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INTERACTION BETWEEN CLAY SOILS AND ACIDIC WASTEWATER: TEXTURAL AND STRUCTURAL EVOLUTION

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1. Introduction

Scientific endorsements concerning barrier performances of mineral liners are indispensable to obtain disposal site reliability, and examinations addressing individual quality of natural clays soils are necessary. The use of argillaceous sites for industrial waste storage is due primarily to their very lowest permeability (hydraulic permeability lower than 10^{-9} m/s) [1, 2]. However, it is necessary to choose the type of the most suitable clay which resists better against the waste aggressiveness (acidic, basic, radioactive wastes…) and have low porosity and high sorption capacity.

Various investigations have been carried out on the clay-polluant systems [3, 4]. Several authors [5–7] reported that the contact of a chemical solution with an argillaceous barrier gives a significant modification of the textural and structural properties. Generally, the acid solutions are the most aggressive compounds, which destroy the crystalline structure of clays, especially the octahedral layer [8]. The clay soils used for the experimental works has been chosen among three Tunisian sites (soil1, Soil2 and Soil3) originated from Gabes region. The industrial waste is consisted of an enormous quantity of solid powder accompanied by a liquid solution of high acidity (pH varies between 2 and 3), this acid solution (leachate) is very charged by a noxious elements (F, Cl, S, P). Moreover, the leachate permeability test of the three soils have been studied in our laboratory using a permeameter [9].

The present study consists to correlate the permeability variations with the textural and structural modifications of clay soils, produced by the acid attack and noxious elements sorption in clay minerals. Firstly, we used N_2 adsorption to determine the surface area and the pore size distribution by MP method. Secondly, we used the scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) to investigate the particles form variation and to detect the noxious elements fixed in clays.

2. Materials and methods

2.1. Soils

Samples used in this work provided from three sites of the south of Tunisia (soil-1, Soil-2 and Soil-3) in the form of intact carrots pack in PVC tubes to avoid any contamination coming from the external environment. The depths of the taking away are respectively 17.60; 10.10 and 12.15 m. The permeability tests are carried out by using the samples without modification, to keep the originality of materials with a view to its use as discharge basin. The mineralogical composition of these samples, are summarized in Table 1. On the other hand, the industrial waste is compound by significant amounts of solid combined with a liquid solution of pH=2.7 heavily loaded with harmful elements (Table 2).

Table 1. Mineralogical composition, of three soils.

Sample	Mineralogical composition of clay samples (%)						
	Paly	Smec	Kao	Il	Q	Ca	Do
Soil-1	35.4	1.7	14.9	-	29.1	18.9	-
Soil-2	-	56.3	6.5	-	12.5	24.7	-
Soil-3	-	-	22.9	62.7	9.7	-	4.7

Paly: palygorskite, Smec: Smectite, Kao: Kaolinite, Il: Illite, Q: Quartz, Ca: Calcite, Do: Dolomite

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Table 2. The composition of the leaching solution

ions	Initial concentration in wastewater (mg/L)
F^-	2360
Cl^-	880
PO_4^{3-}	1500
Na^+	2836
SO_4^{2-}	1563
Ca^{2+}	850

2.2. Permeability test

The permeability has carried out using an odeometer (permeameter) [9]. The hydraulic conductivity k (cm/s) governed by the Darcy law, was calculated by the following equation [10].

$$k = \frac{2.3aL}{At}\log\frac{h_1}{h_2}.$$

Where, “A” is the cross-sectional of the sample, “a” is the cross-sectional area of the presser tube of the water column. “L” is the thickness of the sample, “t” is the time interval between the readings of the levels h_1 and h_2, “h_1” is the initial height of water, “h_2” is the final height of water at the time t.

