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Treatment of controlled discharge leachate by coagulation-flocculation: influence of operational conditions

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ABSTRACT

The aim of this study was to optimize the operational conditions of the coagulation-flocculation process for the clarification of leachate from the landfill Technical Center of Souk-Ahras city. Three coagulants (ferric chloride, aluminum sulfate and ordinary alum) were tested and two types of agitation (mechanical and ultrasound) were implemented. The quality of treatment was assessed via physicochemical and bacteriological analyzes. The parametric study revealed that pH adjustment of leachate was crucial for the success of treatment. The stronger reduction of turbidity was obtained with a coagulant dose of 15%, a stirring speed of 250 rpm and a stirring time of about 5 min for both aluminum sulfate and ordinary alum and 15 min for ferric chloride. An optimum coagulant-to-leachate volume ratio of one was found for the three coagulants, resulting in a turbidity reduction of 99.4%, 98.9% and 98.6% with ferric chloride, aluminum sulfate and ordinary alum, respectively. Bacteriological analyzes highlighted the absence of total germs, fecal coliforms and streptococci for leachates treated with ferric chloride or aluminum sulfate. In contrast, coliforms including 9 total germs, 4 fecal germs and 3 fecal streptococci per 100 mL were detected for leachates treated with ordinary alum. The treatment of leachate was improved by using ultrasound waves with a frequency of 37 kHz and a power of 30 W. Indeed, a significant decrease in the turbidity of supernatants was observed as compared with the use of mechanical agitation, and a value of 0.19 NTU (instead of 0.61 NTU with mechanical agitation) was obtained for a treatment carried out with ferric chloride. The clarification of leachates was optimal at 20°C providing a BOD_5 of 100 mg O_2/L for both ferric chloride and aluminum sulfate, and 200 mg O_2/L for ordinary alum.

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Introduction

The production of household and similar waste causes serious pollution problems; their increasingly complex and heterogeneous nature involves difficulties in their treatment and management. Technology offers effective solutions for waste management, thereby protecting the environment and public health. Several methods are available such as the disposal of waste in controlled landfills, where they are subject to degradation processes.[1] This option makes it possible to recover fermentable waste through production of biogas but also generates leachates, which are sources of contamination for the environment. The leachates are effluents composed of multiple organic and mineral elements including toxic species that pollute soil, groundwater and surface water. The monitoring and treatment of these effluents is then necessary before their release into the natural environment both to prevent health and environmental risks and to collect data whose analysis can be useful to improve their treatment.[2,3]

Treatment methods are constantly evolving in order to meet the specific needs of the treatment stations. They include the most basic treatment types up to the most innovative ones depending on the socio-economic context and regulations that weigh on stations. The treatment of leachates can be biological, chemical and/or physicochemical.[4–7] Among these processes, coagulation-flocculation is viewed as a reliable and economic method due to its high selectivity toward colloidal species and its proven efficiency in the treatment of effluents.[8,9] Coagulation-flocculation allows neutralization or reduction of electrical charges, thus allowing closer approach of the colloidal particles to each other, which then aggregate into flocs.[8] It is a simple and

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cheap technique that can be used successfully to treat landfill leachates. However, the choice of the appropriate coagulant, the determination of optimal operating conditions, the evaluation of the pH effect and the search for the optimum doses of reagents are essential to optimize the efficiency of the treatment.[9–13]

Coagulation-flocculation process is frequently used for treating fresh leachates and often applied as a pretreatment before biological treatment. It is used to remove heavy metals and non-biodegradable organic compounds from landfill leachates.[14]

Other physicochemical methods for processing leachates, such as advanced oxidation processes (AOPs), have been widely used in recent years. The ultrasonic irradiation is one of AOPs and is an attractive method for the elimination of recalcitrant substances. The process is based on the phenomenon of acoustic cavitation, involving the formation, growth, and sudden collapse of micro-bubbles in an irradiated liquid.[15] The cavitation bubbles conduct to high local temperatures and pressures resulting in sonochemical effects such as pyrolytic decomposition or oxidation by generated $H^{\bullet}$ and $OH^{\bullet}$ radicals, which have a very high oxidation potential and are able to oxidize almost all organic pollutants.[16,17] In addition, the irradiation by ultrasound is an efficient technique for the decomposition of ammonia-nitrogen in landfill leachates.[18] Despite its successful and large use in various fields such as industrial wastewater treatment and sludge treatment, literature shows that studies dealing with the use of ultrasounds to improve the efficiency of leachate treatment are scarce.[19]

On the other hand, the irradiation by ultrasound in combination with other treatment methods such as electro-coagulation, biodegradation, electro-oxidation and adsorption was also shown to play an essential role in the removal of organic pollutants.[16,20–22]

The principal aim of the present study was to evaluate the efficiency of the coagulation-flocculation process for the treatment of leachate from the Technical Landfill Center of Souk-Ahras city. Firstly, the conventional Jar test procedure was adapted to the leachate by researching the best operational parameters. In this perspective, the influence of many parameters on the degree of clarification of leachate was investigated, namely, the pH of medium, the nature and dose of coagulant, the stirring speed and stirring time, and finally, the coagulant-to-leachate volume ratio which, to the best of our knowledge, is a parameter rarely studied in the literature.

Experimental

Leachate samples

Leachate samples used in this study were collected in plastic flasks from the lagoon of the landfill Technical Center of Souk-Ahras city, which covers an area of 12 hectares. The center has been in service since 2010 and processes a load of 90 tons of waste per day. All samples were collected manually, sealed hermetically, transferred to the laboratory, stored at 4°C and then analyzed within two days.

Description of coagulation-flocculation tests

A volume of 100 mL of leachate was used for each test. The pH of some leachates was adjusted to 3.5 ± 0.2 by adding a few drops of HCl or H_2SO_4 solutions whereas the pH of others was not changed. Next, a volume of coagulant solution ($V_{Coagulant}/V_{Leachate}$ = 0.5, 1 or 2) with a concentration ranging from 5% to 20%w was added to leachates and the mixtures were mechanically stirred for a given time using a flocculator (Jar test, velp Scientifica JLT 4 positions). Ferric chloride ($FeCl_3$), aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) and ordinary alum $KAl(SO_4)_2.12H_2O$ were used as coagulants. It should be noted that the dissolution of the ordinary alum was made under stirring and light heating. At the end of the stirring step, the pH of leachates for which the pH had been previously adjusted at 3.5 ± 0.2 was readjusted at 7.5 ± 0.2 by adding a few drops of NaOH solution while stirring, to promote the formation of flocs.

All experiments were conducted at room temperature (18 ± 2 °C). The mixtures obtained after this step were decanted for 6 hours in a separator funnel. The flocs obtained after decantation were separated from the supernatant by filtration through filter paper, dried in an oven at 105°C for 6 hours and then weighed by means of an analytical balance. The supernatants were then recovered for analysis.

In a second step, the mechanical agitation provided by the Jar-test procedure was replaced by ultrasonic agitation with a frequency of 37 kHz and a power of 30 W, provided by an ultrasonic bath (Fisher-brand). Its temperature was regulated by connecting it to a thermostatic bath through a copper cooling system.

Analytical

Analyses of the sludge and supernatants recovered after decantation

The sludge collected after the step of decantation/filtration was examined using optical microscopy (LEICA DM R-MN) and Fourier Transform infrared spectroscopy (FTIR) by means of a spectrophotometer of type

IRAffinity-1S SHIMADSU in combination with a single reflection ATR.

The supernatants recovered after decantation, were centrifuged at 3000 rpm for 30 min to quantify the Suspended Solids (SS). The pellet at the bottom of the tubes was weighted after drying in an oven at 105°C.

Analyses performed on both raw leachates and supernatants recovered after decantation

The pH and electric conductivity of raw and treated leachates (supernatants) were measured by a pH-meter and conductimeter from Hanna Instruments. The refractive index was determined using the refractometer Zuzi Model-315 ABBE and turbidity measurements were obtained with the turbidimeter TB 300 IR Lovibond. The turbidity reduction (% of clarity) due to the treatment was calculated as follows:

$$\%\ \text{of clarity} = 100\text{x}\,[(T_{rl} - T_s)/T_{rl}] \quad (1)$$

with T_{rl} the turbidity of raw leachate and T_s the turbidity of supernatant.

