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Use of combination of coagulation and adsorption process for the landfill leachate treatment from Casablanca city

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ABSTRACT

This article presents a combination of coagulation–flocculation and powder activated carbon (PAC) adsorption as a treatment process for landfill leachate. Leachates were collected from a municipal solid waste landfill in Mediouna site, Casablanca city. Ferric chloride ($FeCl_3$) is used here as a coagulant to study the optimum conditions for the removal of chemical oxygen demand (COD), colour, total suspended solids (TSS) and turbidity in jar tests. This coagulant showed the highest removal efficiency in terms of COD (62.5%), turbidity (92.5%), colour (80%) and least sludge volume generation (30% v/v) for an optimum coagulant dose of 12 g Fe^{3+} L^{-1}. Combining coagulation with adsorption process onto PAC enhances the removal of COD, turbidity and colour reduction by a 77%, a 99% and a 99.7%, respectively. These results show that coagulation-adsorption could be used as a promising hybrid process for the treatment of landfill leachates.

Keywords: Coagulation; Flocculation; Adsorption; Jar-Test; Landfill leachate

1. Introduction

Landfill leachate is considered as an important pollution source which threats soil, surface water and groundwater, as they may percolate through soils and subsoils, causing extensive contamination of streams, creeks and water wells, if they are not properly collected, treated and safely disposed.

Various technologies based on physical-chemical processes such as chemical precipitation, coagulation–flocculation, ultrafiltration and reverse osmosis [1–4] have been applied successfully for the treatment of landfill leachates. On the other hand, combined processes, including two or three physical–chemical treatment methods have been widely used in treating landfill leachates, such as; ozonation-activated carbon adsorption [5], coagulation–ozonation [6], and precipitation–reverse osmosis [7].

In particular, coagulation-flocculation is a technique that has been successfully applied as pretreatment method of landfill leachate prior to biological processes, or other physical–chemical techniques [8–10]. In the case of adsorption process, it has been considered as one of the best conventional and economical process to treat the organic matter content [11,12].

Activated carbon is an excellent adsorbent for the removal of organic contaminants, owing to it's of high specific surface area, microporous structure and surface reactivity [13,14]. The combined process of coagulation and

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adsorption can ameliorate the drawbacks of each single process. On one hand, coagulation could remove a fraction of COD, reducing the burden COD for subsequent adsorption and leading to a decrease in AC consumption. On the other hand, activated carbon could provide a charged contact surface where colloidal matter can initiate their destabilisation, contributing to the formation of heavy flocs.

This work aims to study the feasibility to combine the processes of coagulation–flocculation(CF) and adsorption in a single process to treat leachates from a municipal solid waste landfill in Mediouna site, Casablanca city (Morocco). In particular, removal efficiencies in terms of organic matter, solids, colour and sludge production are assessed.

2. Materials and methods

2.1. Materials

2.1.1. Landfillsite and sampling

Landfill leachate samples were collected from Mediouna municipal landfill, located at 10 km south-east of Casablanca near PR7 in Morocco. Leachate samples were stored in a refrigerator at 4°C in the dark to minimise leachate decomposition due to microbial activity.

2.1.2. Chemicals and materials

Ferric chloride ($FeCl_3$) (40%w/w) was supplied by Cadilhac. HCl, and NaOH were supplied by Sigma-Aldrich chemicals. Powder activated carbon (PAC) was provided by Sigma-Aldrich Chemie GmbH ($S_{BET} = 900\ m^2 \cdot g^{-1}$). PAC was dried at 110°C in an oven for 24 h before any use.

2.1.3. Characterization of powder activated carbon (PAC)

Surface area and pore volume of the PAC were determined by using nitrogen adsorption at 77 K in Micromeritics ASAP 2010 instrument. PAC was degassed before analysis at 383K for 4 h under vacuum at $<10^{-2}$ Pa in order to remove all physically adsorbed water molecules and small organic impurities.

The concentration of basic and acid groups on PAC surface were determined by the Boehm titration method [15]. A mass of 0.1 g PAC sample was placed in 40 mL of the following solutions: NaOH (0.1 M) and HCl (0.1 M). After that, vials were sealed and agitated at 200 rpm for 24 h at room temperature. Then, suspensions were filtered and the excess of base or acid were titrated with HCl (0.1M) or NaOH (0.1M), respectively. According to Boehm [15], the number of acidic sites was determined under the assumption that NaOH neutralises acidic sites of different strength (carboxylic, lactonic, and phenolic groups).The content of basic surface groups was determined from the amount of hydrochloric acid consumed by the PAC. Acidic and basic character of the PAC was also characterised by the determination of the point of zero charge (pH_{pzc}).The pH_{pzc} was determined following the method reported by Stumm and Morgan [16]. A volume of 20 mL of NaCl solution (0.1 $mol \cdot L^{-1}$) was transferred in series of flasks. Initial pH values were adjusted in the range of 2–12 by additing HCl or NaOH solutions. Then, 0.1 g of PAC sample were weighed and placed into each bottle and stirred for 72 h at 25°C. Finally, the equilibrium pH was measured in each flask and the pH value required to give a neutral net surface charge density, designated as the pH of the point of zero charge (pH_{PZC}) was determined graphically.

