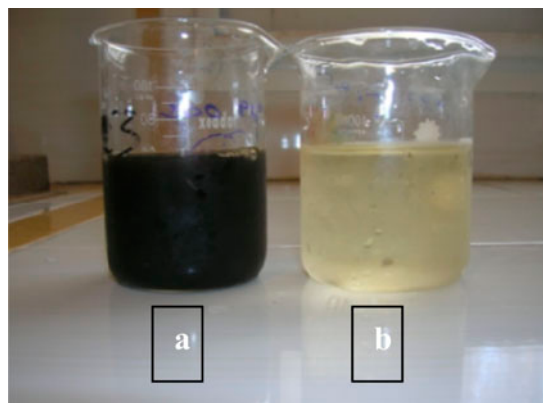

Fig. 4. Landfill leachates, (a) raw solution; and (b) treated solution by combined process of coagulation/flocculation, Fenton and powder zeolite adsorption.

of Fe^{2+} and the results regarding COD abatement are depicted in Fig. 3(c). As shown, COD removal increases

up to 58% for $2.8\,g\,L^{-1}$ of H_2O_2. Therefore, when considering these factors, the dosage of $2.8\,g\,L^{-1}$ of H_2O_2 was appropriate and the mass ratio of removable COD to H_2O_2 is 4,990/2,800. That is, $2,800\,mg\,L^{-1}$ H_2O_2 theoretically removes $4,990\,mg\,L^{-1}$.

In addition, the color of the leachates slowly changed from an initial dark brown to light brown (Fig. 4). The removal of color had a similar trend to COD and turbidity. This suggested that color was mainly produced by organic matter and some insoluble forms, color, which is similar with the respective findings of other researchers [37]. However, the COD RE by Fenton oxidation reached saturation at higher H_2O_2 concentrations, which can be explained by a radical-scavenging capacity of hydrogen peroxide, as mentioned above and further increase in the amount of this reactant would not be economically viable. Therefore, it seems that the molar ratio of H_2O_2 to Fe^{2+} is 2.3 which can be successfully used to enhance the process efficiency.

An optimal molar ratio of H_2O_2 to iron salt required to maximize production of ·OH has been theoretically calculated for some individual organic compounds. For example, Tang and Huang [38] concluded that the optimal molar ratio of H_2O_2 to Fe^{2+} is 11:1, for Fenton oxidation of TCE. Such calculation is not possible for landfill leachates, however, due to its chemical complexity and because a high dosage of iron salt is desired to promote coagulation and flocculation. Roddy and Choi [39] reported that molar ratios of H_2O_2 to Fe^{2+} for batch mode and continuous mode operations were 1.5:1 and 3:1, respectively. The discrepancy in these results reflects the variability in landfill leachates characteristics.

Obviously, the combined treatment coagulation/flocculation-Fenton proved to be the more efficient process for the reduction of COD content to values lower than $5,000\,mg\,L^{-1}$ with BOD_5/COD of 0.4 (initially 0.36). It should be noticed that these methods did not substantially affect the ammonia removal, which did not exceed 45%. This parameter suggests again that these leachates are amenable to biological treatment, as mentioned above. However, the application of coagulation/flocculation and Fenton methods were not efficient enough to produce an effluent with residual COD values lower than $1,000\,mg\,L^{-1}$ in accordance with Tunisian discharge standards in the sewer. Tunisia had labeled these leachates as "priority pollutants," which means that they need to be constantly monitored in the aquatic environment prior to their discharge in the receiving water body. The COD value of $1,000\,mg\,L^{-1}$ is the upper permissible limit of these compounds in publicly supplied water. According to our results, it seems advantageous to substitute the
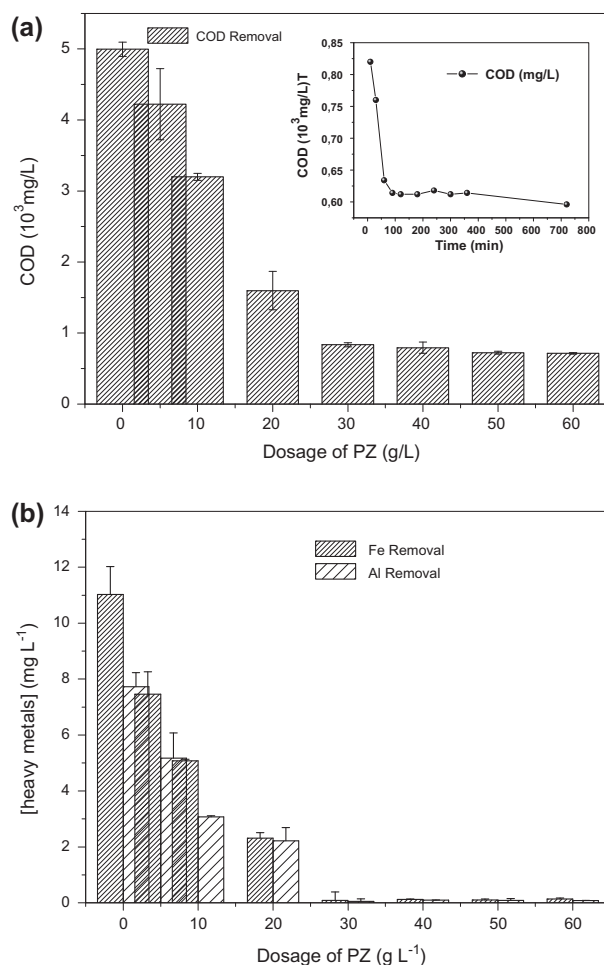

