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Use of coagulation-flocculation process for the treatment of the landfill leachates of Casablanca city (Morocco).

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Abstract

This study aims to investigate the feasibility to apply a coagulation-flocculation process to treat the landfill leachate of the municipal solid waste of Casablanca city (Morocco). Three types of coagulants are assessed: lime ($Ca(OH)_2$), ferric chloride ($FeCl_3$), and alum ($Al_2(SO_4)_3$). Optimum conditions in terms of the removal of chemical oxygen demand (COD), heavy metals, colour and turbidity contents are determined, using a standard jar test apparatus. Optimum coagulant dosages of 52.5 g $Ca(OH)_2.l^{-1}$, 12 g $FeCl_3.l^{-1}$ and 22.5 g $Al_2(SO_4)_3.l^{-1}$ are obtained. Lime allows to remove 66.25% of COD, 98% of turbidity, 80% of colour with a low sludge volume generation (30%). When the optimum coagulant dose of $FeCl_3$ is applied a 62.5% of COD, 92.5% of turbidity, 82% of colour are removed with less sludge volume generation (21%).Whereas when $Al_2(SO_4)_3$ is used 11% COD and 6% of turbidity removal are obtained with a slightly lower sludge volume generation (11%). Regarding the analysis of metallic elements, the results show that a substantial elimination of heavy metals is reached, particularly of Cd, Cr, Cu, Fe, Ni and Pb. Treatment with lime shows a greater affinity to Cr (86%) and lower to Fe (60%). Ferric chloride allows to eliminate most of the detected metal elements with a high affinity toward Cd, Cu, Ni, Cr and Zn. Alum shows to be very suitable for Ni, Pb, Cr elimination with 95 %, 94 % and 93% removal efficiency, respectively. These results show that coagulation-flocculation could be used as a promising process for the pretreatment of landfill leachates of Casablanca city.

1. Introduction

From 1996 to 2015, the landfill of Casablanca (Morocco) has received a large urban and industrial waste amount (about 20 million tons), generating high volume of leachates (around 12000 m^3). Landfill leachate are considered a potential contamination source of surface groundwaters, as they may percolate through soils and subsoils, causing extensive contamination of streams, creeks and water wells, if they are discharged without any kind of treatment [1]. The elimination of landfill leachates has been a serious challenge for several years in many industrial companies which have to accomplish stringent environmental regulations. An adequate leachate treatment system should provide an effective treatment and retention capacity to handle the leachate quantity. Best available technology should be applied in order to prevent and minimise further environmental impacts [2].

Various technologies based on physical-chemical process such as chemical precipitation, coagulation–precipitation, ultrafiltration and reverse osmosis have been applied successfully for the treatment of landfill leachates [3-6]. On the other hand, combined processes including two or three physical–chemical methods have been widely used including ozonation-activated carbon adsorption [7], coagulation–ozonation[8], and precipitation–reverse osmosis [9].

In particular, coagulation-flocculation process has been extensively applied in wastewater treatment plants due to its simplicity of implementation and operation [10], and as a pre-treatment method prior to biological processes, or other physical–chemical techniques in the treatment of landfill leachates [11, 12]. Several studies have been reported, relate to the feasibility to use coagulation-flocculation for the treatment of leachates, focussing at performance optimisation, i.e. selection of the most appropriate coagulant, determination of the best experimental conditions, assessment of the effect pH and flocculant addition [13].

This study aims (a) to characterise the leachates of Mediouna landfill and (b) to examine the efficiency of coagulation-flocculation process in terms of the removal of COD, turbidity, colour and heavy metals, using three types of coagulants (lime, ferric chloride and alum). Finally, optimum dosage of each coagulant is established.

2. Materials and methods

2.1 Materials

2.1.1 Landfill site and sampling

Landfill leachate samples were collected from Mediouna municipal landfill in Morocco. This landfill is located at 10 km south-east of Casablanca city, Morocco (see Fig.1).This site (about 780 000 m^2) has been in operation since 1986, receiving approximately 3000 ton of household wastes per day from different areas of Casablanca. Leachate samples were taken directly from a collection box at the exit of the landfill cell and were collected in plastic bottles of 25 l capacity. Then, samples were transported to the laboratory and stored in a refrigerator at 4 °C in the dark in order to minimize leachate decomposition due to microbial activity.