2.2. Experimental procedure

2.2.1. Coagulation–flocculation

Coagulation–flocculation (CF) tests were performed in a jar-test apparatus equipped with four beakers of 1 L capacity. Ferric chloride was applied at different concentrations in order to determine the optimum coagulant concentration for maximum removal of turbidity and organic matter. Before any test, leachate sample was equilibrated to ambient temperature. All samples (250 mL) were stirred at a constant rapid speed of 200 rpm (10 min) followed by slow stirring at 40 rpm (30 min) to facilitate floc formation. After 60 min of the settling period, supernatants of each beaker were withdrawn, and analytic determination of turbidity, COD, total suspended solids (TSS), and colour, were conducted. Sludge volume was determined from the level of deposited sludge on the bottom of the beakers. The experiments were carried out with and without pH adjustment at different concentrations of coagulant. The pH values of leachate samples were adjusted by the addition of appropriate amounts of HCl or NaOH (1 $mol \cdot L^{-1}$)solutions.

2.2.2. Adsorption isotherm and kinetic experiments

Adsorption experiments were carried out using the batch method in a series of flasks containing the adsorbent material and 40 mL of pre-treated leachate from coagulation-flocculation process with chloride ferric ($FeCl_3$). Samples were constantly stirred at 200 rpm for 72 h. After that, the solid phase was separated from the liquid phase by centrifugation at 5000 rpm for 10 min and supernatants were analysed for the chemical oxygen demand (COD), UV_{254}, colour and metals.

The influence of operating conditions such as contact time, PAC dose ($R = m/V$ where m is the mass and V is the volume of leachate), pH and temperature on the adsorption of COD onto PAC were studied in a batch system.

The effect of adsorbent dose on the adsorption capacity toward COD was performed by mixing different amounts of PAC from 0.5 $g \cdot L^{-1}$ to 20 $g \cdot L^{-1}$ at 25°C with a fixed concentration of organic matter (expressed as COD = 8223 mg $O_2 \cdot L^{-1}$). Adsorption kinetic experiments were carried out under the same conditions, using a fixed dose of adsorbent.

The effect of pH conditions on COD removal was studied by varying the pH of leachate solution (COD = 8223 mg $O_2 \cdot L^{-1}$) from 2 to 12 at 25°C. The initial pH was adjusted using 0.1 $mol \cdot L^{-1}$ of HCl or NaOH solution. Optimum pH was obtained by the highest percentage of removed COD. The effect of temperature on COD adsorption was also investigated. Temperature varied from 25°C to 35°C.

The amount of adsorbed COD per gram of PAC($q_{t,e}$, $mg \cdot g^{-1}$), was determined from a mass balance, as follows:

$$q_{t,e} = \frac{(C_0 - C_{t,e})V}{m} \tag{1}$$

where C_0 (mg·L^{-1}) and $C_{t,e}$ (mg·L^{-1}) are COD concentrations at initial time and at equilibrium, respectively. V is the total volume of the leachate solution (L), and m (g) is the mass of PAC used.

2.2.3. Analytical determinations

Leachate samples were characterised before and after each treatment. Analyses of pH, conductivity (EC), turbidity (NTU), chemical oxygen demand (COD), Cl$^-$, nitrate, nitrite, ammonium, UV absorbance at 254 nm (UV$_{254}$) were conducted according to the Standard Methods for Water and Wastewater Examination [17]. UV–visible absorption measurements were obtained using a UV2300 II spectrophotometer equipped with quartz cuvettes with 1 cm of light path. Colour number (CN) was determined using the method described by Tizaoui et al. [18]. Prior to measurement, the samples were filtered in order to avoid interferences due to the presence of non-dissolved. CN relies on the measurement of the spectral absorption coefficient *(SAC)* in the visible range at three different wavelengths: 436 nm, 525 nm and 620 nm as indicated by Eq. (2):

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \tag{2}$$

with $SAC_i = \dfrac{Abs_i}{x}$

where *Abs* stands for the sample absorbance at specific wavelength and x is the cuvette light path.

COD (mg·L^{-1}) was measured using the colorimetric closed reflux method (5220D) reported in the Standard Methods for the Examination of Water and Wastewater [17], using a UV2300II spectrophotometer at a maximum wavelength of 600 nm.

The organic composition of the leachate was identified after conducting a liquid-liquid extraction with dichloromethane [19] by gas chromatography coupled with mass spectroscopy (GC-MS) using a Finniganpolaris Q GC/MS Benchtop Ion Trap mass spectrometer from Thermo Fisher Scientific (Waltham, Massachussetts, USA).

3. Results and discussion

3.1. Leachate characterisation

Chemical/physical characteristics of the raw leachate from the Mediouna landfill are presented in Table 1. Attending to data listed in Table 1, it can be stated that the landfill leachate is a complex wastewater. The dark colour of the liquid is related to the high values of COD (22000 mgO$_2$·L^{-1}), BOD$_5$ (8500 mgO$_2$·L^{-1}) and to the high turbidity content (1007 NTU) of the leachate; being all these parameters higher than the values of the Morocco Reject Requirements. The total suspended solids are of the order of 33940 mg L^{-1}. The leachate presents also a high content of aromatic compounds, measured in terms of the absorbance at 254 nm (the absorption at this wavelength has been usually associ-

Table 1
Characterisation of Mediounal and fill leachate and comparison to landfill leachates of other countries [20–23]

