Article submitted to the Proceedings Book of the VIth. International Symposium–2022, *Theme: "Biosphere & Environmental Safety"*

Biosphere and Environmental Safety
VI.th International Symposium-2022

ISBN: 978-963-449-285-6
Online
May 5-6, 2022
ICEEE, Óbuda University, Budapest, Hungary

ENVIRONMENTAL IMPACT OF BARITE WASTES FROM THE AIN MIMOUN MINE, KHENCHELA, NORTH-EAST ALGERIA.

Meriem BOUKHATEM*, N. CHABOUR, F. BOUAICHA, R. KOURICHE, H. BOUDRA

Geology and Environment Laboratory, University des Frères mentouri Constantine 1, Road Ain El Bey Zouaghi Slimane Constantine 25 000, Algeria, * Corresponding author : boukhatem.meriem2100@gmail.com

The barytic deposit of Ain Mimoune is a complex vein of hydrothermal type, which represents a very interesting mining potential on an economic level in view of the quality and quantity of the extracted ore. It is located at the northern flanks of the Khenchela anticline. To this effect the mining industry in Algeria occupies of the exploitation of this type of ore especially in the oil field. In spite of the productivity of the factory and good quality of the concentrate resulting from the jig REMER, a loss in useful mineral in the waste rock. This waste presents a serious threat for the environment and the habitat. In order to verify the impacts of these mine wastes, a mineralogical and hydrogeochemical study was carried out. Principal component analysis (PCA) was applied to samples taken from different mining sites in order to better understand the geochemical associations characterizing this study area as well as the possible origin of existing metallic contaminants. The analyses show a high degree of pollution by Ba with a maximum value of 9000 mg/kg for the samples downstream of the treatment plant on soils and 124.66 mg/L for surface and groundwater. Concentrations in waters in some stations largely exceed the norms of potability (W.H.O. norm, AFNOR norm). In the soil, the Ba and Pb content exceed that considered as natural. The results show the degradation of the environment in the proximity of the mining center. This is translated by the high content of barium Ba, lead Pb, NO_3 and NH_4.

***Keywords**: barytic, Ain Mimoune, hydrothermal, environment, pollution, barium*

INTRODUCTION

Since antiquity, humans have always had recourse to mineral substances in various forms for their daily needs. Hence the extractive mineral industry has become an essential activity in the development of research and extraction techniques.

To this effect, extraction activities concerning the exploitation of baryte have been actively developed in Algeria, providing 50 000 tons of baryte used mainly in the oil drilling sector. Among the most important, we find the deposit of Ain Mimoune located in the wilaya of Khenchela.

The treatment of this mineral was carried out by wet gravimetric separation by jigging. Where the rejects of the recovery method on the one hand contains an acceptable content of barite sulfate, but on the other hand occupying thousands of hectares in the vicinity of the plant which cannot be biodegraded and therefore persist in the environment for long periods of time.

Their accumulation in the environment can affect humans and animals by threatening their habitat but also their health. The aim of our work is to know the pollution by heavy metals in the Ain Mimoune region and to evaluate the environmental danger which represents the potential migration of the pollutants towards the ground and the surface water by the chemical characterization of the various environmental components.

STUDY AREA SETTINGS

The Ain Mimoune ore deposit is part of Khenchela province. It's located in the North Eastern of Algeria between the longitude 6°56'55.07" and 6°57'40.27" East and the latitude 35°25'05.87" and 35°25'06.12" North with an area about of 641 Hectare. It was discovered in 1968 during a systematic exploration of the region [1].
The baryte deposit is located in the oriental part of the Auras Mountain range which extends along the NE-SW direction [3]. It is represented by a bundle of veins outcropping at the surface with a strong dip (30°-90°) and with a power of 2.5 to 3 m. The most important extent of the veins is 1km. The highest altitude of the vein (vein N°11) and the lowest altitude (vein N°1) are equal to 1250 m. The veins are distant from the industrial form of the mine by about 6 to 12.5 km [2].
From a geological point of view (Figure 1), the study area is characterized by terrains of Cretaceous age dominated by detrital marl-sandstone in which large limestone banks form ledges sometimes giving important reliefs [1]. These geological formations are affected by a very marked plicative and brittle tectonics whose structures are most often the seat of a very important polymetallic mineralization Ba-Pb (Zn- Cu - Hg)
The climate of the region is of continental Mediterranean type. It is semi-arid characterized by irregular average rainfall of order of 478mm, high temperatures in summer 42 ° and very low in winter (-2°) whose annual average is 24.42 with clouds falling quite frequently [5].
The massif of Khenchela offers a strong orographic represented by moreieure chainon such as djebel aidel 2173 m, Ras kodaleine 1945m, Kef tifekressa 1817m and Rass serdoun 1700m [2].