Fig. 5. (a) COD removal by granular zeolite for different dosages; inset: Kinetics of adsorption at $30\,g\,L^{-1}$ PZ; and (b) Fe and Al removal by granular zeolite for different dosages.

current physicochemical treatments by the adsorption process as an additional treatment step for the reduction of COD content.

3.4. Adsorption process

The treated leachate TL_{CF-F-A} was further subjected to adsorption by powdered zeolite PZ. The experiment was first carried out employing different dosages of PZ ($5–60\,g\,L^{-1}$), with the aim of determining the optimum dosage for high removal of COD. During equilibrium experiments, contact time was set at 3 h in order to ensure its final equilibrium. The residual concentration of COD could be expressed as a function of PZ dosages the results of which are shown in Fig. 5((a) and (b)). It can be observed that the removal

COD efficiency (up to 83%) increased with increasing PZ dosage from 0.5 to 30 g L^{-1}.

In order to determine the equilibrium adsorption time for high removal of COD, adsorption kinetic experiments of leachates were carried out using a dosage of 30 g L^{-1}. The results showed that the equilibrium practically reached in 120 min (Fig. 5(a)). Under these conditions, the RE of COD was about 50%. After these experiments, COD in the leachates was about 620 mg L^{-1}. The *Freundlich* and *Langmuir* adsorption models, Eqs. (9) and (10), respectively, were used to study the media adsorption behavior for COD removal from leachates.

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{9}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \tag{10}$$

where q_e is the adsorbed amount (mg g^{-1}) and C_e is the equilibrium organic concentration (mg L^{-1}). The *Langmuir* constants q_m (mg g^{-1}) and b (L mg^{-1}) are related to maximum adsorption capacity and the *Langmuir* constant, respectively. Whereas K_F (mg g^{-1}) (L mg^{-1}) and $1/n$ are *Freundlich* constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively. The empirical constant values are illustrated in Table 3.

The K_F and $1/n$ can be determined from intercept and slope of the linear plot of $\log q_e$ vs. $\log C_e$. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. The empirical constant (n) value of the *Freundlich* isotherm is closer to 1, implying the valuable adsorption of COD from leachate [40]. According to the R^2 values obtained from two adsorption models, the *Freundlich* isotherm proved to be a better fit for adsorption because the R^2 value is small, higher than that obtained from the *Langmuir* isotherm. *Freundlich* isotherm could thus be used for COD removal using PZ.

The residual concentration of Al and Fe ions decreased with the increase in the dosage of PZ. When the dosage of PZ exceeded 30 g L^{-1}, Al and Fe ions in the solution were hardly detected due to strong adsorption by PZ (Fig. 5(b)). No significant changes in the residual concentration of other heavy metals. One possible explanation is that the initial metal contents were already extremely low. Therefore, when considering these factors, the dosage of 30 g L^{-1} was appropriate. The concentration of Al and Fe ions was about 50 and 85 μg L^{-1}, respectively.