Parameters	Mediouna	Saudi Arabia	Germany	USA	Portugal	Italy	MRR
Conductivity (mS cm^{-1})	38.6	52.83	–	–	17.5–23.6	–	0.27
T (°C)	19	–	–	–	17.6–24.1	–	30
pH	7.61	6.21	5.7–8.1	5.1–6.9	6.9–9.1	6–8.5	6.5–9
TA(meq·L^{-1})	0	–	–	–		–	–
TAC(meq·L^{-1})	1800	50795.2	–	–		–	–
TSS(mg·L^{-1})	3394	5604	–	–	208–796	–	50
Turbidity (NTU)	1007	–	–	–		–	–
COD(g·L^{-1})	22	17	1.63–63.7	1.3–18	3.4–4.58	7.7–38.5	0.5
BOD$_5$(g·L^{-1})	8.5	–	–	–	150–300	–	0.1
BOD$_5$/COD	0.39	–	–	–	0.04–0.07	–	–
UV$_{254nm}$(diluted 1:10)	3.8	–	–	–	–	–	–
Colour Number	5	–	–	–	–	–	–
PO$_4^{3-}$ (mg·L^{-1})	–	–	–	–	2.5–5.7	–	2
NO$_3^-$ (mg·L^{-1})	6.4	–	–	–	16–693	–	–
NO$_2^-$ (mg·L^{-1})	0	–	–	–	325.1–469	–	–
Cl$^-$(mg·L^{-1})	5236	8971.5	–	–	3063–3823	–	3010
Mg^{2+}(mg·L^{-1})	192	1962.5	100–270	233–410	–	827–1469	–
Cd^{2+}(mg·L^{-1})	<0.01	<0.002	–	–	–	–	0.2
Cr^{3+}(mg·L^{-1})	2.86	0.26	–	–	2.2	–	2
Pb^{2+}(mg·L^{-1})	3.58	<0.04	–	0–0.46	<0.01	–	0.5
Cu^{2+}(mg·L^{-1})	0.95	0.182	–	0.01	0.1	–	0.5
Fe^{2+}(mg·L^{-1})	38.8	167.61	8–1979	4.2–1185	–	47–330	3

*Morocco Reject Requirements (MRR)

ated to the presence of aromatics). Another relevant point is the high conductivity (38600 μS·cm^{-1}), attributed to a great concentration of chlorides. It is interesting to note that such values are extremely high, even bigger than the respective values detected in landfill leachates from other countries as indicated by Al-Wabel et al. [20], Rowe et al. [21], Al-Yaqout and Hamoda [22] and Rocha et al. [23] (see Table 1).

Contrary to the low content of heavy metals (Mg, Cd, Cr, Pb, Cu, Fe, etc); the value of salinity is very high, principally due to the amount of chlorides (5236 mg L^{-1}), and nitrates (6.4 mg L^{-1}).

Fig. 1 illustrates a chromatogram with the main organic components of the Mediouna landfill leachate. Humic substances, aromatics carboxylics acids, phenolics, heterocyclics, polycyclics and aromatic hydrocarbons are indentified here as the predominant organic components of the landfill leachate. Normally, these products may have been released from the material deposited in the landfill or are generated during the degradation of fats, proteins, and carbohydrates.

3.2. Characterisation of PAC

Fig. 2 shows N_2 adsorption–desorption isotherms of the PAC used in this work at 77 K. Nitrogen adsorption onto PAC follows a type I isotherm with features of a low porosity material according to the IUPAC classification. It can be seen a remarkable uptake at low relative pressure due to the presence of micro pores in this material [24–25].

As it can be observed, this PAC has a high value of specific surface area, expressed as S_{BET} of 900 m^2·g^{-1},with an average pore diameter of 3.5 nm.

Quantification of PAC surface functional groups by the Boehm method is shown in Table 2. Functional surface groups of PAC have very important implications on the adsorption process since they act as active sites capable of interact with organic molecules [26].

The pH value at the point of zero charge (pH_{PZC}) is determined when the correlation between the initial pH and ΔpH is zero [27]. A value of pH_{PZC} 9.0 confirms the basic character of the PAC. Thus, the material has positive surface charge when the solution's pH is less than pH_{PZC} and negative surface charge for pH values higher than pH_{PZC} due to the deprotonation of acidic oxygen-containing functional groups.

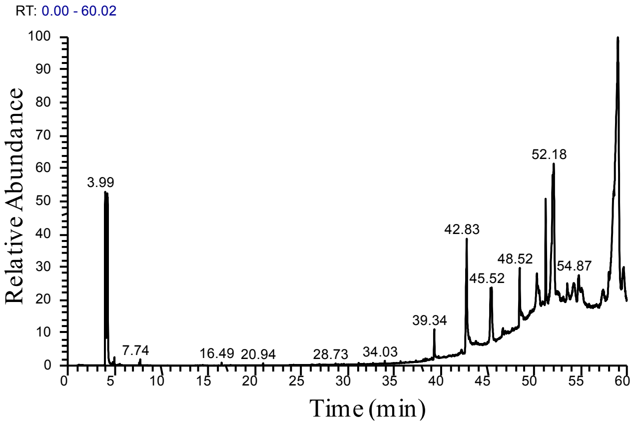

Fig. 1. Chromatogram of the Mediouna landfill leachate, after extraction with dichloromethane.