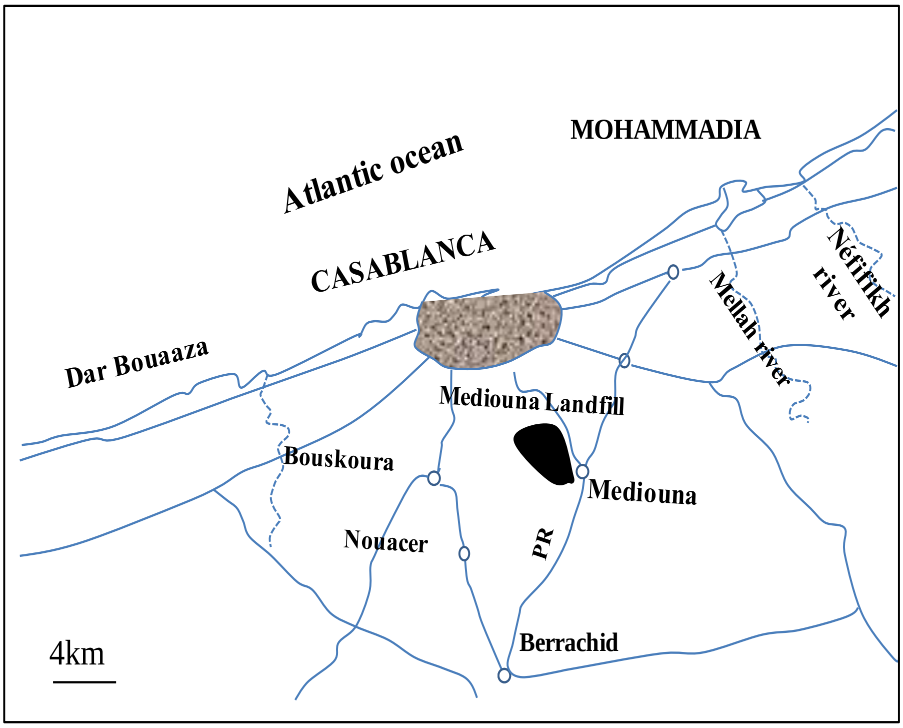

Figure 1: Location of Casablanca Landfill site.

2.1.2. Chemicals and materials

Lime ($Ca(OH)_2$, 80%w/w), ferric chloride ($FeCl_3$, 40% w/w) and alum ($Al_2(SO_4)_3 \cdot 18H_2O$, 17% w/w) were supplied by Cadilhac, Casablanca Morocco and were used as coagulants. Hydrochloric acid and sodium hydroxide were supplied by Sigma-Aldrich chemicals, Saint-Quentin Fallavier, France.

2.2 Experimental procedure

2.2.1 Coagulation/flocculation

Coagulation/flocculation (CF) tests were performed in a jar-test apparatus (FC4S Flocculator Velp) equipped with four beakers of 1 l volume. Coagulants (lime, ferric chloride and alum) were applied at various concentrations in order to determine the optimum concentration for maximum turbidity, colour and organic matter removal. In each test, 400 ml of sample was poured into the beakers. Before any test, leachate samples were equilibrated to ambient temperature.

CF process included three sequential operating stages. An initial rapid mixing stage that took place during 10 min at 200 rpm, followed by a slow mixing stage of 30 min at 60 rpm, and finally a settling step of 60 min. After the settling period, supernatants were withdrawn from the beakers and were taken for chemical analysis (pH, turbidity, COD, total suspended solids (TSS), and color rmeasurements). Sludge volume was determined from the level of deposited sludge in the bottom of beakers after the 60 min of settling.

2.2.2. Analytical determinations

Leachate samples were characterised before and after the CF treatment. Physical-chemical parameters such as pH, conductivity, turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD_5), Cl^-, total suspended solids (TSS), nitrate, nitrite, ammonium, phosphorus, UV absorbance at 254 nm (UV_{254}) were determined according to the Standard Methods for the Examination of Water and Wastewater [14]. UV–visible absorption measurements were performed using a spectrophotometer UV2300 II. Color number (CN) was determined using the method described by Tizaoui et al. [15].

The removal efficiency of turbidity, color, heavy metals and COD was obtained using the following equation:

$$\mathrm{Re}\,moval(\%) = \left[\frac{(C_i - C_f)}{C_i}\right].100 \qquad \text{(Eq. 1)}$$

Where C_i and C_f are the original content and the residual content in leachate, respectively.

Organic composition of leachate was identified after conducting a liquid-liquid extraction procedure using dichloromethane and hexane by gas chromatography coupled to mass spectrometry (GC-MS) using a Finnigan polaris Q GC/MS Bench top Ion Trap mass spectrometer from Thermo Fisher Scientific (Waltham, Massachusetts, USA). This method allows to separate organics based on their chemical structure in three conditional groups: aromatic, polar and aliphatic compounds [16]. Inductively coupled plasma atomic emission spectroscopy analysis ICP-AES (Activa, Jobinyvon) was used to quantify the concentration of metals after samples were filtered through 0.45 μmfilter. Scanning Electron Microscopy assays (SEM) were conducted with a Quanta-200 SEM (Philips) to characterise formed flocs in relation to their basic constituents and surface morphological information.

3. Results and discussion

3.1 Leachate characterisation

Chemical-physical characteristics of raw leachate from the Casablanca landfill are presented in Table 1. Attending to data presented in Table 1, this landfill leachate result to be a complex wastewater.

The dark colour of the liquid is related to the high values of COD (7680 mg O_2. l^{-1}), BOD_5 (300 mg $O_2.l^{-1}$) and to the high turbidity content (106 NTU). All these parameters are higher than the values set by the Moroccan standard discharge limits. The high concentration of COD is due to the presence of different kinds of dissolved organic matter. Figure 2 presents a chromatogram with the main organic components of the Mediouna landfill leachate. Humic substances, phenolic, heterocyclic, aromatic hydrocarbons, carboxylic acids, and carbohydrates are identified as the predominant dissolved organic matter of the landfill leachate. Another relevant point is the high conductivity (23000 μS. cm^{-1}) that could be related to the high salinity value, principally due to the amount of chlorides (6002 mg. l^{-1}), potassium, sodium (>1000 mg. l^{-1}), nitrates (169 mg. l^{-1}), nitrites (3.2 mg. l^{-1}), phosphates (3 mg. l^{-1}) and ammonia (139 mg. l^{-1}). The BOD_5/COD ratio is close to 0.039 with a pH of 7.6, indicating that this leachate may be defined as stabilised leachate and difficult to further biodegradation. In addition, the landfill leachate contains Al, Cd, Cr, Pb, Cu and Fe with concentration of 6.3, 0.01, 0.5, 0.02, 0.74 and 3 mg. l^{-1}, respectively. The total suspended solids are of the order of 5.7 $mg.l^{-1}$.