The nitrate amount was determined by UV–visible spectrophotometry (Secomam UviLine 9400 model) at 415 nm. Sodium salicylate was used to obtain, in the presence of nitrate, sodium para-nitro salicylate, which is colored in yellow. It should be noted that the sodium salicylate method is adopted by the French Standardization Agency (AFNOR, 1975, standard FNT 90–012).[23] The dissolved oxygen (DO) content was measured by means of an oximeter (JPSJ-605, DO Analyzer) whereas the Chemical Oxygen Demand (COD) and (Biological Oxygen Demand) BOD_5 were determined using a reactor COD-Hanna (model C 9800) and an Oxitop (WTW), respectively. Analyses were repeated two times.

Analyses of supernatants recovered after centrifugation

Several analyses were performed on the supernatants recovered after centrifugation. The concentration of calcium and magnesium ions (Hydrotimetric Title, HT) was determined by complexation reaction with ethylenediaminetetraacetate (EDTA) in an ammoniacal buffer medium (pH = 10) with a few drops of Black Eriochrome T (BET) to detect the equivalence. The Alkalimetric Title (AT) and Complete Alkalimetric Title (CAT) were determined by acid-base titration by means of hydrochloric acid with phenolphthalein and methyl orange as an indicator, respectively. All the analyses were performed according to standard methods.[24,25]

Bacteriological analyzes aiming at identifying and counting the germs were also performed on the supernatants. A usual method of bacteriological examination of water with search for bacteria indicative of pollution (total coliforms, fecal coliforms and fecal streptococci) was implemented. The identification and enumeration of coliform bacteria was made in liquid medium on BromoCresol Purple broth with Lactose (BCPL) by the technique of the most probable number.[26] The BCPL liquid medium technique uses two consecutive tests, namely, the presumption test, which is dedicated to the search for total coliforms and the confirmation test, which is dedicated to the search for fecal coliforms from positive tubes of the presumption test. The search and enumeration of fecal streptococci are performed using the technique of colimetry in liquid media. The media used are: the single-concentration Rothe medium, which contains sodium azide as selective agent (Gram-negative secondary flora inhibitor) and the Litsky-Eva medium, which contains in addition to sodium azide a low concentration of crystal violet, which slows the growth of Gram positive bacteria.

Results and discussion

In this section, the characterization of raw leachate, and then the investigation of operational conditions for coagulation-flocculation first using the conventional Jar test procedure and then an ultrasonic process is presented.

Characterization of raw leachate

The leachate was brownish in color and had a pH of 8.15 ± 0.1. Its COD has proven to be very high due to a high organic matter content (see Table 1). It is well known that the strong presence of organic matter allows microorganisms to develop while consuming oxygen. The DO content is therefore a useful parameter in the biological diagnosis of aqueous media. The low oxygen value of 31.7 mg O_2/L shows the presence of high amount of both microbial population (COD > 15000 mg O_2/L) and organic matter (BOD_5 = 700 mg O_2/L). The values of conductivity, turbidity and

Table 1. Physicochemical characterization of raw leachate.

Parameters	Results	Units
pH	8.16	-
COD	>15000	mg O_2/L
BOD_5	700	mg O_2/L
DO	31.7	mg O_2/L
Turbidity	95.2	NTU
Refractive index	1.3405	-
Conductivity	90.3	mS/cm
NO_3^-	909.23	mg/L

refractive index are also high because of the presence of minerals ions and colloidal particles.

Optimization of operational parameters for the Jar-test procedure

Effect of pH

Liquid discharges naturally contain different suspended particles such as colloidal particles and biopolymers, which are responsible for their color and turbidity.[27,28] The pH adjustment of the raw leachate (at 3.5 ±0.2 and 7.5 ± 0.2) gave a supernatant with a better clarity than without pH adjustment (Fig. 1a). The percentage of clarity with pH adjustment is: 95.3% (T_s = 4.5 NTU), 92.0% (T_s = 7.59 NTU) and 73.2% (T_s = 25.5 NTU) for ferric chloride, aluminum sulfate and ordinary alum, respectively, at a coagulant concentration of 5%. It is found that ferric chloride is the most efficient. The acidification of the raw leachate at pH 3.5 ± 0.2 provides a more favorable environment for neutralization of colloidal particles while the increase of pH at 7.5 ± 0.2 (after addition of coagulant) allows the formation of flocs.[29,30]

Electric conductivity provides information on the totality of the soluble salts in the water.[31] As shown in Fig. 1b, for a treatment performed without any pH adjustment, the conductivity of supernatants drops significantly as compared with the conductivity of the raw leachate (90.3 mS/cm). The conductivity drops are: ~53%, ~78% and ~66% for ferric chloride, aluminum sulfate and ordinary alum, respectively. However, the conductivity of supernatants slightly increases when the pH of leachate was adjusted, precisely because of the addition of acid and base.

Figure 1c shows the pH measurements made on the different supernatants. In the case of no pH adjustment, all the supernatants have an acidic pH. This result can be explained by the acidic nature of the added coagulants. On the other hand, when the pH of leachate was adjusted, the pH of supernatants was between 7 and 8. This can be explained by the stabilization of the flocculation process.[29]

The measured refractive indices indicate values close to that of pure water (1.33) for all supernatants with or without pH adjustment. This is due to the efficiency of the coagulation-flocculation treatment (Fig. 1d).

As can be seen from Fig. 1e, treatments carried out with pH adjustment ensures a better elimination of SS (except for the treatment performed with ordinary alum) as compared with those performed without pH adjustment. This result is consistent with the clarity increase (i.e., turbidity reduction) shown in Fig. 1a.

Fig. 1f shows that treatment of raw leachate without any pH adjustment produces less sludge as compared with that performed with a pH adjustment, regardless of coagulants. This result is due to the formation of iron hydroxide or aluminum hydroxide flocs at pH 7.5 ± 0.2. The treatment with pH adjustment is therefore more efficient.

Effect of concentration and nature of coagulant

Figure 2a shows the effect of coagulant dose on the clarity of leachate (i.e. the turbidity reduction). An optimal dose of 15% is observed for the three coagulants, the concentration effect being more significant for ordinary alum than for the other two. The clarity increase with the amount of coagulant can be explained by a more efficient neutralization of colloids resulting in a lower zeta potential that promotes the formation of flocs and therefore, a better clarification.

The same phenomenon was observed during the clarification of solutions loaded with sodium humate thanks to the use of aluminum sulfate. A better clarification was also achieved for a higher coagulant concentration.[32]

On the other hand, an excessive rise in the coagulant dose may no longer be efficient (as in the case of ordinary alum) when the solution becomes saturated with reagents, which badly influences the clarity of the solution. The same trend was observed in the case of leachate treated with ferric chloride or aluminum sulfate. It was found that the dark brown color of raw leachate turned after sludge separation with increasing coagulant dose. This color change can be explained by the redissolution of metal hydroxides causing darkening of the supernatant and increase in turbidity.[33]

As can be seen in Fig. 2a, the clarity sequence follows the following order: ferric chloride > aluminum sulfate > ordinary alum, with values of 98.7% (T_s = 1.25 NTU), 96.6% (T_s = 3.25 NTU) and 88.1% (T_s = 11.35 NTU) at the coagulant dose of 15%, respectively. The best efficiency of ferric salts as compared with aluminum salts has already been reported by many authors and can be attributed to the stronger reduction power of ferric coagulant.[34,35]

Effect of stirring speed

The stirring speed is a very important factor in the coagulation-flocculation process because it contributes to the destabilization of colloidal particles by giving them the possibility of sticking together.[36]