3.3. Coagulation-flocculation process

Fig. 3 shows the removal efficiency in terms of turbidity, COD, and sludge volume generation at different dose of coagulant at pH = 7.6. An optimum coagulant dose is found when 12 g Fe^{3+} L^{-1} is applied, corresponding to a maximum removal of turbidity (93%) and COD (62.7%).

Various test for turbidity and COD removal efficiency using the optimum dosage (12g Fe^{3+}·L^{-1}) of $FeCl_3$ were car-

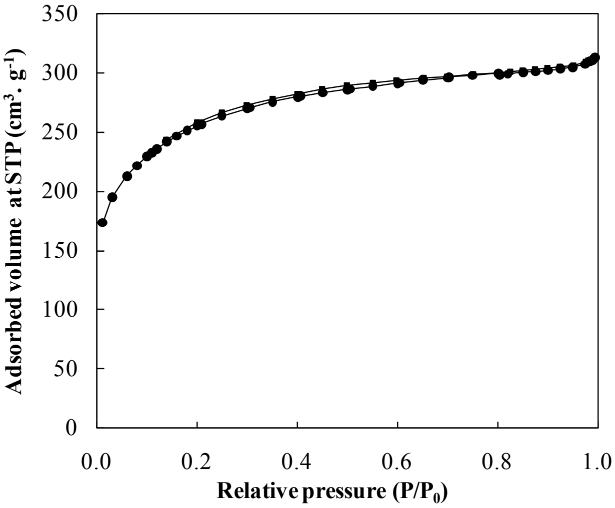

Fig. 2. N_2 adsorption-desoprtion isotherms of the PAC used in this work.

Table 2
Content of surface functional groups in PAC determined by Boehm method

PAC	Values
Acid sites (mmol·g^{-1})	0.31
Basic sites (mmol·g^{-1})	1.03
Total sites (mmol·g^{-1})	1.34

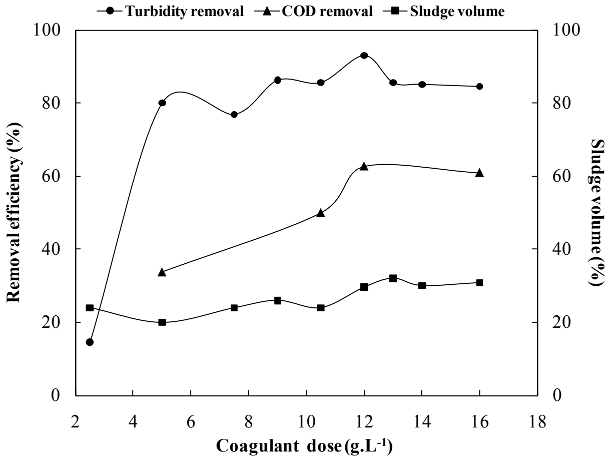

Fig. 3. Effect of ferric chloride ($FeCl_3$) addition on removal efficiency: (•) turbidity, (■) COD and (▲) sludge volume at pH = 7.6.

ried out at different pH values from 2 to 12 (results not shown here). The best result was obtained when raw leachate (before the addition of the coagulant), with a solution pH of 7.6 was used.

At this pH value, results show that the removal efficiency expressed in terms of turbidity increases with the increase in the coagulant dosage until reaching an optimum value (12 g $Fe^{3+}\cdot L^{-1}$). After that, the removal of turbidity decreases slightly. When the coagulant is added to the leachate, cations and its hydrolysed products interacts with negative colloids, neutralising their charges and promoting colloid destabilisation. However, after reaching the optimum value of coagulant dosage, the removal of turbidity decreases due to restabilisation of colloidal particulates [18]. In Fig. 3 it can also be seen that the volume of the sludge generated increases gradually with the increase of coagulant dose, resulting in a ~30%v/v (mL of sludge·mL^{-1} leachate). The increase in coagulant dose decreases the pH of supernatant reaching a pH value of 5.7 at the optimal dose of ferric chloride applied (12 g $Fe^{3+}\cdot L^{-1}$). This reduction on pH could be explained by the acidic character of Fe^{3+} (acid of Lewis). Fe^{3+} could react with the OH^- ions of the leachate, generating, iron precipitates in the form of $Fe(OH)_3$ [28].

Fig. 4 displays UV-vis spectra in a wavelength range between 200 and 700 nm for leachate before and after the coagulation–flocculation treatment process. It should be noted that the absorbances at all wavelengths (200–700 nm) decreases significantly with the increase in the dose of $FeCl_3$. The UV values at 254 nm (UV_{254}) is used here as indicator of the presence of aromatic or conjugated double-bond compounds [19,24–25]. It is observed that the removal efficiency for UV_{254} increases as the applied $FeCl_3$ dose increases. These results indicate that aromatic compounds could be partly removed by coagulation–flocculation. The removal efficiency for UV_{254} reaches a maximum value of 95%. This performance is likely to be due to the charge neutralisation capacity of Ferric chloride that provides a higher reduction in the electrostatic repulsion between flocs and the dissolved organic molecules, facilitating their adsorption.

Pictures at the upright side of Fig. 4 show that, increasing the coagulant dose leads to a colour transformation of the landfill leachate. Thus, the original dark brown colour of the raw leachate turns, into a clear brown after sludge separation, then to yellow and finally becomes clear yellow at a coagulant dose near to the optimal coagulant dose. It is also noticed that the removal of colour is found to be 96% by measuring the absorbance in the visible range at wavelengths of 436, 525 and 620 nm [18].