It should be noticed that the adsorption by PZ substantially affects the ammonia removal, which exceed 91% (Table 2). Zeolite was widely used as a natural ion exchanger to remove ammonia and other inorganic pollutants from leachate or other wastewater. A similar behavior has been observed in ammonia and COD adsorption on zeolite, activated carbon, and composite materials in landfill leachate treatment by Halim et al. [41]. The kinetic study showed that adsorption rate of ammonia on composite adsorbent
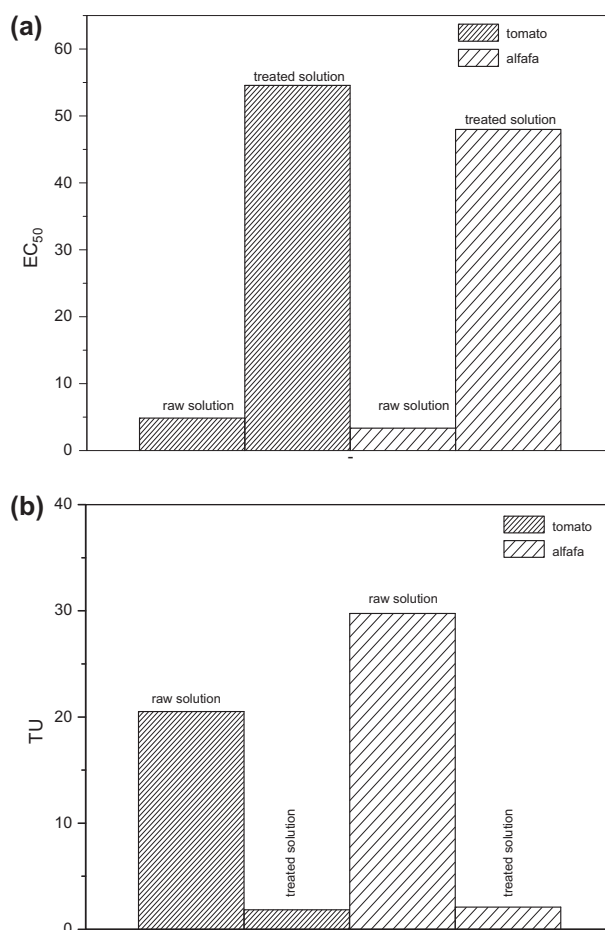

Fig. 6. (a) EC$_{50}$ of sample before and after treatment of landfill leachates; and (b) variation of toxic units.

Table 3
Isotherm parameters for the adsorption of COD on PZ

Langmuir isotherm model			Freundlich isotherm model		
Q (mg g^{-1})	b (L mg^{-1})	R^2	*K_F	$1/n$	R^2
3.935	0.013	0.8212	0.0243	1.044	0.9115

*Unit of K_F was (mg g^{-1}) (L mg^{-1}).

was the fastest to reach equilibrium (30 min), followed by zeolite (60 min) and activated carbon (105 min). These results suggested that the chemisorption or ion exchange was the dominant mechanism for the adsorption of ammonia on zeolite, and the physical adsorption for activated carbon. The removal efficiencies of COD, ammonia, iron, and aluminum were 97, 91, 99, and 97%, respectively. In this condition, a high biodegradability enhancement is achieved leading to a BOD_5/COD of 0.63 (Table 2), in accordance with the Tunisian discharge standards in the sewer.

3.5. Toxicity reduction

The RL showed a toxic effect, since the raw effluent completely inhibited the germination of tomato (*L. esculentum*) and Alfafa (*M. sativa*). The toxicity unit of the initial landfill leachates was 20.51 and 29.76, respectively. The phytotoxicity could be primarily attributed to the presence of toxic compounds such as $N-NH_4^+$, hydrocarbons, and phenolic compounds. The toxicity of raw and treated leachates by the combined process of coagulation–flocculation- Fenton and PZ adsorption are shown in Fig. 6((a) and (b)).

The results showed that the toxicity reduction was about 91 and 93% for the two species, which means the efficiency of the combined process in the treatment of leachates. The total information on the different kind of contaminants in the leachates is needed for the hazard and risk assessment of landfill emissions.

4. Conclusion

Our results add another approach to an already complex picture. The combined process of coagulation/flocculation, Fenton, and adsorption process for landfill leachates proved to be an efficient and promising method. The single coagulation process led to very high removals of turbidity (up to 84%), but moderate COD (53%) for a dosage of $0.6 \, g \, L^{-1}$ of Al^{3+}, when the pH value-coagulated sample was adjusted at the neutral region. The combined treatment of coagulation/flocculation and Fenton proved to be the more efficient process for the reduction of COD content. In this case, the optimum COD removal value reached about 80% for a dosage of $1.2 \, g \, L^{-1}$ of Fe^{2+} and $2.8 \, g \, L^{-1}$ of H_2O_2 when the pH value was adjusted at 3. Nevertheless, almost complete removal of color was obtained in all cases. The pH control of samples in the alkaline region was found to deeply affect the process efficiency. However, the application of a subsequent coagulation/flocculation followed by Fenton stage still did not fulfill the legal requirements of Tunisian

discharge standards in the sewer in what regards COD ($1,000 \, mg \, L^{-1}$). Therefore, reduction of COD to the imposed legislative limits can be accomplished by the application adsorption process in an additional step, using powder zeolite PZ for a dosage of $30 \, g \, L^{-1}$. However, the legal limits for discharge were accomplished with the RE of COD was 97% ($620 \, mg \, L^{-1}$). Under the optimum condition, the removal efficiencies of heavy of Fe, Al, and ammonia reaching were up to 97, 98, and 91%. The toxicological assays showed a reduction of toxicity after the treatment of landfill leachates by the new method, indicating that the combined process corresponds to an actual detoxification of the leachates.

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