2.3. Textural measurements

Nitrogen sorption isotherms at liquid nitrogen temperature (77 K) were obtained with a Quantachrom-Autosorb1 unit using a volumetric technique. Prior to analysis, all samples have been degassed in vacuum at 160 °C during 4 hours. BET surface areas were calculated from the nitrogen adsorption isotherm at relative pressures ranging from 0.05 to 0.35. The total pore volume was derived from the amount of nitrogen adsorbed at a relative pressure close to unity ($p/p_0 = 0.99$) by assuming that all accessible pores had been filled with condensed nitrogen in the normal liquid state. We proposed here a micropore analysis method, termed as the MP method, to calculate the micropore size distribution. In the MP method [11], surface area of a group of pores with similar pore size is obtained from the difference in slopes of the tangents drawn at two adjacent points on the *t*-plot. In addition, the pore volume of the pores group is then calculated from the information of surface area and pore size assuming a pore shape. For seeing the argillaceous modification textural inside the grain we well reached measurement of total specific surface of clays using adsorption of ethylene-glycol [12]. The interest of this protocol is that the molecular value of obstruction of the ethylene glycol is independent of the nature of the compensation cation of load, it is equal to 2.22 m^2/mg of ethylene glycol. The total surface area is given by $S_T = 2.22$ p, where p is the weight of ethylene-glycol retained after adsorption stability by mg per gram of sample.

2.4. Scanning electron microscopy (SEM)

Morphological observation was undertaken by PHILIPS FEI QUANTA 200 Scanning Electron Microscope which was employed in conventional high-vacuum mode using gaseous secondary electron and secondary electron detectors respectively. To investigate compositional variation of the untreated soil after permeability test, semiquantitative micro-probe chemical analysis by energy–dispersive spectroscopy (EDS) was performed in SEM in order to characterize the new chemical elements adsorbed in clays soils.

2.5. Instruments for F- , PO_4^{3-}, Cl^- and pH measurements

The fluoride concentrations and pH were measured using a Metrohm 781 pH/Ion Meter and an HI9321 pH meter (HANNA Instruments) respectively. Phosphate concentration was measured by the standard method [13] (vanadomolybdophosphoric acid colorimetric method) using the spectrophotometer Hach DR/4000. Chloride was analysed by Metrohm 716 DMS Titrino, using Silver nitrate solution.

3. Results and Discussion

3.1. Permeability

The permeability study is composed by two parties, first the determination of the permeability coefficient by water, second follow the kinetic permeability using the acidic waste solution. However, Table 3 summarized the coefficient permeability k (m/s), we observe that for soil-1 and soil-3 the permeability $k<10^{-9}$ m/s. But, since the waste solution which will be stored have acidic character (pH=2.7), it is indispensable to follow permeability using leachate solution as function of time (>200 days) Figures 1, 2 and 3. These results show that, it exist an interaction between waste solution and soils. Where, the permeability decreases according to time in the case of soil1-2 and increase from 6.8 10^{-10} to 1.1 10^{-8} m/s for soil-3. This amelioration of permeability found in the case of soil1-2 can be due to the precipitation of some compounds which blocked the water circuit in the specimen. Which are the consequences of the carbonate fraction degradation, relatively higher in both soils see Table 4. In contrary, in the case of soil-3 there is probably formation of inter-connected microcracks which increase the solution flow, because this soil has a few percentage of carbonate and a low plasticity (illitic clay) which is affected moreover by acidic attack. After leachate permeability test, the specimen recovered from permeameter was prepared for the textural and structural study.