Additionally, metal concentrations were determined in some of experiments before and after conducting the coagulation–flocculation treatment. Results of heavy metal analyses conducted to the raw and treated leachate (under optimal conditions); show the presence of metal elements, in particular Cd, Cu, Mg and Pb. The removal of heavy metals is found to be higher after the coagulation–flocculation treatment, for Cr, Pb and Cd with more than 60% removal achieved; while for other metals (Cu and Mg) are just removed to a less extent (0–30% removal).

3.4. Removal of COD in the pretreated leachate by adsorption

3.4.1. Effect of adsorbent dosage, pH and contact time on the adsorptive removal of COD, UV_{254} and colour

The dose of the adsorbent is a very important parameter that affects the cost of the adsorption process. Thus, in this work the elimination of the remaining COD (8223 $mgO_2\cdot L^{-1}$) and turbidity (70 NTU) after a coagulation–flocculation-sedimentation process using 12g·L^{-1} of $FeCl_3$ is carried out by an adsorption process using an amount of PAC in the range of 0–20 g·L^{-1}. Fig. 5 shows the variation of adsorbent dosage on the removal of COD and UV_{254} onto PAC at 25°C.

It is clearly revealed that by increasing the PAC dose from 1 g·L^{-1} to 3 g·L^{-1}, increases the removal efficiency of COD and UV_{254}, due to a greater availability of adsorption sites at higher PAC dose. However, further increase in adsorbent dosage does not exert an appreciable enhancement in the adsorptive removal of COD (~7%) and UV_{254} (~2%) as a consequence of the saturation of adsorption sites. Moreover,

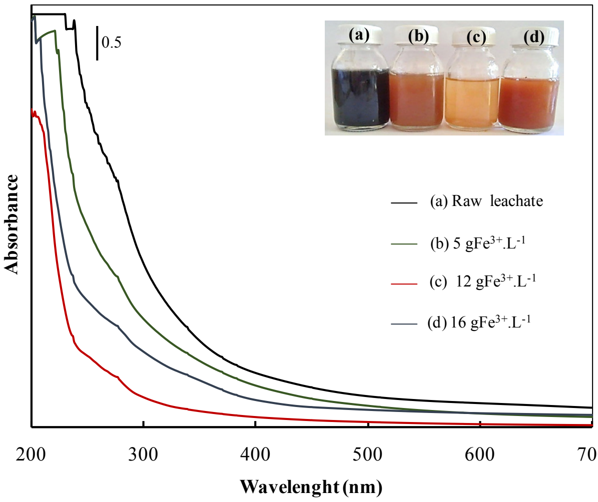

Fig. 4. UV-vis absorbance spectra of the landfill leachate (diluted ×10) before and after the treatment with $FeCl_3$.

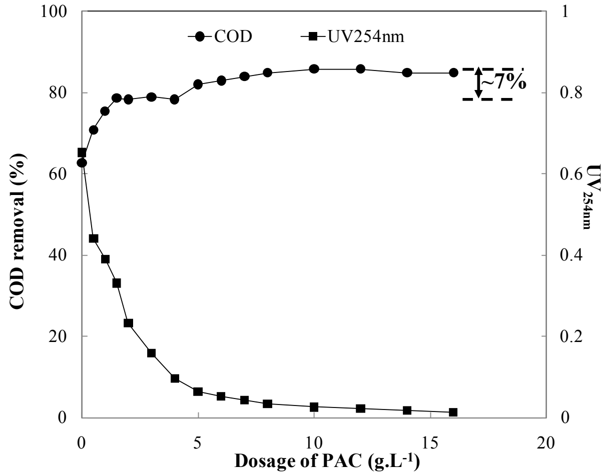

Fig. 5. Removal of COD and UV_{254} for different dosages of PAC without prior adjustment of pH (5.3–5.9).

higher adsorbent dosage could impose particle interactions, resulting from the aggregation and overcrowding adsorbent particles that would lead to a decrease in the probability of molecules to contact all available adsorption sites of the PAC, lowering the pollutant removal per unit of adsorbent [29].

When only coagulation–flocculation treatment is applied using ferric chloride, removal efficiencies in terms of COD, turbidity and UV$_{254}$ reach ~63% (22000 to 8223 mg·L^{-1}), 93% (1004 to 70NTU), and 83% (38.7 to 6.53 (a.u)) respectively; whereas when a combination of coagulation–flocculation and adsorption treatment is used (CF 12 g Fe^{3+}·L^{-1} + (3gPAC L^{-1}), a 79% of COD removal (22000 to 4631 mg·L^{-1}), 99.8% of turbidity removal (1004 to 1.55 NTU) and 96% of UV$_{254}$ (38.7 to 1.59 (a.u)) are obtained.

Fig. 6 displays the UV-vis spectra in a wavelength range 200–700 nm during the adsorption process onto PAC. It should be noted that the absorbance of the UV-vis decreases significantly with the adsorption process.

Pictures inserted in Fig. 6 show the colour changes during the adsorption process. The dark brown colour of raw leachate turn into a clear brown, after sludge separation, then to yellow and finally became colour less when PAC is applied. It is noted that colour removal efficiency reaches 99.8% value by measuring the absorbance in the visible range at 436 nm, 525 nm and 620 nm.