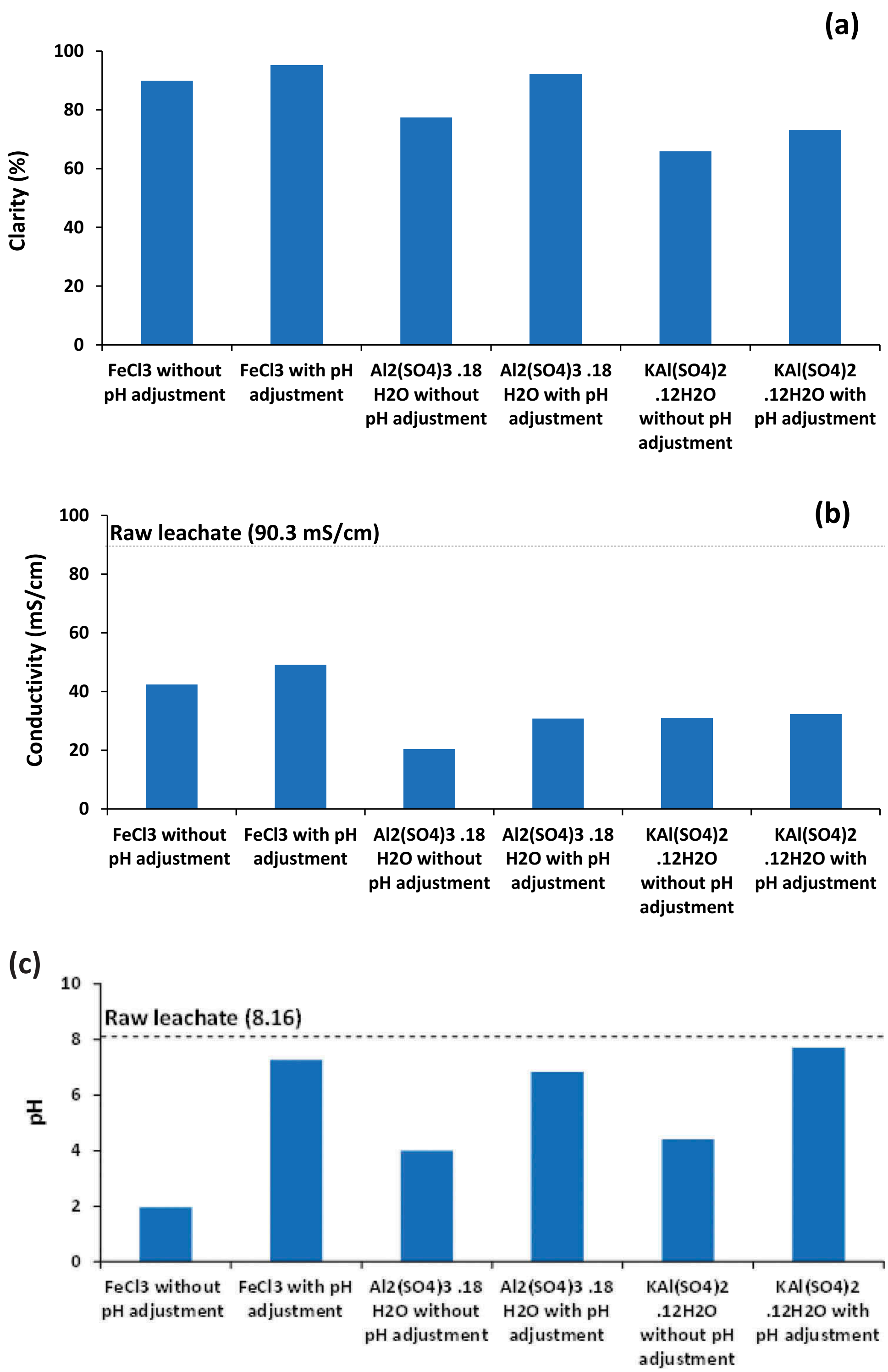


Figure 1. (a–f) Effect of pH adjustment of the leachate on some physicochemical parameters of supernatants recovered after treatment by coagulation-flocculation using conventional Jar test procedure. T_{rl} = 95.2 NTU; Stirring speed: 150 rpm; Stirring time: 15 min; Coagulant dose: 5%; $V_{Coagulant}/V_{Leachate}$ = 1.

Fig. 2b shows that an optimum clarity is obtained for a stirring speed of 250 rpm, regardless of the coagulant used. It is of 99.4% (T_s = 0.61 NTU), 98.6% (T_s = 1.35 NTU) and 98.3% (T_s = 1.62 NTU) for ferric chloride, aluminum sulfate and ordinary alum, respectively. Beyond this speed,

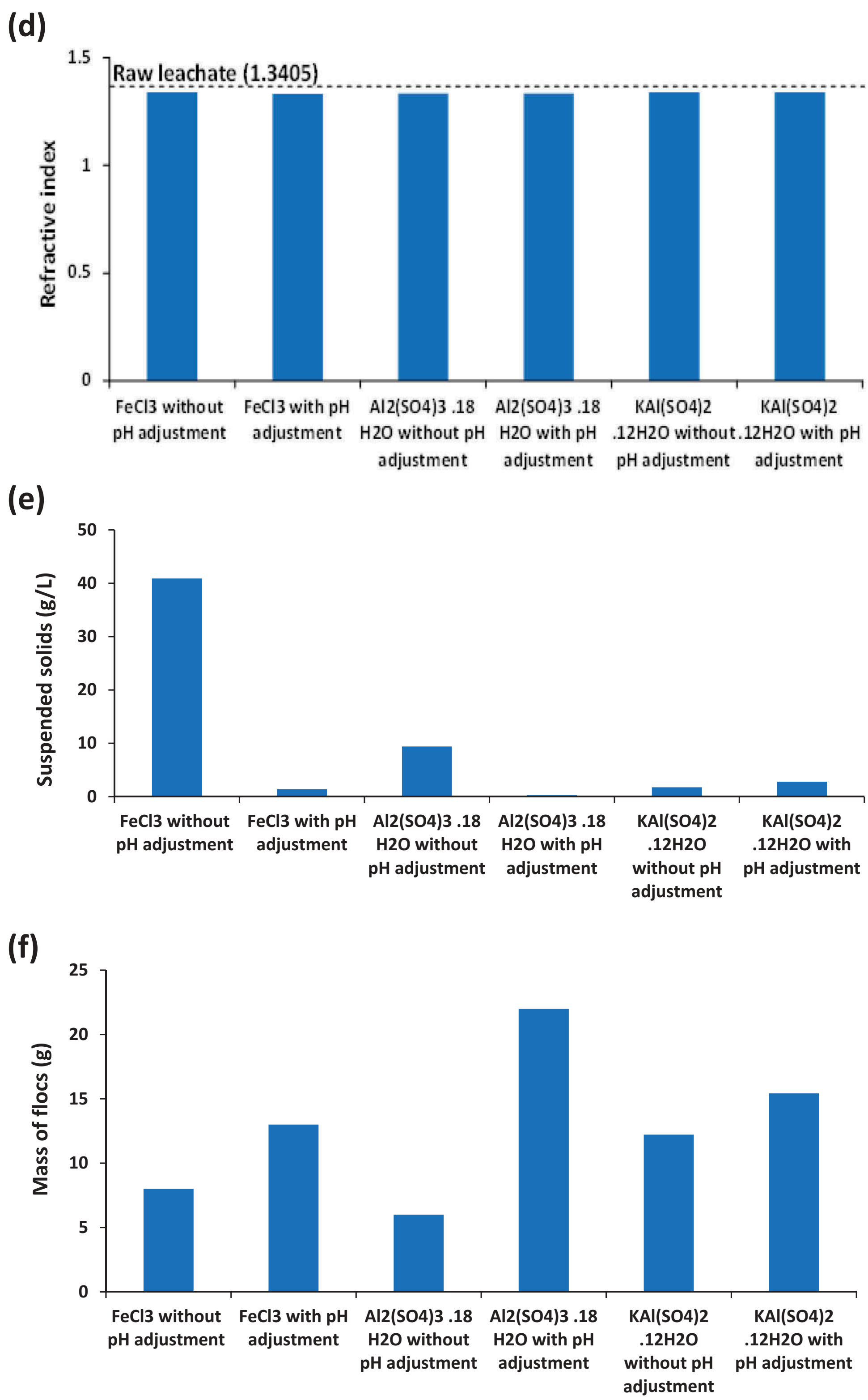


Figure 1. (Continued).