Table 1: Characterisation of Mediouna landfill leachate and Morocco Reject Requirements (MRR)

Parameters	Value	MRR
Conductivity (mS cm^{-1})	23	0.27
T ($^{\circ}$C)	19	30
pH	7.6	6.5-9
TSS (mg. l^{-1})	5.7	50
Turbidity (NTU)	106	--
COD (mg. l^{-1})	7680	500
BOD_5 (mg. l^{-1})	300	100
BOD_5/COD	0.039	--
Colour Number	4.87	--
PO_4^{3-} (mg. l^{-1})	3	2
NO_3^- (mg. l^{-1})	169	--
NO_2^- (mg. l^{-1})	3.2	--
NH_4^+ (mg. l^{-1})	139	
Cl^- (mg. l^{-1})	6002	3010
Al^{3+} (mg. l^{-1})	6.3	--
Cd^{2+} (mg. l^{-1})	0.01	0.2
Cr^{3+} (mg. l^{-1})	0.5	2
Pb^{2+} (mg. l^{-1})	0.02	0.5
Cu^{2+} (mg. l^{-1})	0.74	0.5
Fe^{2+} (mg. l^{-1})	3	3

*Morocco Reject Requirements (MRR)

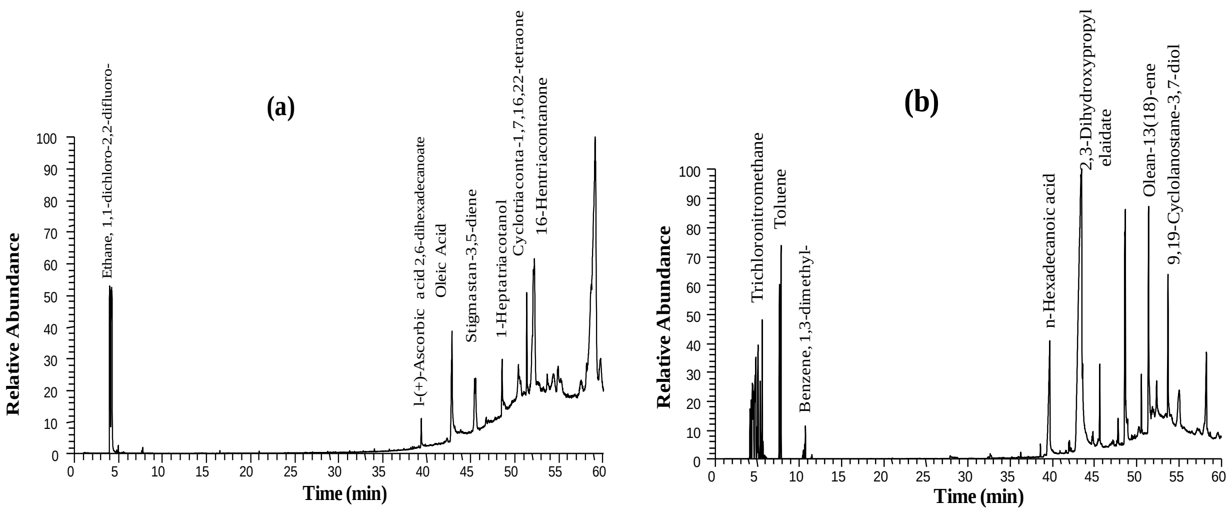

Figure 2: Main organic components of the Mediouna landfill leachate detected by GC-MS chemical extraction with (a) dichloromethane and (b) hexane

3.2. Coagulation-flocculation process

3.2.1 Lime

Lime is one of the most common chemicals used in coagulation-flocculation and chemical precipitation because of its low cost and availability. Experiments were conducted without prior adjustment of pH using different lime dosages, with the aim to determine the optimum coagulants dosage. Figure 3 shows the removal efficiency in terms of turbidity, COD, and sludge amount at different dose of coagulant.

An optimum coagulant dose (OpCD) is found when 52.5 g Ca^{2+}. l^{-1} is applied, corresponding to a maximum removal of turbidity (98%) and COD (66.25%). Results show that the removal efficiency expressed as turbidity increases with an increase in coagulant dosage until reaching an optimum value. After that, the turbidity removal decreases slightly.