Table 3 summarises leachate quality before and after treatment by a combination of coagulation–flocculation and adsorption with Morocco Reject Requirements. As it can seen the combination of coagulation–flocculation and adsorption is still not enough to achieve the national standard regulations. Under these conditions the treated leachate cannot be discharged in natural water bodies but its quality has been improved with a removal of COD, turbidity and colour of 79%, 99.8% and 99% respectively. These results indicate that a combination of coagulation–flocculation and adsorption could be used as a pretreatment process.

The pH of the leachate is considered as the most controlling factor in the adsorbate–adsorbent interactions. Experiments were carried out using an initial concentration of COD of 8223 mg O$_2$·L^{-1}, 3 g L^{-1} of PAC suspension at 25°C and in a pH range of 2–12 as it displayed in Fig. 7. As it can be seen the highest COD removal (79%) was obtained at pH 5.5 using 3 g L^{-1} of PAC.

According to Cossu and Rossetti [30], in landfill leachates among all different organic fractions, the fulvic fraction is preferentially removed by adsorption onto activated carbons, normally, with a molecular mass ranging between 100 and 10,000 g·mol^{-1}.

In the present work, an increase in the pH value from 2 to 5.5 shows an enhancement on COD removal from 71 to 79 %, and then it gradually decreases. At low pH values (2–4), COD removal is moderately low compared to the results found at pH = 5.5. These results, can be attributed to the high mobility of positives charges of H$_3$O$^+$ ions competing with organic cations for the adsorption sites. At basic pH conditions (8–12), the abundance of OH$^-$ions would hinder the diffusion of the organic anions. These kind interactions can mutually inhibit the adsorption of organic matter onto the PAC, expressed as COD.

The kinetic of the adsorption process was investigated in order to determine the contact time necessary to reach the equilibrium, and to elucidate the adsorption mechanism. Fig. 8 presents the adsorbed amount of COD as a function of contact time. Experiments were conducted using a

Table 3
Comparison of landfill leachate before and after treatment by a combination of coagulation–flocculation and adsorption process with Morocco Rejet Requirements (MRR)

Parameters	Before treatment	After treatment (CF + adsorption)	MRR
TSS (mg·L^{-1})	3394	1900	50
Turbidity (NTU)	1007	1.55	–
COD (mg·L^{-1})	22000	4631	500
BOD$_5$(mg·L^{-1})	8500	200	100
UV$_{254}$	38.7	1.59	–
Colour number	5	0.009	–

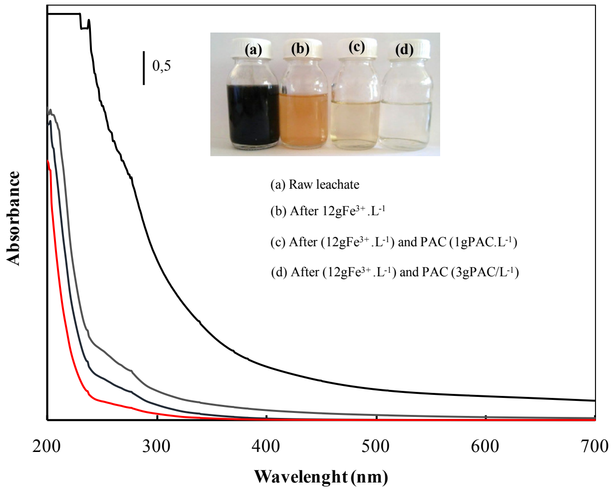

Fig. 6. UV–vis absorbance spectra of the landfill leachate (diluted ×10) before and after treatment by FeCl$_3$ and adsorption onto PAC.

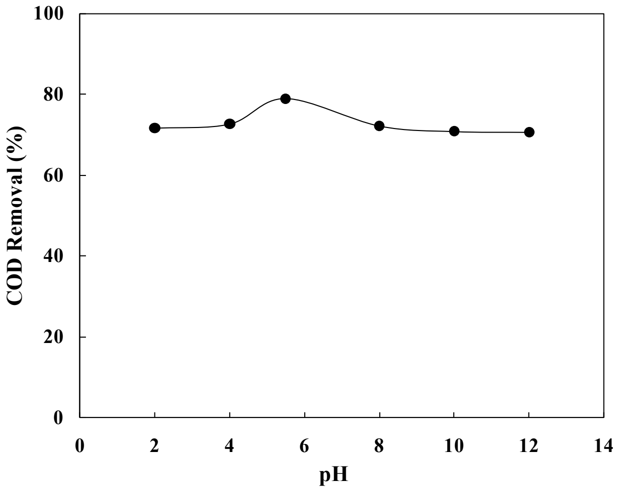

Fig. 7. Effect of solution pH on COD removal from pretreated landfill leachate by adsorption onto PAC at 25°C.

constant volume of leachate of 800 mL with an the initial concentration of organic matter expressed as COD (COD = 2742 $mgO_2{\cdot}L^{-1}$), and 3g·L^{-1} of mass of adsorbent per liter of aqueous solution. Results show that adsorption equilibrium is practically reached in 10 h. Under these conditions, the removal efficiency of COD is about 20%. After having treated by PAC at the dosage of 3 g·L^{-1} for 10 h, COD in the leachate is about 170 mg·L^{-1}.