a drop in the clarity is observed, which would mean that the speed gradient imposed during the orthokinetic phase would have little influence on the clarification of the medium.[32]

Effect of stirring time

Fig. 2c shows that a maximum clarity (minimum turbidity) is reached after a stirring time of 5 min. for both aluminum sulfate (98.9% i.e. T_s = 1.01 NTU) and

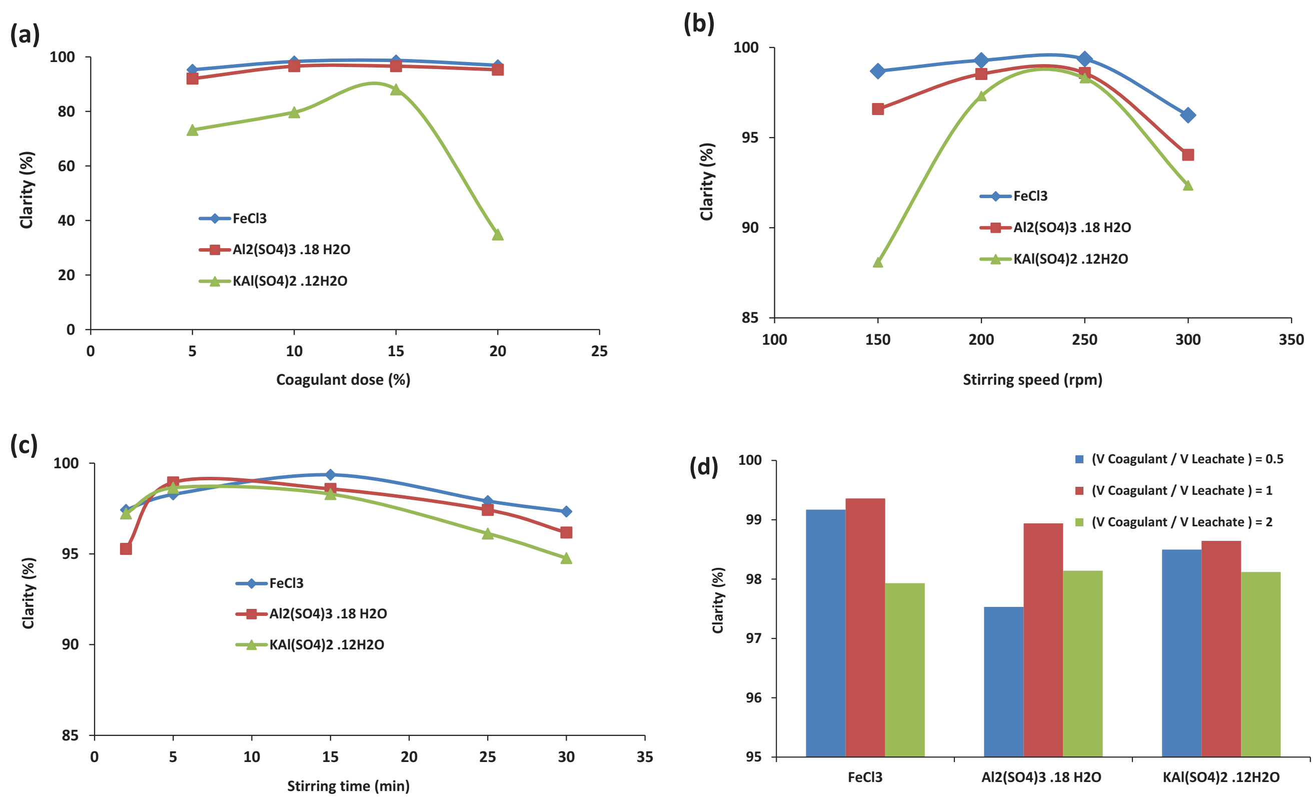


Figure 2. (a-d) Effect of the operating condition on the clarity of leachates treated by coagulation-flocculation using conventional Jar test procedure. T_{rl} = 95.2 NTU; pH of the leachate was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant.

ordinary alum (98.6% i.e. T_s = 1.29 NTU). For ferric chloride, the best clarity (99.4% i.e. Ts = 0.61 NTU) is obtained after a stirring time of 15 min. This difference can be assigned to faster hydrolysis reactions for aluminum sulfate and ordinary alum than for ferric chloride. Similar results have been reported about treatment of solutions polluted with organic substances by aluminum sulfate. However, the optimum stirring time varied from a few seconds to 10 min. This was explained by the fact that hydrolysis reactions of coagulants were very rapid.[32]

Effect of the volume ratio of coagulant to leachate

For each coagulant, the parameters previously studied were fixed at their optimum value to investigate the effect of the volume ratio of coagulant to leachate. Ratios of 0.5, 1 and 2 were considered. The assessment of this new parameter was extended not only to physicochemical but also biochemical and bacteriological analyzes. As can be seen in Fig. 2d, the optimum clarity of the supernatant was obtained for a ratio $V_{Coagulant}/V_{Leachate}$ of 1 providing a clarity of 99.4%, 98.9% and 98.6% for ferric chloride, aluminum sulfate and ordinary alum, respectively. The clarity of the supernatants improved by increasing the ratio from 0.5 to 1 since the amount of coagulant has been increased, which results in more metal cations in solution to neutralize the surface charge of colloidal particles, thus promoting their coagulation and decantation.[37] However, the increase in the ratio $V_{Coagulant}/V_{Leachate}$ to 2 has a negative effect on the reduction of turbidity. This can be explained by the fact that for this ratio, the amount of coagulant may be in excess relative to the charge of colloidal particles, which leads to a saturation in reagents resulting in a clarity drop.[38]

Figure S1 displays the AT, CAT and HT of supernatants for the three coagulants used. It appears that the AT is zero and the CAT is low, irrespective of the coagulant used. On the other hand, the HT is more or less high depending on the coagulant used. However, the lowest value was systematically obtained for a ratio $V_{Coagulant}/V_{Leachate}$ of 1.

Figure 3 shows that nitrates are also present in the supernatants. Their high concentration is essentially due to a strong bacterial nitrification by a mineralization of ammoniacal nitrogen to nitrates.[39] It is found that the nitrate content of the supernatants depends on the ratio $V_{Coagulant}/V_{Leachate}$, the minimum values being obtained for a ratio of 1. The lowest nitrate concentration (about

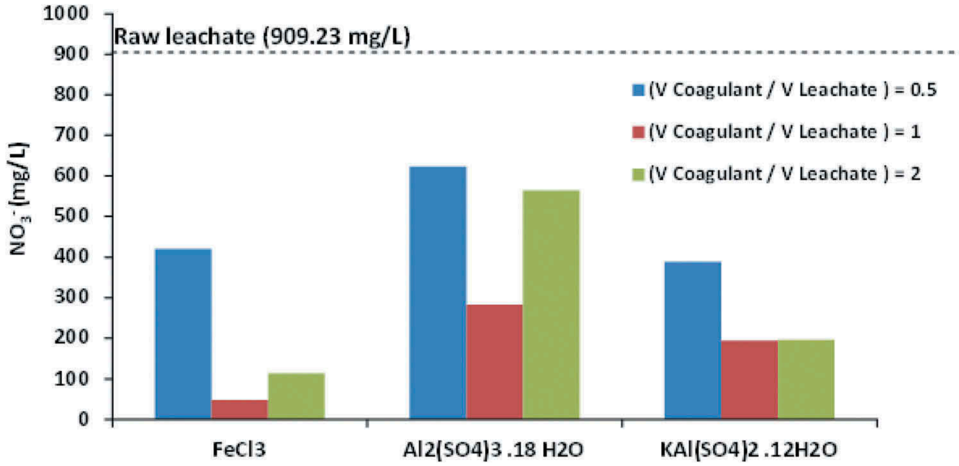


Figure 3. Effect of volume ratio ($V_{Coagulant}/V_{Leachate}$) on nitrate concentration of leachates treated by coagulation-flocculation using conventional Jar test procedure. Stirring speed: 250 rpm; Stirring time: 5 min for both $Al_2(SO_4)_3.18H_2O$ and $KAl(SO_4)_2.12H_2O$ and 15 min for $FeCl_3$; Coagulant dose: 15%; pH of the leachate was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant.