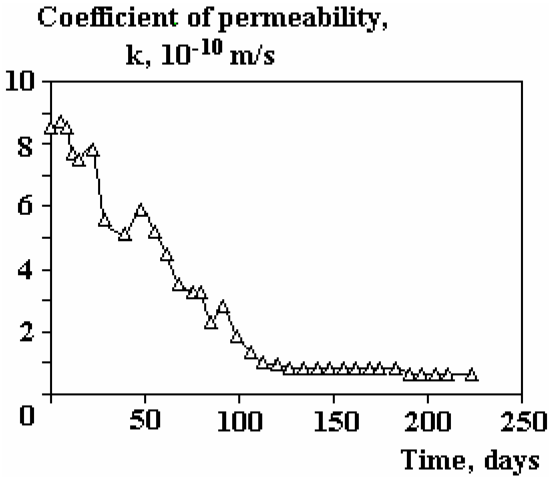


Fig. 1. Variations of leachate permeability with time for soil-1

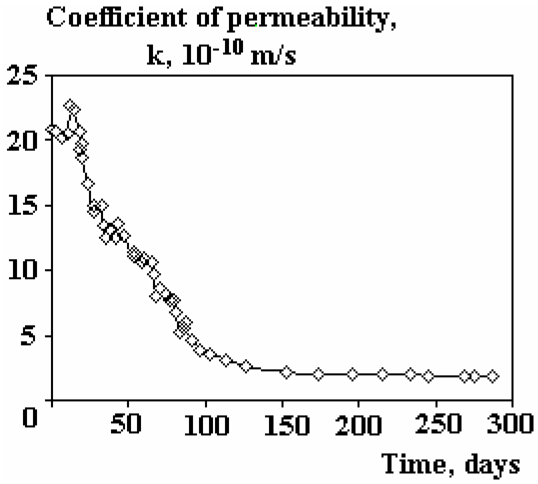


Fig. 2. Variations of leachate permeability with time for soil-2

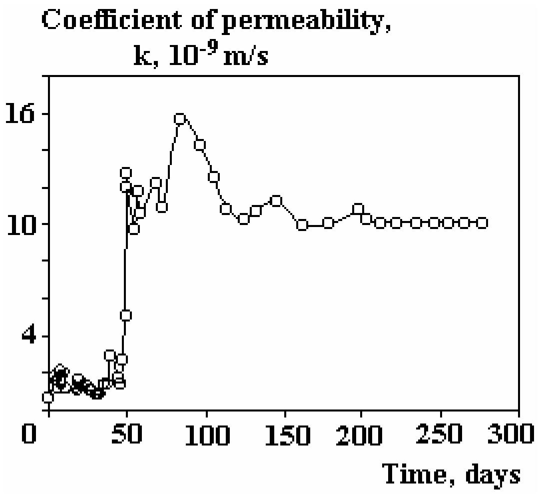


Fig. 3. Variations of leachate permeability with time for soil-3

Table 3. Results of permeability for three soils obtained by odometer

Samples	Water permeability (m/s)	Permeability test using waste solution	
		Permeability (m/s)	Test duration (days)
Soil-1	8.5 10^{-10}	6.2 10^{-11}	223
Soil-2	2.8 10^{-9}	1.9 10^{-10}	287
Soi-l3	6.8 10^{-10}	1.1 10^{-8}	276

Table 4. Percentage of carbonate of soils before and after permeability test

Samples	% of carbonate
Soil-1 crude	18.9
Soil-1 after permeability test	7.7
Soil-2 crude	24.7
Soil-2 after permeability test	12.1
Soil-3 crude	4.7
Soil-3 after permeability test	3.1

3.2. Textural characterization

3.2.1. Nitrogen adsorption isotherms

Figure 4 shows the nitrogen adsorption-desorption isotherms for the three soils before and after permeability test. The shape of the isotherms for all samples corresponds to type II in IUPACs classification and for all isotherms curves, the hysterisis was very clear of H_3 type characteristic of layered materials with slit-shaped pores [14]. Then the isotherms of Soil-1, Soil-2 and Soil-3 don't present a plateau exactly parallel to the pressure axis, which can correspond to the adsorption in some kind of mesoporosity [15].

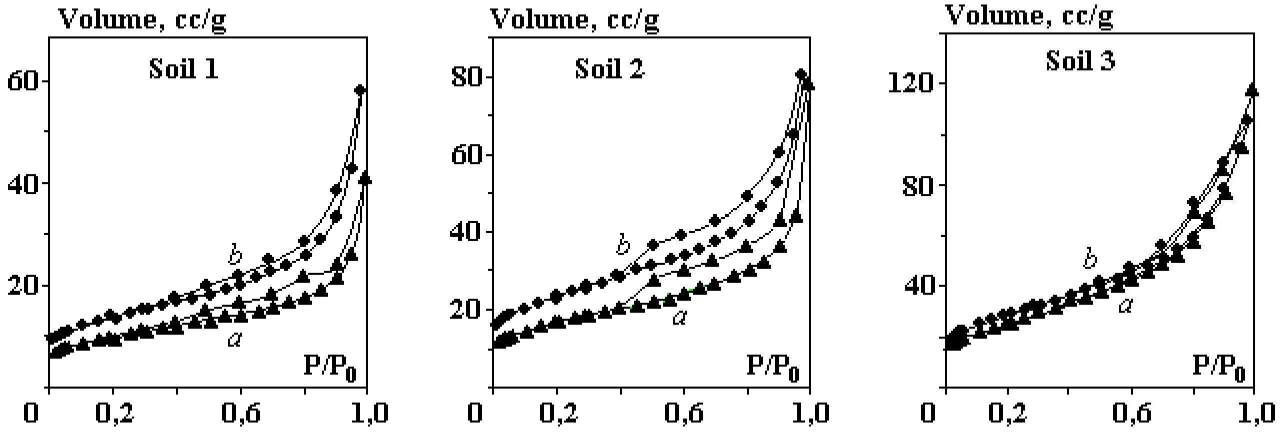


Fig. 4. Nitrogen isotherms of three soils, where; a) raw Soils, b) samples after leachate permeability test