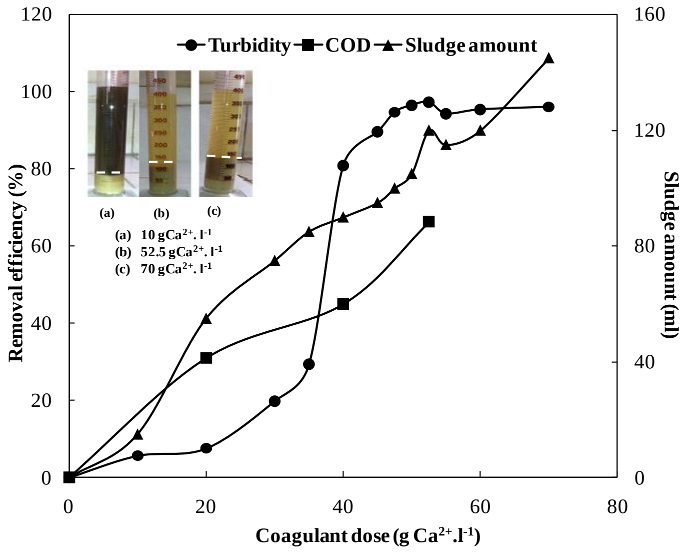

Figure 3: Effect of lime dosages on removal efficiency in terms of turbidity, COD and sludge amount.

When 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 coagulant dosage, the values of turbidity removal decrease due to restabilisation of colloidal particulates [17]. It can also be seen that the volume of generated sludge increases gradually with the increase on the coagulant dose, resulting in a 30% of sludge generation**.**

Results indicate that the pH of the supernatant increases continuously with the increase of coagulant dose, giving a pH value of 13.5 for OpCD of lime. This increase on pH could be explained by the basic character of Ca^{2+} ions (Lewis base).

Figure 4 displays the influence of different lime dosage on colour variation. UV–vis spectra in the wavelength range between 200 and 700 nm for leachate before and after coagulation-flocculation treatment process is shown. It should be noted that the absorbance at all the wavelengths range (200-700nm) decreases significantly with the increase in lime dose. To further investigate the characteristics of organic matter, the absorbance values at 254 nm (UV_{254nm}) are used here as indicator of aromatic or conjugated double-bond compounds [13-15]. It is observed that the absorbance at UV_{254nm} decreases as the applied dose of $Ca(OH)_2$ increases (see figure 4) indicating that aromatic compounds could be partially removed by the coagulation-flocculation process. This performance is likely to be due to the charge neutralisation capacity of the lime that provides a higher reduction in the electrostatic repulsion between flocs and the dissolved organic molecules, facilitating their adsorption.

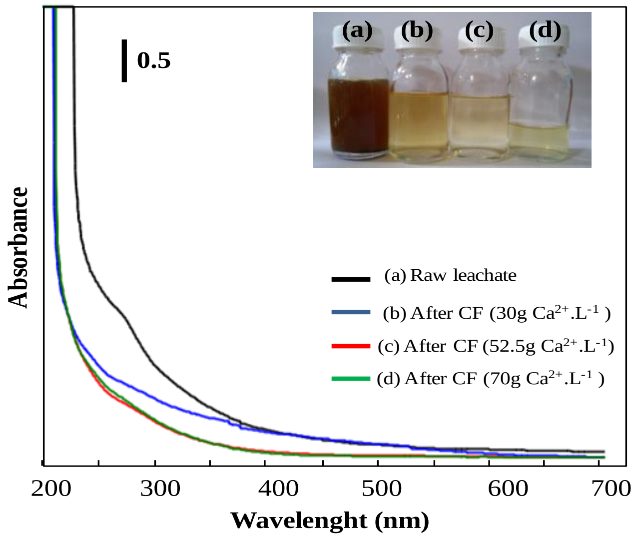

Figure 4: Colour variation and UV–vis absorbance spectra of the landfill leachate before and after the coagulation-flocculation-sedimentation treatment by the lime coagulant

Inserted pictures at the upright side of Figure 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 yellow at a coagulant dose near to the optimal coagulant dose. Colour removal is found to be 80% by measuring the absorbance in the visible range at wavelengths of 436, 525 and 620 nm.

Additionally, heavy metal concentrations were determined before and after the coagulation-flocculation treatment using OpCD of lime. Results shown in Table 1 lists the presence of metal elements in the raw leachate, in particular Cd, Al, Cr, Cu, Mg, Al, Pb, Ca and Zn. Heavy metals contents is found to be reduced after coagulation-flocculation treatment, where maximum removal efficiencies are obtained for Cr, Fe and Mn with 86%, 60% and 88% elimination, respectively.

Figure 5 (A-B) presents SEM images coupled with EDS analysis (Fig 5-C) of a floc sample obtained from the sediments after the CF process when lime was used under the optimum conditions. SEM pictures display precipate structures with large aggregates. This voluminous floc structure provides optimum conditions for trapping particles even though the surface charges of the particles have been only partially neutralised. EDS analysis shows that Ca, Mg, Na and Al are the most abundant elements (see Figure 5-C), whereas Cl, K, N, C, and Fe are detected at relatively low concentrations. The percentage of carbon on the floc surfaces is high which indicates that organic compounds are removed during the CF process. These results evidence that the coagulation-flocculation process using lime does not only remove dissolved organic matter, but also traps other pollutants from the leachate inside the flocs, such as metal ions, due to the adsorption or through complexation process.