48 mg/L) is obtained when $FeCl_3$ was used causing a nitrate reduction of 95% (the nitrate concentration of the raw leachate is 909.23 mg/L). Some authors have also reported that coagulation-flocculation process was of practical interest for treating raw waters heavily loaded with nitrates and denitrification yields could be improved by adding activated carbon powder as a coagulation aid.[40]

Figure 4 shows the results of DO, BOD_5 and COD for the three coagulants used. The significant decrease of DO, BOD_5 and COD shows the beneficial effect of the coagulation-flocculation process for the reduction of polluting organic matter. This result can be explained by the adsorption of the polluting mineral and organic substances on the metal hydroxides involving Van Der Waals forces or hydrogen bonds.[32,41] The best abatements were obtained for a ratio $V_{Coagulant}/V_{Leachate}$ of 1 for all coagulants. The treatment performed with $FeCl_3$ gave the highest drops, i.e. 90.7% for DO (final DO = 2.94 mg O_2/L), 85.7% for BOD_5 (final BOD_5 = 100 mg O_2/L) and 96.8% for COD (final COD = 474 mg O_2/L).

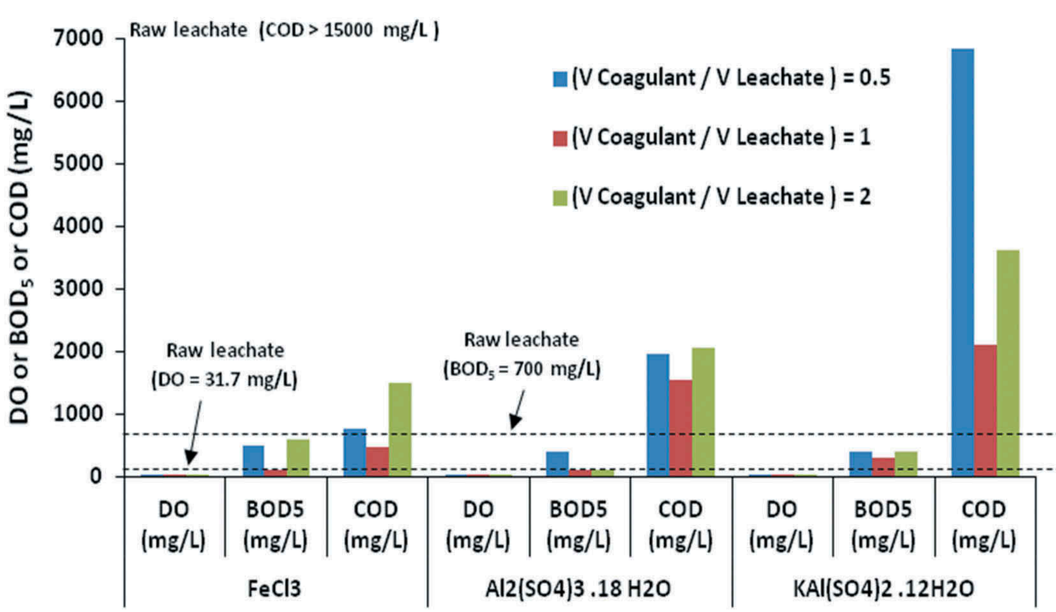


Figure 4. Effect of volume ratio ($V_{Coagulant}/V_{Leachate}$) on DO, BOD_5 and COD concentrations of leachates treated by coagulation-flocculation using conventional Jar test procedure. Stirring speed: 250 rpm; Stirring time: 5 min for both $Al_2(SO_4)_3.18H_2O$ and $KAl(SO_4)_2.12H_2O$ and 15 min for $FeCl_3$; Coagulant dose: 15%; pH of the leachate was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant.

Ferric chloride is therefore a more effective coagulant than aluminum sulfate and ordinary alum to reduce dissolved matter.[35,42]

The sludge recovered after leachate treatment was analyzed under the optical microscope. Table 2 shows micrographs of sludge obtained for each coagulant used. This sewage sludge mainly consists of solid particles containing organic matter, mineral matter and microorganisms. Photos show a somewhat similar texture, especially for sludge recovered from leachate treatment with ferric chloride and aluminum sulfate. The difference lies rather in the color depending on the ratio $V_{Coagulant}/V_{Leachate}$ used. The most blackish sludge was obtained for a volume ratio of 1. This can be explained by the difference in the chemical composition where the carbon content is probably high in these sludge samples, this being supported by a better clarity of the supernatants.

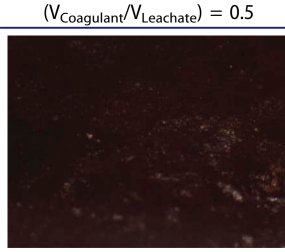
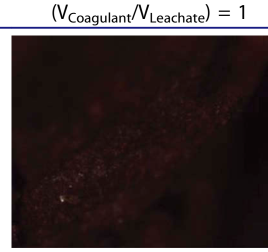
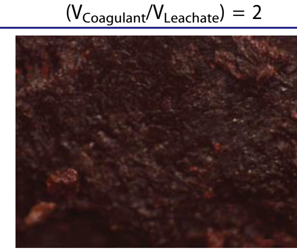
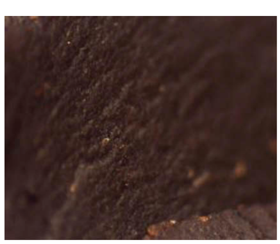
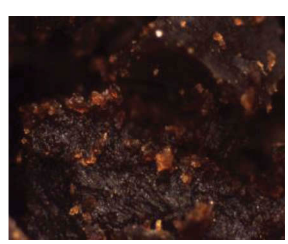
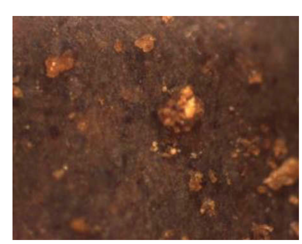
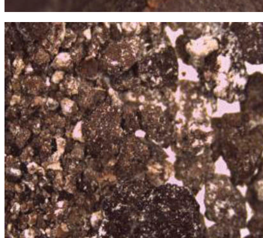
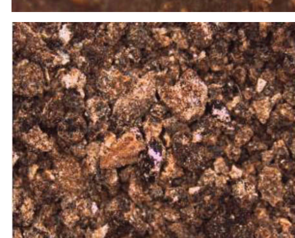
The sludge recovered after a treatment performed with a ratio $V_{Coagulant}/V_{Leachate}$ equal to 1 have also been analyzed by FTIR. As can be seen in Fig. 5, similar spectra were obtained for sludges formed after treatment with ferric chloride or aluminum sulfate whereas the spectrum obtained for sludges formed after treatment with ordinary alum displays some differences.

On the spectra concerning ferric chloride and aluminum sulfate, two peak appears at 657 and 1535 cm^{-1}, which can be assigned to C-Br stretching vibration bond of bromoalkanes and C = C stretching vibrations of alkenes, respectively. The picks observed at 2310 and 2372 cm^{-1} can be attributed to C ≡N stretching vibration bonds. For wavenumbers higher than 3500 cm^{-1}, the spectrum for aluminum sulfate shows additional peaks at 3603, 3724 and 3857 cm^{-1}, which corresponds to the free O-H bonds, these hydroxyl groups can be due to alcohols or carboxylic acids and/or to simple hydroxyls belonging to the free water circulating in the sludge

For the sludge recovered after treatment with ordinary alum, only the presence of the bond C-Br is detected (at 623 cm^{-1}) as compared with other two spectra. In contrast, a thin band of strong intensity is observed around 1099 cm^{-1}, which is characteristic of the stretching vibrations of C-O bonds belonging to alcohol and phenol functions. Two other peaks resulting from the C = C stretching vibrations also appear at 1423 and 1645 cm^{-1}. As for the wide band centered at 3410 cm^{-1}, it can be assigned to the vibration of linked O-H bonds.