The increase in adsorbed volumes of the leached samples with attack time can be explained by increasing pores numbers in the samples soil-1 and soil-2 [16]. The adsorption and desorption branches of hysteresis loop of the soil-3 before and after permeability test are similar. We can notice that in the cases of soil-1 and soil-2 the pores volume increases after the leachate permeability test, it is clear that the isotherms move upwards with the adsorbing N_2 volume.

3.2.2. Surface Area, porosity and Microporosity

The specific areas and total pores volume of the samples before and after permeability test, as obtained from the isotherms data are collected in Table 5. In the three samples, the acid attack caused by the waste solution after permeability test produces an increase of the specific surface S_{BET} and micropore volume V_{mp}. High specific surface area (S_{BET}) was obtained for soil-3 is due to the important illitic fraction in this sample. Moreover, in the soil3 the textural variation (S_{BET} and V_{mp}) remains very weak. However, higher total specific surface (S_T) was determined for the soil2 because it is constituted by smectic clay which has a significant intern specific surface. Before and after permeability test, the specific surface, total pores and the micropores volumes of soil1 are remained the weakest.

Table 5. Textural parameters of soils before and after permeability test

Samples	S_{BET} (m^2/g)	S_T (m^2/g)	V_{Tp} (cm^3/g)	V_{mp} (cm^3/g)
Soil-1 crude	35 .4	55.7	0.064	0.013
Soil-1 after permeability test	47.4	77.7	0.090	0.019
Soil-2 crude	57.1	209.8	0.122	0.023
Soil-2 after permeability test	70.8	224.2	0.124	0.032
Soil-3 crude	91.5	133.4	0.216	0.035
Soil-3 after permeability test	92.2	134.9	0.164	0.039

S_{BET}: specific surface BET; S_T: total specific surface areas; V_{Tp}: total pores volume at P/P_0 =0.99; V_{mp}: micropore volume

Figure 5 shows the micropore size distributions (MPSD) of the samples calculated by the MP method. For all samples the height of the MPSD curve increase after permeability test indicates the increase of the micropores number and the maximum of micropores volume corresponds to the pores size (12 Å). It's due to the attack of the impurity essentially the carbonate by the acid lixiviat. The micropores volume highest is that of soil-3, also the three curves have a Gaussian form where it represents a more uniform micropores size distributions in the 11–13 Å range.