It is clear from Fig. 8 that the adsorption process increases sharply at the initial stage, indicating the availability of accessible sites [31]. As the equilibrium approaches, the process is gradually slower. This phenomena is attributed to a reduction on instant solute adsorption due to the lack available sites for COD uptake, which in turn supports film diffusion [32]. The time required to attain the equilibrium is 10 h. COD uptake profile is a single, smooth and continuous curve leading to the saturation and suggesting the formation of a COD monolayer onto the PAC surface.

In order to understand the behaviour of the PAC adsorbent and to examine the controlling mechanism during the adsorption process, a pseudo first-order and a pseudo second order models were applied to test the experimental data.

The models were analysed based on the regression coefficient, (R^2), and the amount of COD adsorbed at equilibrium.

The pseudo-first-order kinetic model [33] is given by:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{3}$$

where q_t and q_e (mg g^{-1}) are the adsorption capacity at time t and equilibrium time, respectively and k_1 (h^{-1}) is the pseudo-first order model rate constant. Pseudo-first order constant of the kinetic model is obtained by plotting q_t versus t.

The pseudo-second-order kinetic model reported by Ho and Mckay [34] is represented as:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

where k_2 (g·mg^{-1}·h^{-1}) is the adsorption rate constant.

The parameters of the two kinetic models were, calculated using the software Origin, and are listed in Table 4.

As can be observed in Table 4, the values of the coefficient of determination (R^2) of the adjusted models indicate that the pseudo-second-order model describes very well the experimental data (R^2~0.98) with a calculated value of the adsorption capacity (q_e) very close to the experimental one (q_{exp}).The applicability of the pseudo-second order model suggests that chemical interactions are responsible for the adsorption of COD on PAC.

3.4.2. Adsorption isotherms

Adsorption isotherms are usually carried out to obtain the necessary information for optimisation, scale up and final design of the adsorption systems. Adsorption isotherms represent the relationship between the amount adsorbed per unit mass of adsorbent and the amount of adsorbate that remains in the solution when the equilibrium is reached.

The amounts of adsorbed COD at the equilibrium (q_e), vs. the concentration of COD at equilibrium were drawn in Fig 9. Experimental data of the adsorption of COD onto PAC at three different temperature (25°C, 30°C and 35°C)

Table 4
Kinetic parameters for the adsorption of COD onto PAC

Kinetic model	Parameters	Values
	q_{exp}(mg·g^{-1})	185
Pseudo-first-order	q_e(mg·g^{-1})	178.0
	k_1 (h^{-1})	2.68
	R^2	0.940
Pseudo-second-order	q_e(mg.g^{-1})	184.8
	k_2 (g·mg^{-1} h^{-1})	0.023
	R^2	0.98

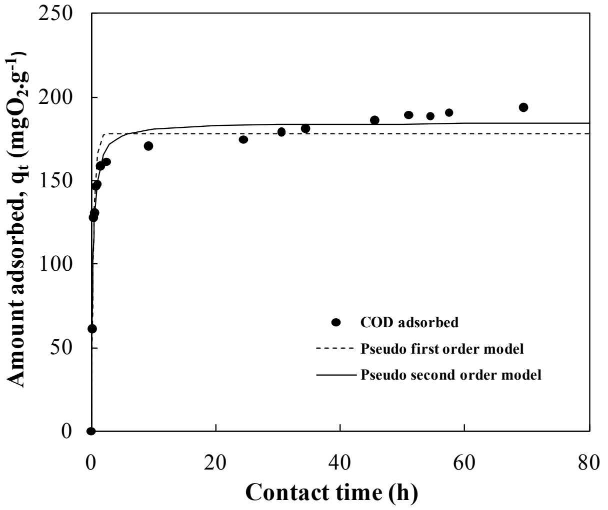

Fig. 8. Kinetics of the adsorption of the organic mater content of the leachate onto PAC, expressed as COD.

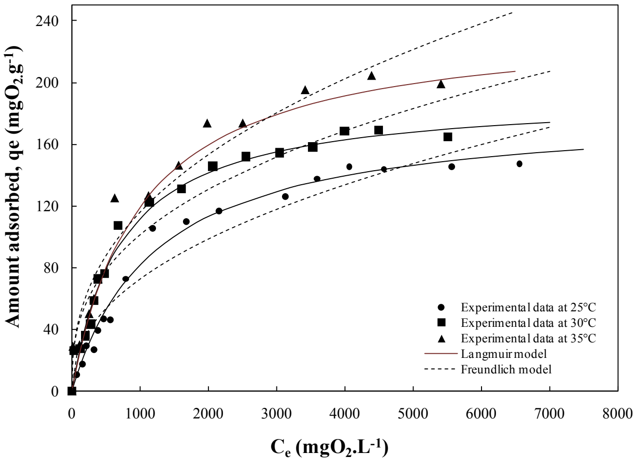

Fig. 9. Equilibrium data of COD adsorption onto PAC: model fitting to different adsorption models. Experimental conditions: 3 g of PAC, agitated during 10 h at 200 rpm.

are fitted to Langmuir [35] and Freundlich [36], adsorption isotherms models (see Fig. 9). Isotherm parameters are listed in Table 4.