In conclusion, the bands in the IR spectra proves the elimination of colloidal species of organic and/or inorganic nature from the leachate by coagulation process,

Table 2. Sludge under Leica microscope recovered from leachate treatment by coagulation-flocculation assisted with test jar procedure. Stirring speed = 250 rpm; stirring time = 5min for both $Al_2(SO_4)_3.18H_2O$ and $KAl(SO_4)_2.12H_2O$ and 15min for $FeCl_3$; coagulant dose = 15%; pH of the medium was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant.

	$(V_{Coagulant}/V_{Leachate}) = 0.5$	$(V_{Coagulant}/V_{Leachate}) = 1$	$(V_{Coagulant}/V_{Leachate}) = 2$
$FeCl_3$			
$Al_2 (SO_4)_3 .18 H_2O$			
$KAl(SO_4)_2.12H_2O$			

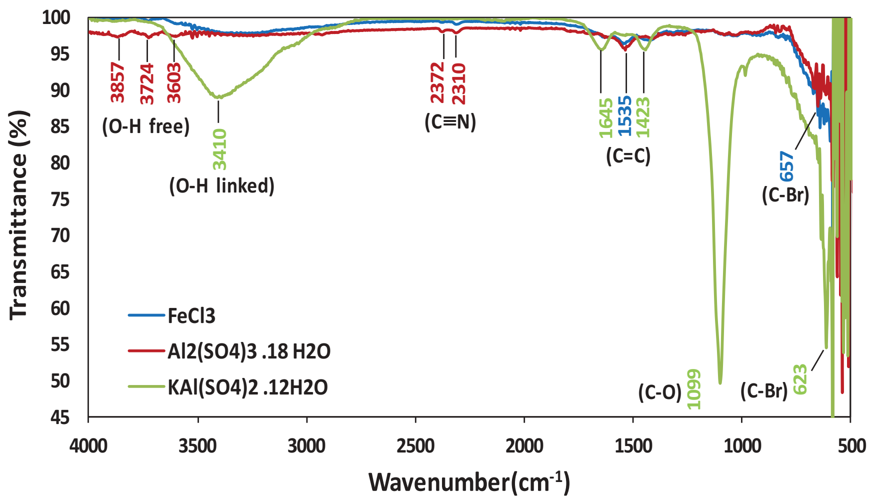


Figure 5. Infrared spectra of sludge recovered after leachate treatment by coagulation-flocculation using conventional Jar test procedure. Stirring speed: 250 rpm; Stirring time: 5 min for both $Al_2(SO_4)_3.18H_2O$ and $KAl(SO_4)_2.12H_2O$ and 15 min for $FeCl_3$; Coagulant dose: 15%; $V_{Coagulant}/V_{Leachate} = 1$; pH of the leachate was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant.

which leads to the formation of flocs rich in different functions. Similar results showing that metal hydroxides formed during the coagulation-flocculation process are able to adsorb and sweep the organic matter have been reported in literature.[31,43]

The enumeration of total germs is an overall indicator of microbiological pollution, which measures the totality of the bacterial load. The stability of bacterial counts is therefore a good sign of protection. As shown in Table 3, the results of bacteriological quality analysis of leachates treated with $FeCl_3$ and $Al_2(SO_4)_3.18\ H_2O$ revealed the absence of total germs, fecal coliforms, and streptococci. The germs enumeration in supernatants was performed according to the Most Probable Number (MPN) from the table of Mac Grady.[44]

For the supernatant sample treated with ordinary alum and a ratio $V_{coagulant}/V_{lixiviat}$ of 0.5, the characteristic numbers related to the enumeration of total coliforms are "311" and "210", which corresponds (in the MPN table) to 75 total coliforms and 15 fecal coliforms per 100 mL, respectively, while the characteristic number related to the Fecal Streptococci enumeration count is "010", which corresponds to 3 fecal Streptococci per 100 mL.

For the supernatant sample, the ratio $V_{Coagulant}/V_{Leachate}$ of which is 1, the coliforms include 9 total germs, 4 fecal germs and 3 fecal Streptococci per 100 mL.

For the supernatant sample, the ratio $V_{Coagulant}/V_{Leachate}$ of which is 2, the coliforms include 28 total germs, 20 fecal germs and 4 fecal Streptococci per 100 mL. These results comply with the standards prescribed by the Algerian regulations (≤ 10 germs

Table 3. Germs enumeration in supernatants recovered from leachate treatment by coagulation-flocculation assisted with test jar procedure according to the NPP table (results of bacteriological analyzes). Stirring speed = 250 rpm; stirring time = 5min for both $Al_2(SO_4)_3.18H_2O$ and $KAl(SO_4)_2.12H_2O$ and 15min for $FeCl_3$; coagulant dose = 15%; pH of the medium was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant.

		BCPL				ROTHE	
Coagulant	($V_{coagulant}/V_{lixiviat}$)	Characteristic number	Number of total coliforms in 100 mL	Characteristic number	Number of faecal coliforms in 100 mL	Characteristic number	Number of Faecal Streptococci in 100 mL
$FeCl_3$	0.5	000	**0**	000	**0**	000	**0**
	1	000	**0**	000	**0**	000	**0**
	2	000	**0**	000	**0**	000	**0**
$Al_2(SO_4)_3.\ 18\ H_2O$	0.5	000	**0**	000	**0**	000	**0**
	1	000	**0**	000	**0**	000	**0**
	2	000	**0**	000	**0**	000	**0**
KAl(SO4)2 .12H2O	0.5	311	**75**	210	**15**	010	**3**
	1	200	**9**	100	**4**	010	**3**
	2	221	**28**	211	**20**	100	**4**