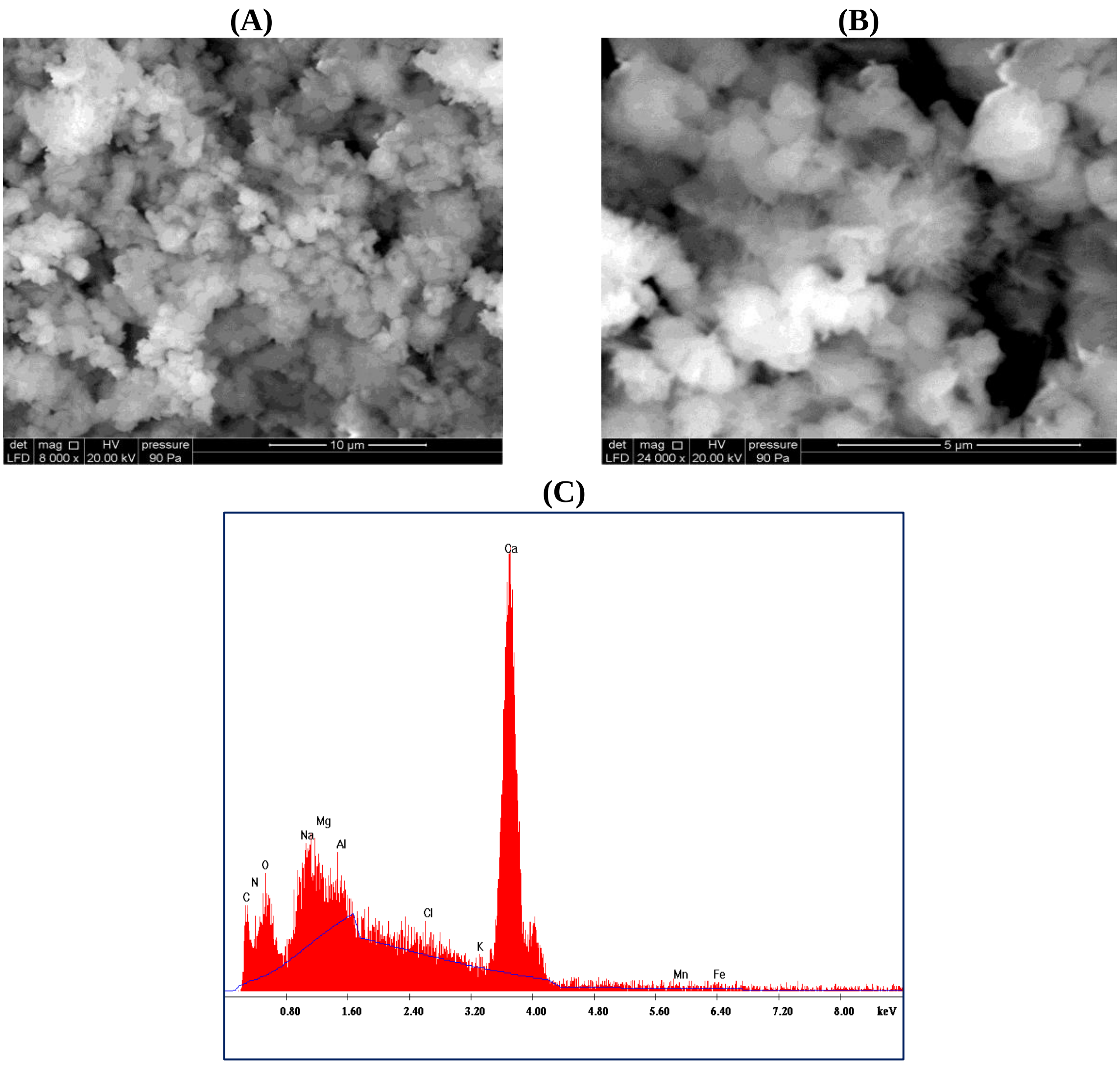

Figure 5: (A-B) SEM images of the flocs obtained after the coagulation-flocculation process using a lime dose of 52.5 g $Ca^{2+}.l^{-1}$ and (C) EDS spectrum

3.2.2 Ferric chloride ($FeCl_3$)

Figure 6 shows turbidity and COD removal efficiencies together with sludge volume generation as a function of ferric chloride dosage. Results show that the removal of turbidity increases with the increase in the coagulant dose until reaching an optimum value (12g Fe^{3+}. l^{-1}) where a 90% of turbidity is removed, corresponding to 62.5% COD elimination and a 21% of sludge volume generation. After that, the removal of turbidity decreases slightly. Hence, when coagulant is added to the leachate, cations and its hydrolysed products interact with negative colloids, neutralising their charges and promoting colloid destabilisation. However, when coagulant dosages are higher than the observed optimum value, turbidity removal rate decreases due to restabilisation of colloidal particulates [17]. The increase in ferric chloride dose decreases continuously the supernatant pH, reaching a value of 4.15 at the OpCD (results not shown here). This reduction on pH could be explained by the acidic character of Fe^{3+} (Lewis acids). Fe^{3+} could react with the OH^- ions of the leachate, producing, iron precipitates in the form of $Fe(OH)_3$ [10]. Under the optimum coagulant dose more than 50% removal is achieved for Cr, Al, and Cd, while other metals (Cu and Mg) are removed to a lesser extent (0- 40%).