Adsorption isotherm models express the adsorbed quantity of COD per mass of PAC, q_e (mg g^{-1}), as a function of COD concentration at the equilibrium, C_e (mgO$_2$·L^{-1}), as follows:

Langmuir equation:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{5}$$

where q_m (mg O$_2$·g^{-1}) is the maximum adsorption capacity of adsorbent that is related to the monolayer adsorption capacity and K_L (L·mg^{-1}) is the Langmuir adsorption equilibrium constant related to the affinity of the binding sites (L·mg^{-1}).

The affinity between PAC and COD is evaluated based on the separation factor, R_L, determined from the Langmuir adsorption isotherm model [37]. The value of R_L is calculated using Eq. (6):

$$R_L = \frac{1}{1+K_L C_0} \tag{6}$$

where C_0 (mg O$_2$·L^{-1}) is the initial concentration of COD and K_L (L mg^{-1}) is the Langmuir constant related to the energy of adsorption. If the R_L value is >1, the adsorption process is unfavorable. Whether the R_L value is equal to 1 or the value lies in between 0 and 1 indicates that the adsorption is linear and favorable. $R_L = 0$ indicates irreversible adsorption process [38].The R_L values ranged from 0.16 to 0.93 for concentrations of 1–7000 mg L^{-1}, indicating that the adsorption process of COD onto PAC occurs favourably in this concentration range.

Freundlich equation:

$$q_e = K_F C_e^{1/n} \tag{7}$$

where K_F (mgO$_2$ g^{-1}) (L mg^{-1})$^{1/n}$ stands for the adsorption equilibrium constant and n is the empirical constant of the Freundlich model.

As it can be observed in Fig. 8, the equilibrium data for the adsorption of COD onto PAC were fitted to Langmuir adsorption model at the three tested temperatures, with R^2~0.98 (see Table 5 and Fig. 9), while the correlation coefficients obtained for Freundlich isotherm model were found lowers than those obtained for the Langmuir isotherm model.

Langmuir coefficient; q_m: maximum monolayer adsorption capacity parameter, k_L: adsorption equilibrium constant and; n: empirical constant of the Freundlich model.

As it can be seen in Fig. 9, the amount of adsorbed COD at equilibrium on PAC at 25°C reaches a plateau at 182 mgO$_2$ g^{-1}.

The adsorbent used in this work shows high adsorption capacity at 25°C for COD as compared to some previous works using different adsorbents under similar conditions as reported in the literature [39–42].

Table 6 exhibits a comparison of maximum monolayer adsorption capacities of COD onto different adsorbents [39–42]. It can be noticed, that the adsorption capacity of PAC used here toward COD is considerably high in comparison with type observed values using other adsorbents.

Table 5
Isotherm model parameters for COD adsorption onto PAC

Models	Parameters	T = 25°C	T = 30°C	T = 35°C
Langmuir	q_m(mg g^{-1})	182	192	239
	K_L(L mg^{-1})	0.000814	0.0014	0.001
	R^2	0.99	0.98	0.98
Freundlich	K_F(mg g^{-1}) (L mg^{-1})$^{1/n}$	3.48	8	7.23
	N	2.27	2.72	2.49
	R^2	0.94	0.95	0.94

Langmuir coefficient; q_m: maximum monolayer adsorption capacity parameter, k_L: adsorption equilibrium constant and; n: empirical constant of the Freundlich model.

Table 6
Comparative evaluation of adsorption capacities onto different adsorbents

Adsorbent	Monolayer adsorption capacity (mg·g^{-1})	Reference
Powder activated carbon (PAC)	182	This study
Granular activated carbon (TSAC)	64.93	[39]
Sugarcane bagasse activated carbon	20.16	[40]
Activated carbon	37.88	[41]
Composite	22.99	[41]
Zeolite	2.35	[41]
Periwinkle shell activated carbon	0.03	[42]
Commercial activated carbon	0.08	[42]

4. Conclusions

Results show that a combined process of coagulation and adsorption results to be an efficient and promising method for the treatment of leachates from Casablanca landfill. The efficiency of the process is evaluated in terms of COD, metal pollution, turbidity, sludge production and colour removal. Single coagulation process using a dosage of 12g Fe^{3+}·L^{-1} lead to very high removal rate of turbidity (up to 92.5%), but moderate in terms of COD reduction (62.5%), and low sludge volume generation (30% v/v). Combining a coagulation process with an adsorption process onto PAC lead to an enhancement on COD and turbidity reduction of 77% and 99%, respectively. The adsorption of COD onto PAC was best described by the Langmuir isotherm model, with a monolayer adsorption capacity of 182 mg·g^{-1} at 25°C.

However, due to the high pollutant load of the leachate of Casablanca landfill, the effluent from this combined process still needs further treatment in order to fulfil local standard regulations.

Symbols

C_0 — COD concentrations at the beginning
C — COD concentrations at equilibrium or specific time
m — Mass of adsorbent (PAC)
V — Total volume of liquid
q_t — Adsorption capacity at time t
q_e — Adsorption capacity at equilibrium time
k_1 — Pseudo-first order model rate constant
k_2 — Pseudo-second order model rate constant
q_{m} — Maximum adsorption capacity of adsorbent
K_L — Langmuir model constant
K_F — Adsorption equilibrium constant
N — Empirical constant of the Freundlich model
R_L — separation factor

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