Figure 1. (A) Geographical location of the study area, (B) satellite Google Earth photo of the spatial distribution of sampling.

MATERIALS AND METHODS

In order to verify the degree of metallic contamination generated by the mining of Ain Mimoune, a sampling campaign was carried out in dry period between June and July 2018. We took care of sampling on a large surface of the study area. Three solid samples were taken from the soil, sterile. Similarly, ten liquid samples containing dissolved matter and or in suspension were taken from the wadi, wells and water source.
For each water point, we measured in situ the physico-chemical parameters such as temperature, pH by pH-meter E520 Metrohm Herisau and the electrical conductivity of the water by a Hanna conductivity meter (HI 9035). The liquid samples were stored in plastic bottles with a capacity of 1.5L and transported in a cooler at a temperature of about 4°C until they were analysed [6]. The soil samples were dried in an oven at a temperature of 450°C for 24 hours and then the samples were acid-

etched and filtered. The analysis of chemical samples elements (Ca^{2+}, Mg^{2+}, Cl^-, and HCO_3^-) was carried out in the laboratory of geology and environment at the university of Constantine 01 by the volumetric method (Table 1). The determining elements of the pollution (NO_2^-, NO_3^-, Br_2, NH_4^+ and Ba) and the heavy minerals (Cd, Zn, Cu, Pb and Hg) were analysed at the laboratory of environmental analysis and chemical test on minerals (Ain Mlila, Algeria).

The statistical study was based on the diagrams and the PCA. The intermediate correlations, the correlation coefficients between the variables and the two axes F1 and F2 and the projection of the variables in the space of the axes F1 and F2 were obtained with a software XLSTAT

Table 1. Equipment used for the determination of the different elements analysed

Analysis method	Chemical element	Laboratory
The spectrometry	NO_2^-, NO_3^-, Br_2, NH_4^+	L.A.C.I.P. Ain M'LILA
Atomic absorption	Ba	
AAS PERKINELMER	Cd, Zn, Cu, Pb, Hg	
Turbidimeter	SO_4^{2-}	
Flame photometer	Na^+, K^+	

RESULTS AND DISCUSSION

Mineralogical Study

The deposit of Ain Mimoune is in the form of a vein structure, with barytic reserves (geological resources of 1.86 MT and exploitable reserves estimated at 1.25 MT) and with an average content of 70% in BaSO4 as types of mineralization in the mine of Ain Mimoune [4]. We find the hydrothermal mineralization of malachite, azurite and sometimes of cinnabar, sphalerite and chalcopyrite. In addition to the baryte veins, there are many other occurrences such as copper, lead, quartz and calcite mineralisation:

- **Barite 1:** is characterized by coarse crystals with elongated emanations or in the form of aggregates with fibrous and actiniform structure.
- **Barite 2:** is presented by crystals forming ranges in the form of isometric grains.
- **Quartz 1:** develops in contact with the vein and contains numerous field rock intercalations.
- **Quartz 2:** is found in the barite mass in the form of automorphic crystals.
- **Dioptase**: appears as rounded and angular grains disseminated in the baryte.
- **Chalcopyrite:** occurs in the form of irregular separation along the fissures in the barium.
- **Sphalerite:** is presented in the form of rounded grains.
- **Cinnabar:** is represented in dissemination in the pane base.
- **Calcite:** gives irregular contact separations.
- **Dolomite:** is developed in the central part in the form of vienules and irregular separation.
- **Iron hydroxides**: are arranged irregularly in the contact along the cracks.
- **Malachite and azurite:** occur as isolated separates and nests. All these metalliferous occurrences have negligible quantities and are of no economic interest [2].

Sample Analysis

The qualitative study of surface and ground water in the vicinity of the mine Ain Minoune was revealed by a physico-chemical study of sampled water (Table 2). It shows that the water temperature varied between 10.9-21.6°C. These temperatures are both influenced by the ambient temperature of the atmosphere. A

ll the surface waters present relatively alkaline pH because of the enrichment in calcite which are due to the dissolution of the carbonate formations present in the big limestone banks and the Mio-Pliocene deposits where these waters percolate (Figure 2).

Table 2. Chemical analysis results (July 2018).