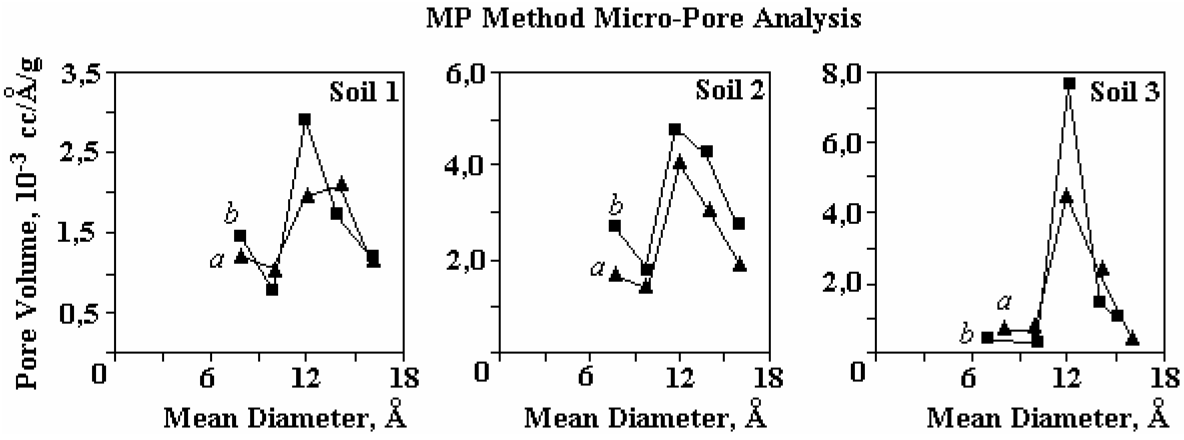
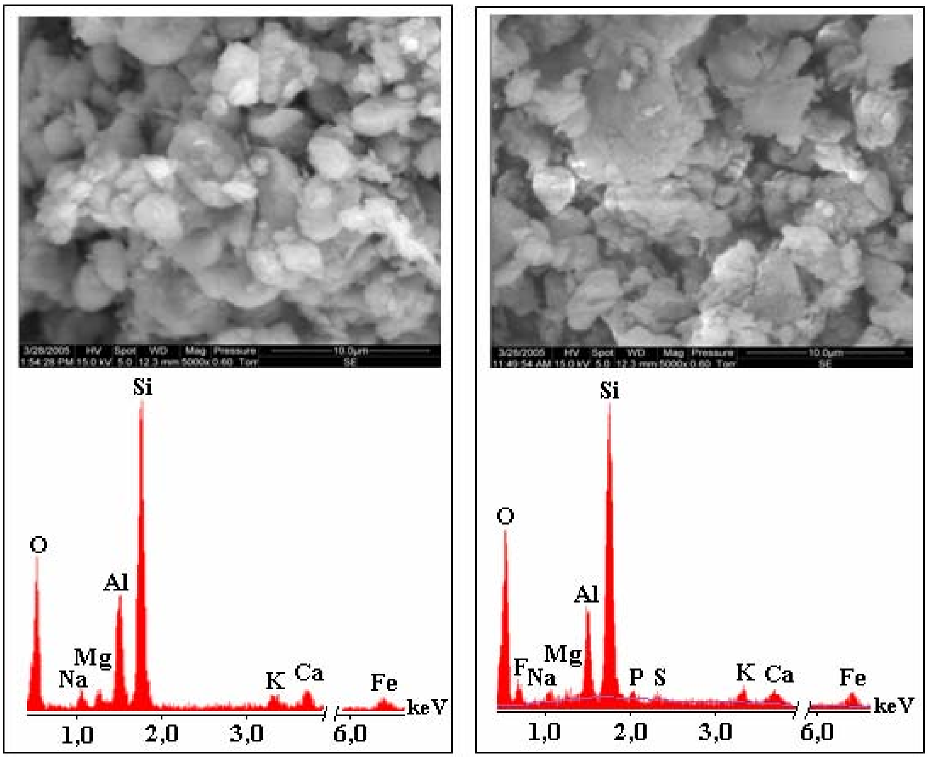


Fig. 5. Distribution micro-pore volume by the MP method of three soils, Where a) raw sample, b) sample after permeability test

3.3. Structural characterization

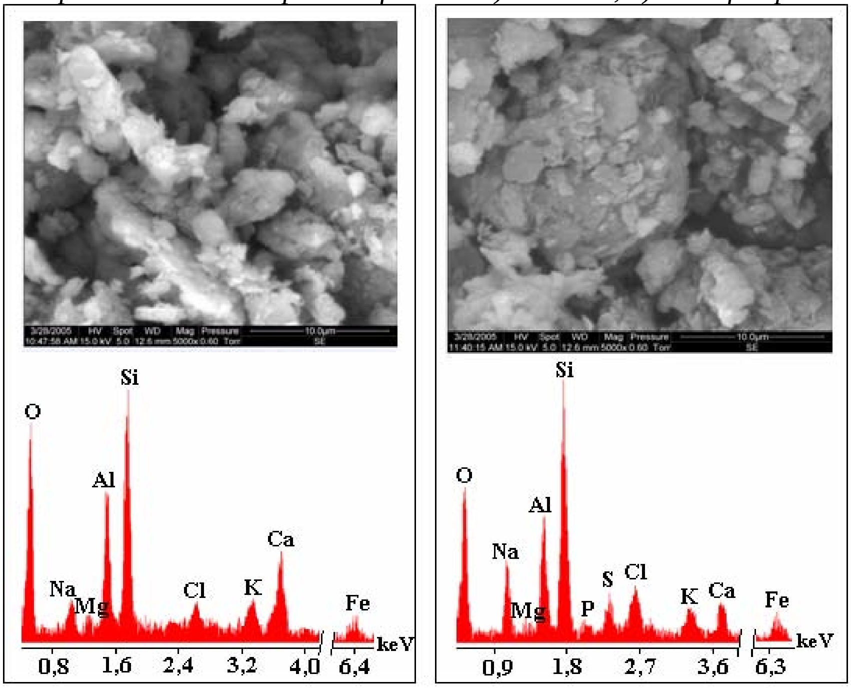
The SEM/EDS analysis shown in Figure 6, 7 and 8 exhibit a morphology and chemical composition of the three soils before and after leachate permeability test. The composition of the untreated soil1 is given in Figure 6a (EDS spectra). The major elements are O, Si and Al, the others Mg, Fe, Na, Ca and K are the minor.