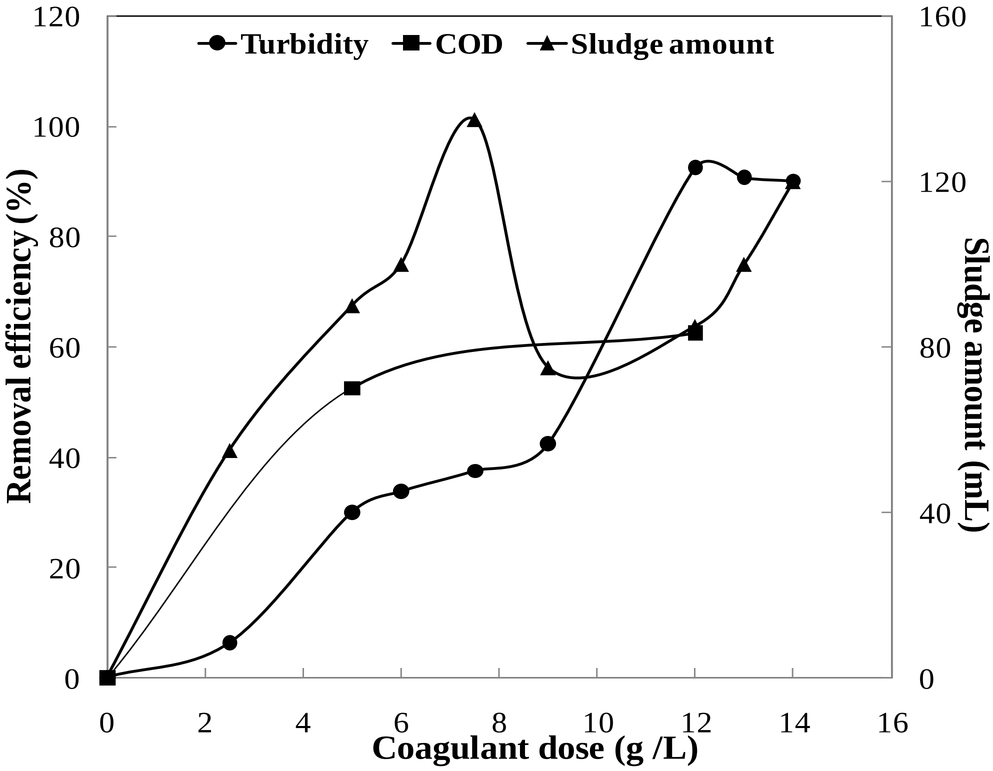

Figure 6: Effect of ferric chloride dosages on removal efficiency in terms of turbidity, COD and sludge amount.

Figure 7 displays the variation of the UV–vis spectra in a wavelength range between 200 and 700 nm before and after the coagulation-flocculation treatment process using $FeCl_3$. It should be noted that the UV-Vis absorbance decreases with the dose of $FeCl_3$ confirming the above results. It is also observed that the absorbance at 254 nm decreases as the applied of $FeCl_3$ dose increases (see figure 7) which indicates that the organic compound in the form of aromatics could be partly removed by the coagulation-flocculation process (the absorbance at 254 nm is surveyed [18 - 20] as characteristics of organic matter). At the optimum coagulant dose an 80% and 82% of removal efficiency are obtained in terms of UV_{254nm} and $UV_{,450nm}$, respectively. This performance is likely to be due to the charge neutralization capacity of ferric chloride that provides a higher reduction in the electrostatic repulsion between flocs and dissolved organic molecules, leading to higher floc formation.

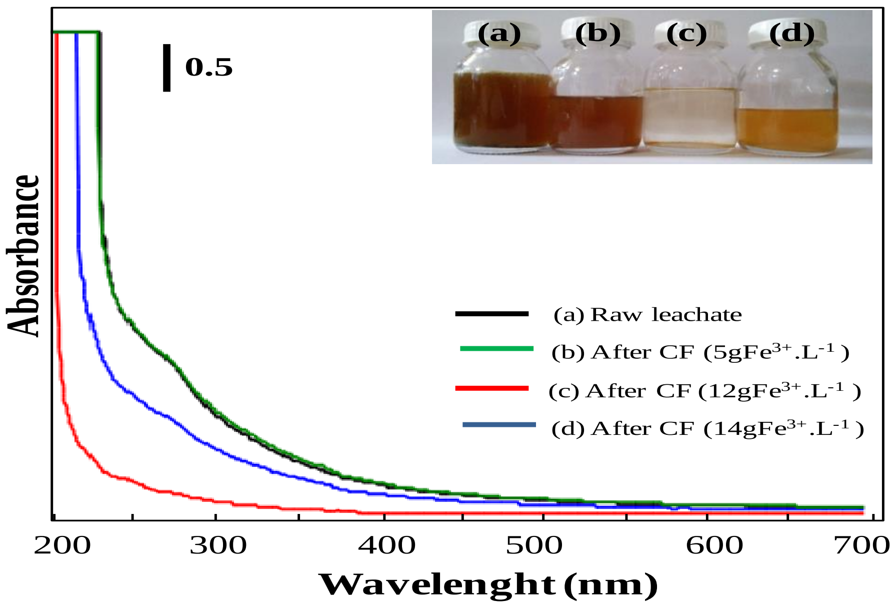

Figure 7: UV–vis absorbance spectra of the leachate before and after treatment by $FeCl_3$.

Pictures at the upright side of Fig. 7 (picture a →d) show that an increase on coagulant dose of $FeCl_3$, transforms, the dark brown colour of raw leachate into a clear brown, then turns into yellow and finally becomes clear at the optimal coagulant dose**.**

3.2.3 Alum ($Al_2(SO_4)_3$)

Results of coagulation-flocculation using alum are presented in Fig. 8. In this figure, the removal of turbidity, COD and sludge volume formation as a function of alum dosage is shown, without any pH control. Coagulant dose ranges from 0 to 30 g. 1^{-1}. It can be seen that the results are similar to those obtained when $FeCl_3$ and lime are applied.