Variable	Minimum	Maximum	Mean	Standard deviation
pH	7,550	8,380	8,093	0,282
T°C	10,900	21,600	18,560	3,479
Conductivity (ppm)	128,000	259,000	195,200	37,774
TAT F	11,750	30,450	15,580	5,803
Ca^{2+} (mg/l)	6,130	104,810	47,519	24,554
Mg^{2+} (mg/l)	4,070	66,170	11,196	19,405
Na^{+}, K^{+} (mg/l)	49,400	81,600	58,115	11,944
HCO_3^- (mg/l)	53,910	209,770	85,188	55,246
SO_4^{2-} (mg/l)	83,650	203,120	120,576	49,072
Cl^- (mg/l)	17,150	91,400	32,593	26,205
NH_4^+ (mg/l)	0,011	3,460	0,388	1,080
NO_3^- (mg/l)	9,470	85,130	48,508	24,114
NO_2^- (mg/l)	0,007	0,314	0,045	0,095
Ba (mg/l)	2,340	124,660	22,328	36,387
Pb (mg/l)	0,006	0,082	0,046	0,023
Zn (mg/l)	0,054	0,210	0,085	0,055
Cd (mg/l)	0,000	0,203	0,074	0,062
Cu (mg/l)	0,017	0,091	0,033	0,026
Hg (mg/l)	0,000	0,003	0,000	0,001

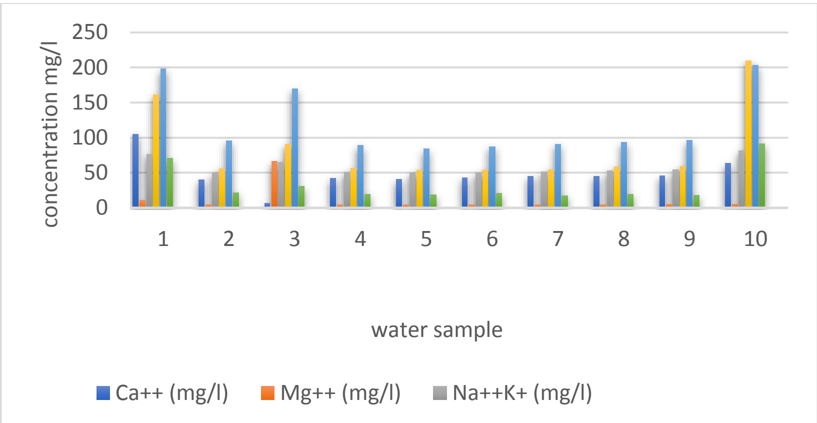

Figure 2. Spatial variation of chemical elements in the study area.

The results of the chemical analysis amount that the most abundant cations in surface waters are sodium (Na^+) and calcium (Ca^{2+}), their contents oscillate between 49.4 mg/l to 81.6 mg/l for Na^+ and 6.13 mg/l to 104. 81 mg/l for Ca^+, followed by magnesium (Mg^{2+}) and (k^+) with low concentrations of 66.17 mg/l to 4.07 mg/l, therefore we can classify by increasing order the cations as follows: r% k < r% Mg+< r% Ca< %r Na+.

The most abundant anions in the study area are sulfate ($S0_4^-$). The concentrations vary between 83.65 mg/l to 203.12 mg/l for sulfate due to the dissolution of the Cretaceous terrain which is predominantly marl, 53.91 mg/l to 209.77 mg/l for carbonates and 17.15 mg/l to 94.4 mg/l for chlorides (Figure 3).