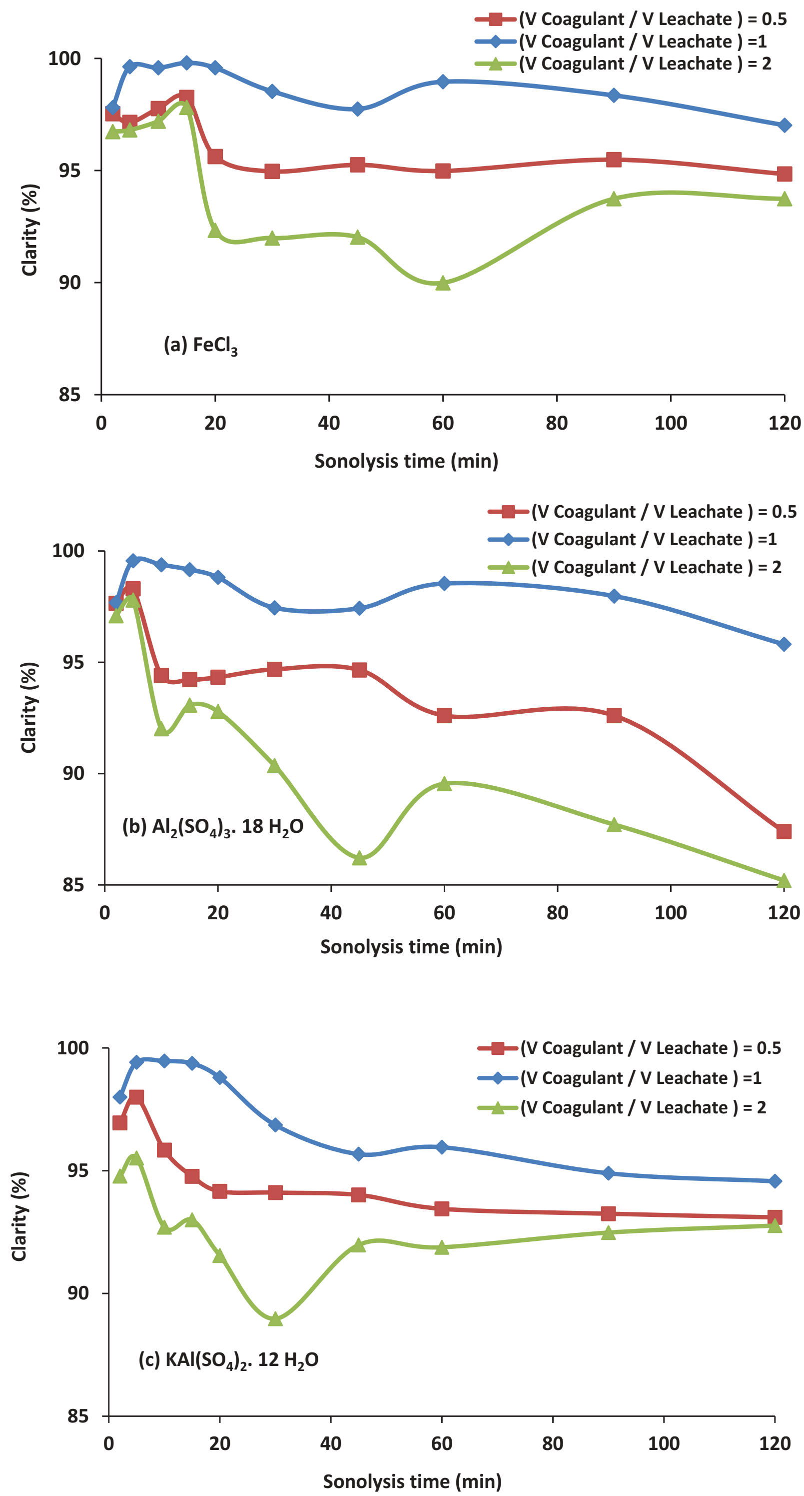


Figure 6. (a-c) Effect of sonolysis time on the clarity of leachates treated by coagulation-flocculation. T_{rl} = 95.2 NTU; Coagulant dose: 15%; pH of the leachate was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant.

per ml at 37°C and ≤ 100 germs per ml at 22°C). It should be noted that the number of fecal streptococci is very low, thus meeting the potability standards of the recovered water. The number of total and fecal coliforms as well as the number of fecal streptococci of the supernatant sample (for which the ratio $V_{Coagulant}/V_{Leachate}$ was equal to 1), are close to those of water. The near total absence of fecal coliforms can be explained by the absence of pollution, in particular by Escherichia-Coli.

Coagulation process under ultrasonic waves

Effect of sonolysis time

Preliminary tests were performed by exposing raw leachate (V = 50 mL) to ultrasonic radiation for a contact time varying between 2 min and 18 hr. After this step, the leachate was left for decantation for 6 hr. However, no separation was found. This can be explained by the fact that the frequency of the ultrasonic radiation (37 kHz) is not energizing enough to enable particles in solution to combine and separate from the liquid.

In the following tests, leachate-coagulant mixtures were exposed to ultrasound waves for 2 to 120 min. All experiments were conducted at a controlled pH: at pH = 3.5 ± 0.2 before addition of coagulant and pH = 7.5 ± 0.2 after addition of coagulant.

The best clarity of supernatants was obtained for a volume ratio $V_{Coagulant}/V_{Leachate}$ of 1 irrespective of the coagulant agent employed (Fig. 6a-c).

Turbidity reduction reached 99.8% (T_s = 0.19 NTU) for a treatment carried out with ferric chloride and for a sonolysis time of 15 min. It was 99,6% (T_s = 0.42 NTU) and 99.4% (T_s = 0.56 NTU) for a treatment performed with aluminum sulfate and ordinary alum, respectively, and for a sonolysis time of 5 min.

This hybrid method using ultrasound-assisted coagulation-flocculation technique has proved to be efficient. This can be explained by the agitation of the leachate-coagulant mixture induced by the fluid jet created by cavitation.[45] This agitation causes the destabilization of the colloidal particles and their neutralization.

As can be seen in Fig. 6, for the three coagulants, the turbidity drops more when the ratio $V_{Coagulant}/V_{Leachate}$ is increased from 0.5 to 1. This is due to the introduction of a higher quantity of metal cations, which can more neutralize the surface charge of colloidal particles.[46] On the contrary, the treatment becomes less efficient with the increase of the ratio $V_{Coagulant}/V_{Leachate}$ from 1 to 2. This is probably due to an excess of coagulant that can cause the formation of various species making the solution less clear. For these ultrasound-assisted experiments, it is also found that the supernatants recovered after treatment with ferric chloride are the clearest. This finding has already been reported by many authors.[35,42,47] Fig. 6 show that long exposure to ultrasound causes an increase in the turbidity. This phenomenon can be due to the effect of ultrasound on chemical reactions, which can generate inhibitory ions. The presence of these ions in the solution causes the reduction of the vapor pressure and an increase of the surface tension thus favoring a more violent collapse of the cavitation bubble.[48]

For all experiments, it was found that the temperature of the reaction mixture increased with the sonolyis time, steadily up to about 50 min, and then less strongly for longer times. An example (chloride ferric as coagulant and volume ratio of 1) is shown in Figure S2. From these results, it is found that the temperature increased by 57% for the mixture. This phenomenon can be attributed to the generation of cavitation bubbles. The formation of these bubbles produces areas of voids in the medium. These vacuum zones create a sector with high pressure and high temperature.[49]

A comparison between the percentages of clarity of the supernatants obtained after coagulation-flocculation treatment assisted by ultrasound and those obtained using the conventional Jar test procedure is presented in Fig. 7a-c. As can be seen, better results are obtained when ultrasound are used. The formation and evolution of the cavitation bubbles are the essential events of the ultrasound action for the medium. When water vapor, dissolved gases and substances are exposed to the extreme conditions of the cavitation bubble, the breakage of chemical bonds occurs instantly.[45] In other words, it results from the sonolysis of water induced reactions that lead to the formation of oxidizing species such as $O^{\bullet}$, $HO^{\bullet}$, $HOO^{\bullet}$ and H_2O_2 capable of degrading pollutants. Cavitation bubbles are considered as microreactors and are the locus of all sonochemical reactions.[49] When aqueous sonolysis occurs in the presence of solutes, a number of chemical processes may occur depending on their physical and chemical nature.

Effect of temperature

To investigate the effect of temperature on the leachate clarity, the procedure used was as follows: pH adjustment of leachate before and after addition of coagulant. The sonolysis time was 15 min. for $FeCl_3$ treatment and 5 min. for $KAl(SO_4)_2.12H_2O$ and $Al_2(SO_4)_3.18H_2O$.

It is clear that the percentage of clarity of the supernatants decreases with temperature (Fig. 8a-c) and BOD_5 increases with temperature (Figures S3 a-c). The decrease in the efficiency of ultrasound with increasing temperature can be explained by the fact that temperature changes the viscosity of the medium, the concentration of dissolved gas and the vapor pressure. Most sonochemical reactions are promoted by lowering temperature.[50,51] The best results are obtained at a temperature of 20°C and for a volume ratio equals to 1, for the three coagulants used. For these conditions, the clarities were 99.8% when treatment was performed with $FeCl_3$ and for sonolysis time of 15 min., 99.6% and 99.4%