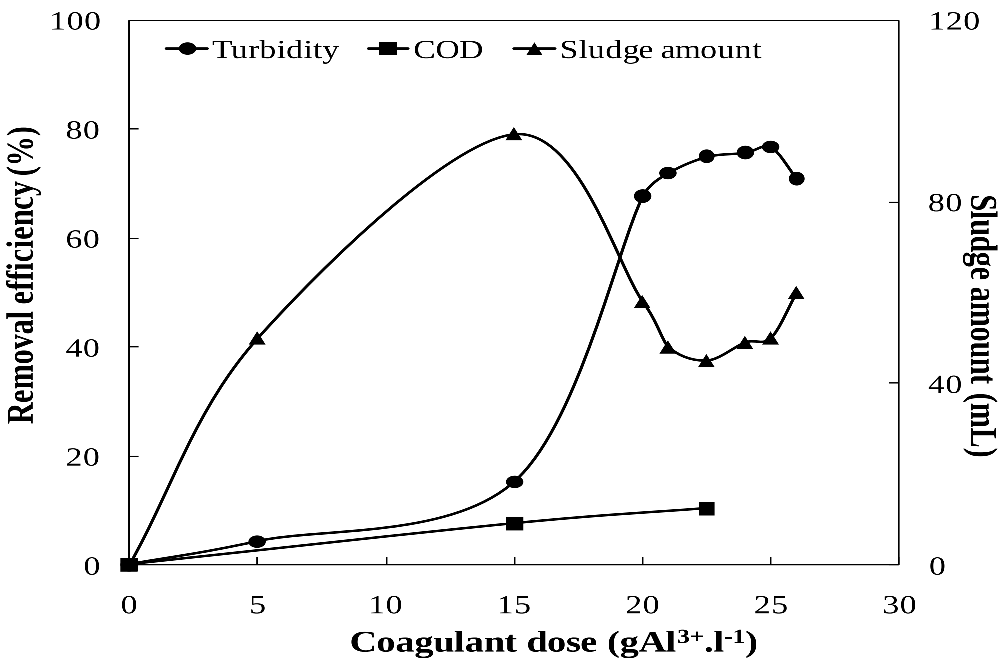

Figure 8: Effect of alum dosages on removal efficiency in terms of turbidity, COD and sludge amount from leachate for different doses of alum

The treatment efficiency of alum increases as coagulant dosage increases up to an optimum value of 22.5 g Al^{3+}. l^{-1} beyond that value the removal efficiency decreases slowly. Thus, the addition of alum to the leachate results in only 11% COD reduction and 6% of turbidity removal. As a consequence lower heavy metals removal is observed during the coagulation-flocculation process using alum. After a settling period of 60 min, the amount of sludge produced represents only about 11% of the total volume of sample used in the experiment. Related to the colour of the leachate, it changes with the increase of coagulant dose from dark brown colour of the untreated leachate into a clear brown, then to yellow and finally becomes clear yellow at the optimal coagulant dose (see figure 9). These findings are in agreement with those obtained by Tatsi et al [6].

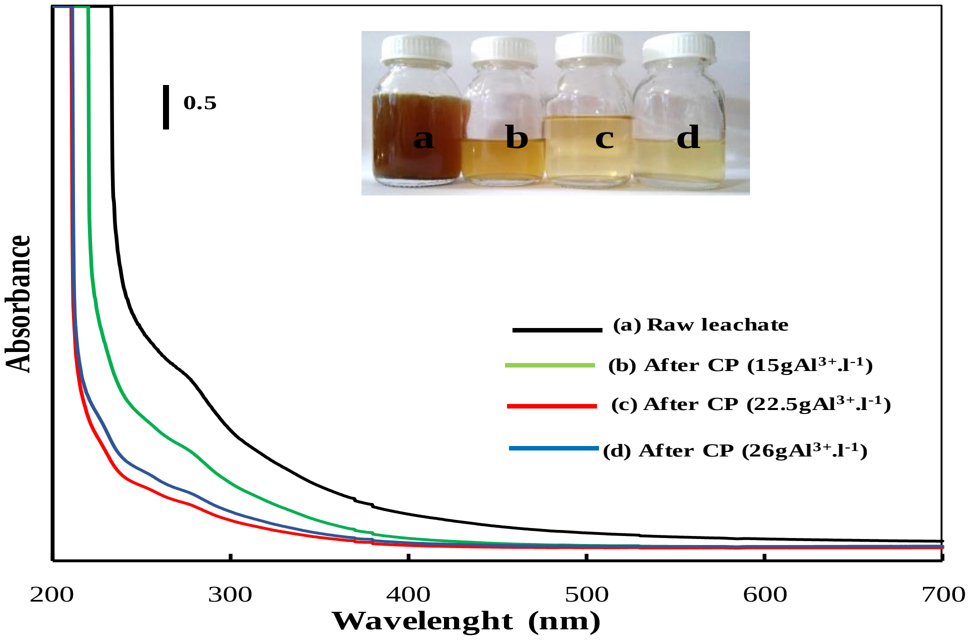

Figure 9: Color variation and UV–vis absorbance spectra of the landfill leachate before and after the coagulation-flocculation treatment by alum

3.2.4 Comparison of the application of different coagulants

Figure 10 compares the best results obtained from each of the tested coagulant at the optimal conditions. It can be seen that the removal of turbidity is very high, reaching values about 90% for two of the coagulants (lime and ferric chloride).