After permeability test, the SEM imaging (Figure 6b) show that the particles morphology become more laminated, this is due to the attack of impurity by the acidic waste thus ensure an purification of clay presented by the layers argillaceous form. In addition the news EDS peaks after permeability test (Figure 6b) are attributed to fluoride (F), sulphur (S) and phosphorus (P), corresponds to the fixation of these elements in this sample. Also, when the EDS probe was focused on group or only one particle on within the same aggregates, all show the existence of F and S atoms. This shows the fixing uniformity of these noxious elements and reveals that this soil (palygorskitic clay) does not let pass the harmful ions to the underground water.



a *b*

Fig. 6. SEM images and representative EDS spectra of Soil-1. a) Raw soil, b) Soil after permeability test

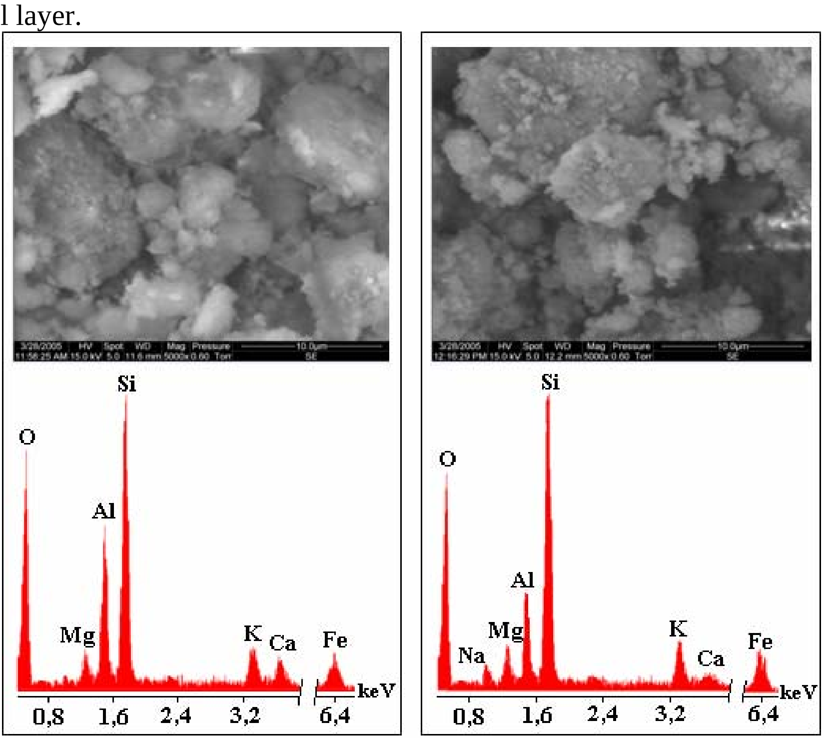


a *b*

Fig. 7. SEM images and representative EDS spectra of Soil2. a) raw soil, b) Soil after permeability test

In the case of soil-2, Figure 7 reveals that the morphology was modified completely and the particle becomes finer and dispersed after acidic treated. Therefore, the EDS analysis (Figure 7b) shows a remarkable reduction in the Ca percentage revealing the attack of carbonates. In addition, we observe the fixation others elements as sulphur (S), phosphorus (P) and chlorine (Cl).