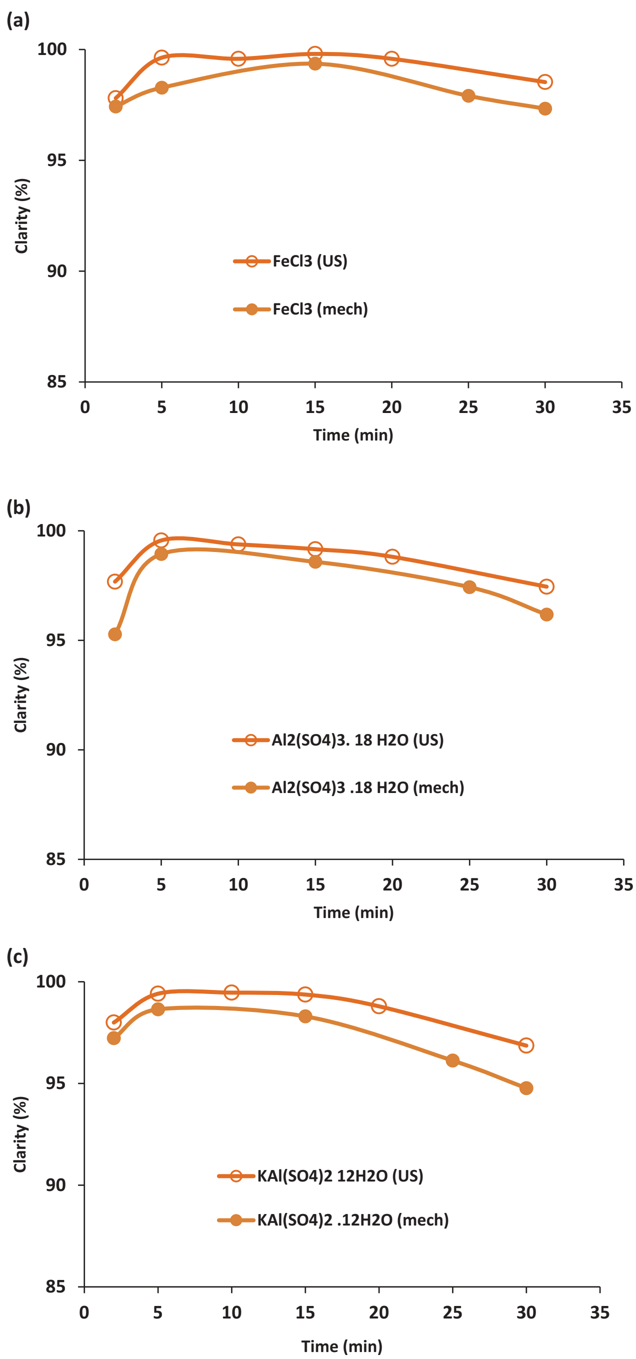


Figure 7. Comparison between clarities of leachates treated by coagulation-flocculation using conventional Jar test procedure and ultrasonic procedure. T_{rl} = 95.2 NTU; Stirring speed: 250 rpm; Coagulant dose: 15%; $V_{Coagulant}/V_{Leachate}$ = 1; pH of the leachate was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant.

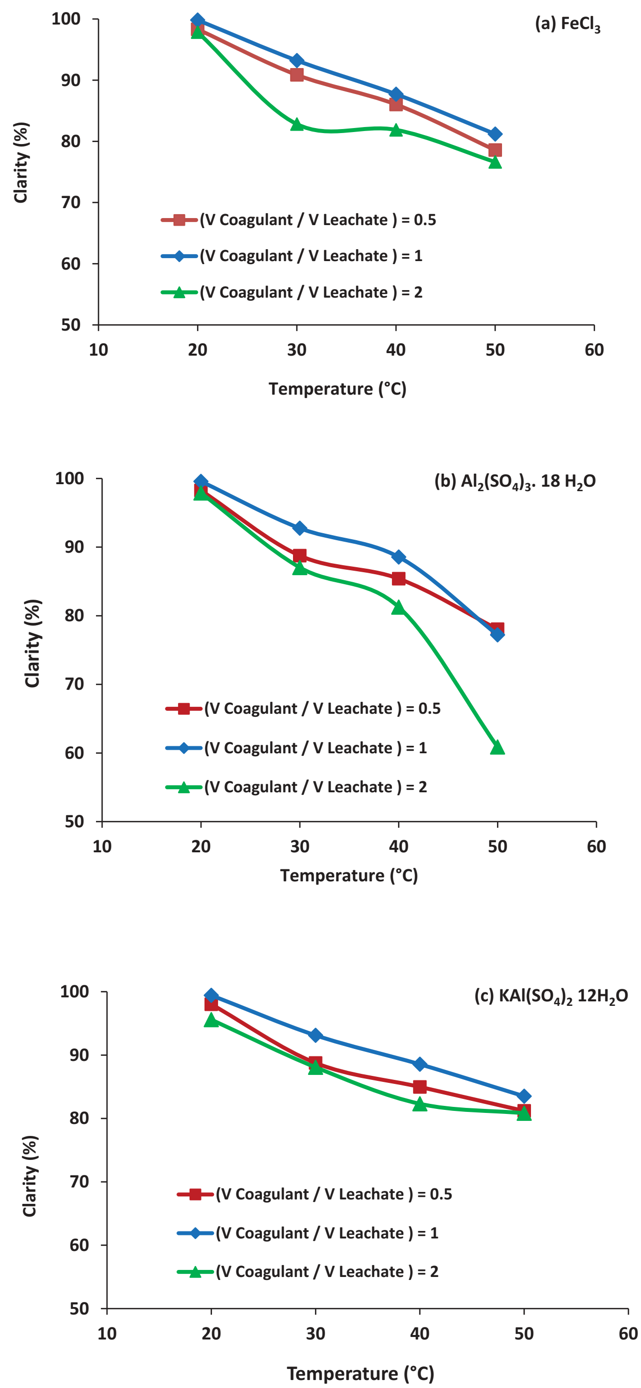


Figure 8. (a-c) Effect of the temperature on the clarity of leachates treated by coagulation-flocculation assisted with ultrasound. T_{rl} = 95.2 NTU; Coagulant dose: 15%; pH of the leachate was adjusted to 3.5 ± 0.2 before adding coagulant and to 7.5 ± 0.2 after adding coagulant. Sonolysis time of 15 min for $FeCl_3$ and 5 min for both $KAl(SO_4)_2.12H_2O$ and $Al_2(SO_4)_3.18H_2O$.

when it was carried out with $Al_2(SO_4)_3.18H_2O$ and $KAl(SO_4)_2.12H_2O$, respectively, and for sonolysis time of 5 min. The best results for BOD_5 were 100 mg O_2/L for both $FeCl_3$ and $Al_2(SO_4)_3.18H_2O$ and 200 mg O_2/mg for $KAl(SO_4)_2.12H_2O$.

Conclusion

The optimization of the coagulation-flocculation process for the treatment of leachate from the Technical Landfill Center of Souk-Ahras city was investigated through the variation of several operational parameters. The efficiency of the process was assessed by monitoring both physicochemical and biochemical parameters before and after treatment. The best conditions for leatchate treatment by the conventional Jar test procedure are: coagulant dose of 15%, stirring speed of 250 rpm and stirring time of 5 min. for both aluminum sulfate and ordinary alum, and 15 min for the ferric chloride, a volume ratio of coagulant to leachate equals to 1. For these conditions, the percentage of clarity is about 99.4%, 98.9% and 98.6% for ferric chloride, aluminum sulfate and ordinary alum, respectively. The characterization of sludge by infrared spectroscopy showed the presence of some functional groups proving the adsorption of organic matter on the hydroxides formed during the flocculation step. On the bacteriological level, the enumeration of total and fecal coliforms as well as fecal streptococci gave values consistent with the standards prescribed by the Algerian regulations. The treatment has therefore proved to be efficient. Moreover, it was shown that the ultrasound agitation in place of mechanical agitation improved the clarity of supernatants. It was also found that the increase in temperature has a negative effect on the clarification of leachate.

Highlights

- The efficiency of the coagulation-flocculation process for the treatment of leachate was assessed by monitoring both physicochemical (turbidity, DO, COD, etc) and biochemical (BOD_5, germs enumeration, etc) parameters.
- The ultrasound agitation improved the clarity of supernatants as compared with mechanical agitation.
- Clarities of 99.8%, 99.6% and 99.4% were obtained for a treatment performed with ferric chloride, aluminium sulphate and ordinary alum, respectively.
- The increase in temperature has a negative effect on the clarification of leachate.

Conflicts of interest

The authors declare no conflicts of interest.

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