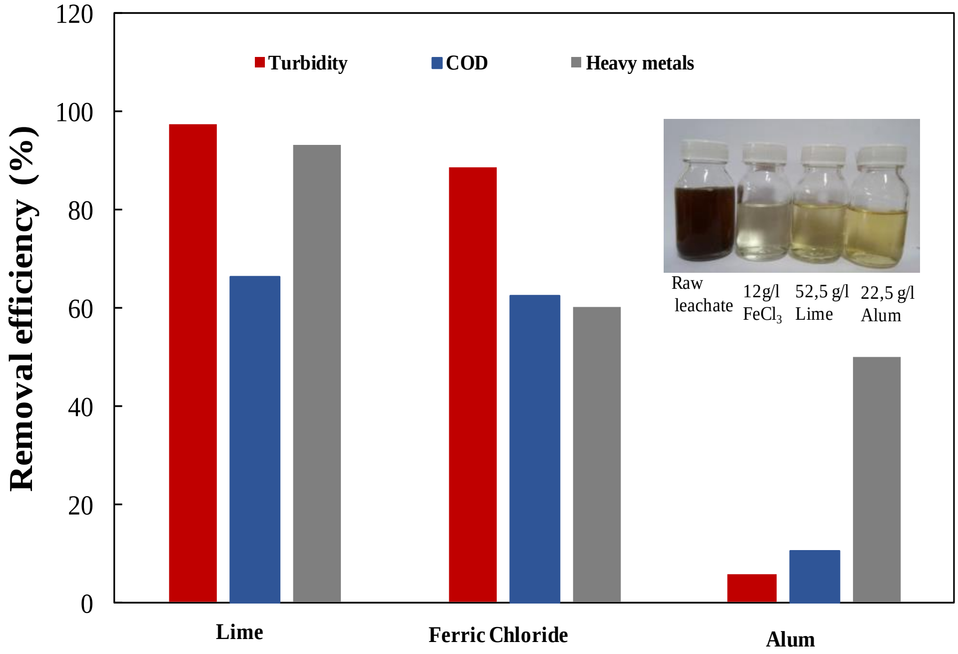

Figure 10: Comparison of COD, turbidity, color, and heavy metals removals from leachate using different coagulants.

$FeCl_3$ and lime were found to be generally superior to the alum in removing all the parameters (COD, turbidity, coulor and heavy metals). Concerning to the organic matter, COD removal efficiency is higher for lime followed by $FeCl_3$ and then by alum. From the figure 10, good removal of turbidity, colour and COD were achieved with reasonably lower amount of $FeCl_3$ coagulant (12 g. l^{-1}). This is in agreement with the findings of Amokrane et al [11] who indicated that ferric chloride was more effective than aluminium sulphate or lime for turbidity, colour and COD removal. Iron flocs are denser than the aluminum flocs. Daud et al. [21] also reported ferric chloride as the most efficient chemical in their study which led to 84% of colour removal and 37% of COD elimination. It is obvious that $FeCl_3$ showed the highest treatment efficiency and lowest sludge volume generation, which confirms that ferric chloride is highly efficient in coagulation process [22] and one of the most promising coagulants.

A rough economic analysis of the operating costs associated with CF treatment process is conducted here base on the acquiring costs of reagents. It is important to note that this analysis is just an approximate tool to differentiate the trends in the operating cost associated with the use of CF treatment. A more rigorous economic analysis should consider initial investment, prices at plant scale, energy, maintenance and labour costs.

Ferric chloride consumption is 12 g Fe^{3+}. l^{-1}, it is almost ~2 to 4 times lower than the values of lime and alum. If it is considered an estimated average price of ferric chloride to be around US$ 300 ton^{-1}, the total reagent cost will be US$ 3.6 m^{-3}. Nevertheless, comparing the cost of reagent per treated leachate volume (US$.$m^{-3}$), values of 3.6; 5.25 and 5.85 US$.$m^{-3}$ are obtained for ferric chloride lime and alum, respectively. This is 1.4 -1.6 times in favour of ferric chloride, being acceptable for the treatment of landfill leachate. Thus, given the fact of low cost, ferric Chloride is likely to become a strong coagulant candidate for leachate pretreatment of Casablanca city.

Conclusions

In this research, treatment of leachate from the Casablanca landfill by coagulation -flocculation process was evaluated. Several jar-test experiments were carried out to determine the optimum conditions to eliminate pollution using three different coagulants (lime, ferric chloride and alum). The efficiency of the process was evaluated in terms of the removal of COD, metal content, turbidity, colour and sludge production and colour. The optimum dose obtained by the $FeCl_3$ is estimated at 12 g. l^{-1} with removal efficiencies of COD and turbidity of 62.5 and 92.5%, respectively. The amount of sludge produced is 21%. Economic analysis shows that the operating cost of the CF process is US$ 3.6 per m^3 of treated landfill leachate. CF process results to be a feasible alternative to treat landfill leachates of Casablanca city.

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