According to Figure 8 the EDS analysis indicates that the soil-3 is composed dominantly of O, Si, Al where (Si/Al mass ratio near 2 unity), also a greater amounts of potassium (K) are clearly observed on the Figure 7a relative to the cation no exchangeable of illite. This sample is not evidently enriched by noxious elements (Figure 7b) after permeability test, just a weak adsorption of sodium (Na). Moreover, we notice a reduction in the percentage of Al, confirming that soil-3 has been attacked by the acidic waste solution especially the octahedral layer.



a *b*

Fig. 8. SEM images and representative EDS spectra of Soil3; a) raw soil, b) soil after permeability test

3.4. Sorption study of anions into three soils

In the aim of to argue the results found by EDS analysis and quantify the removal of all anions by these sample. A sorption study of F$^-$, PO$_4^{3-}$ and Cl$^-$ from waste solution was carried out using 1g of powder soil in 30 mL of solution; the agitation time is about 48 hours. The results for all three samples are shown in Table 6. It can be seen that the sorption capacity of anions into three soils are in agreement with the results found by EDS analysis, in the majority of cases. Fluoride is the more selective element by soil-1, and the sorption capacity is very interesting, is about 60mg/g. Table 3 shows that the selectivity of the fluoride adsorption onto three samples was 25–50 times greater than others anions.

Table 6. Sorption of anions (PO$_4^{3-}$, F$^-$ and Cl$^-$) from wastewater into three soils

Anions	Removal capacity (mg/g) at pH=2.7 and S/L ratio=3.33%		
	Soil-2	Soil-1	Soil-3
F$^-$	57.04	60.01	51.92
PO$_4^{3-}$	2.43	1.52	1.12
Cl$^-$	2.17	1.45	0.05

4. Conclusion

Basing on the difference of mineralogical composition of three soils (soil-1 is essentially palygorskite clay mixed with kaolinite, the soil-3 was illito-kaolinitic clay and soil-2 was smectic clay associated with kaolinite and calcite). Following this study, the results of leachate permeability show that in the cases of Soil-1 and soil-2, k decrease with leached time. In the contrary, the soil-3 shows an increase of the permeability according to time. This was clearly due to the higher resistance to acid attack and the lowest textural size of soil-1 and soil-2. Moreover, in all samples the specific surface area and micropores volume increase after permeability test has derived essentially of carbonates attack. The EDS/SEM analysis indicates the remove of the noxious elements like the fluoride (F), sulphur (S) and phosphorus (P) by the soil-1 after permeability test and the fixation of the (Cl) in the place of (F) by the soil-2. However, the sorption study of *F*$^-$,

PO_4^{3-} and Cl^- from waste solution into three soils shows that the fluoride is more selective by all samples, and is in order to 60mg/g for soil-1. Basing on these results the suitable site for waste storage is Soil-1 or soil-2.

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Summary

This paper reports the interaction between clay and acidic wastewater (pH=2.7 and rich in F^-, PO_4^{3-}, Cl^-…). However, this work investigates the structural and textural evolution after the leachate permeability test of clay soils from three potentials sites for acid effluents storage in the south of Tunisia (Soil-1, Soil-2 and Soil-3). We can notice, that the coefficient of permeability decreases according to time in the case of soil-1 and soil-2 and increase from 6.8 10^{-10} to 1.1 10^{-8} m/s for soil-3. The textural changes for the three varieties of clay soils obtained after leachate permeability test were studied through nitrogen gas adsorption at liquid nitrogen temperature; we determined the specific surface areas (S_{BET}), total pore and micropore volume. The textural study data have indicated that the soil-1 had lowest textural properties with a pore volume in the 0.06-0.09 $cm^3 g^{-1}$ ranges and with a surface area (S_{BET}) vary between 35.4 and 47.4 m^2g^{-1}. A detailed structural and morphologic modification were undertaken by scanning electron microscopy (SEM) equipped by an energy–dispersive spectroscopy (EDS), their results shows that soil-1 and soil-2 able to uptake the noxious elements. By comparison, the selectivity of eliminate these elements are in this order F>P>S for soil1. The quantitative analysis of anions shows that the sorption capacity of fluoride for soil-1 is about 60mg/g and is very higher comparing to others anions.