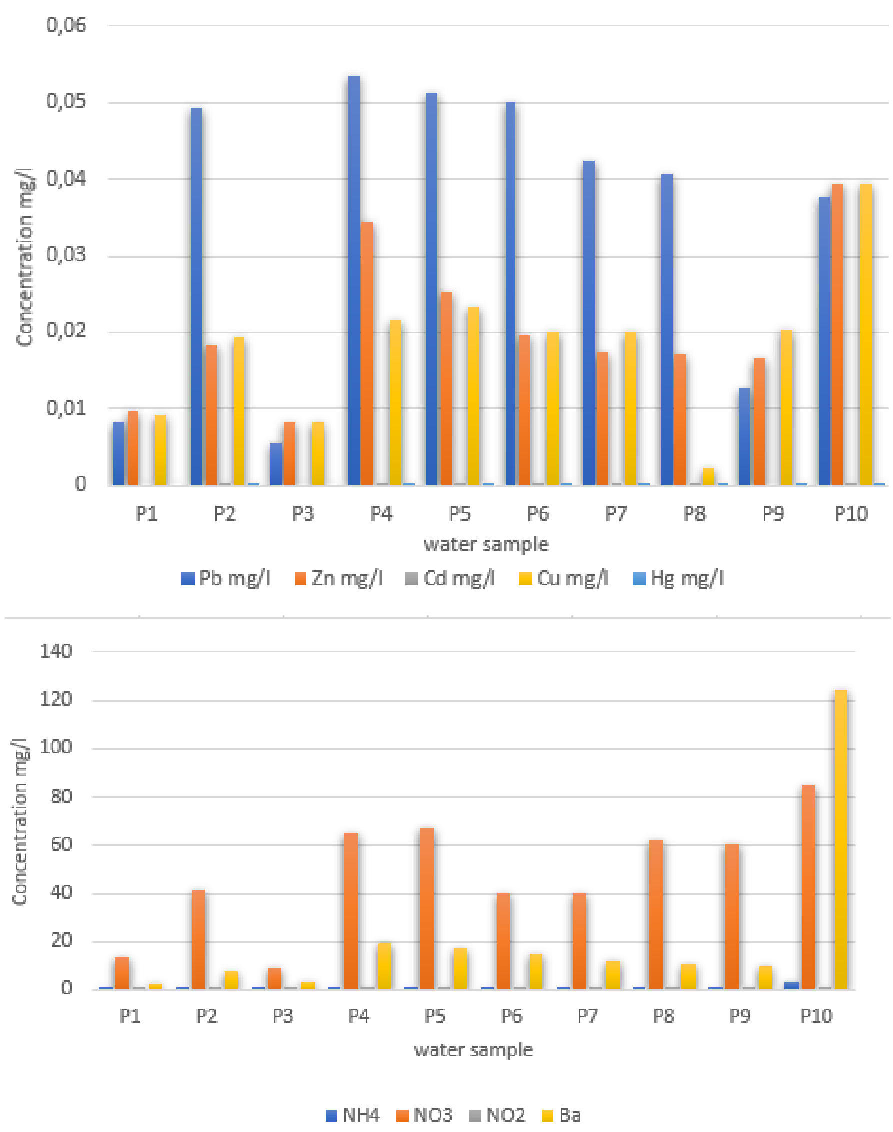

Figure 3. Spatial variation of chemical elements in water sample

The contents of Zn, Ca, Cu and Hg in the water samples remain lower than that admitted by the World Health Organization (WHO) for drinking water. The order of abundance in most element is as follows Zn>Cu>Cd>Hg (Figure 4).

The metallic contents varying respectively from 8.3 mg/l to 39.4 mg/l, from 2.3 mg/l to 39.3 mg/l, from 0 mg/l to 0.11 and from 0 mg/l a 0.3 mg/l. In fact, the levels of Pb and Ba exceed the national and WHO standards in several places, with the highest levels at the site of the mine workings and discharge.

The remarkable enrichments in Pb and Ba taken in the proximity of the mine's treatment discharge, which ranged from 8.3 mg/l to 53.6 mg/l and from 2.34 mg/l to 124.66 mg/l, respectively. These two compounds are not very water soluble and have low geochemical mobility.

In our case lead is associated with barite ore in the form of lead sulfide. These high values may be due to the impact of the mine and tailings on the surface water in the vicinity of the mining centre. To define the potability of the studied waters we are based on norms established by the WHO, the potability of the waters and not drinkable to the human consumption and are met at the level of all the point of waters of the region of study whose agricultural solution constitutes the main type of the pollution of also that of industrial origin caused by Ba.

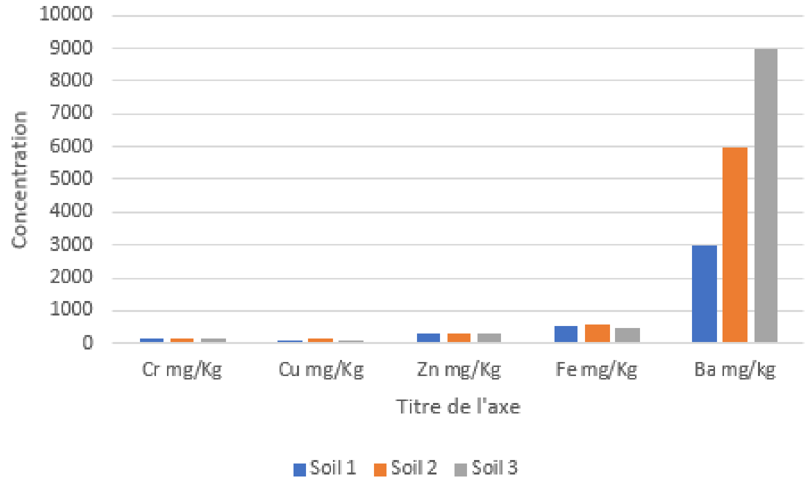

Figure 4. Spatial variation of metallic elements in soil sample

For the metal element in the soil sample, the analysis showed a relatively high concentration of TME, the order of abundance in most elements is as follows: BA>Fe>Zn>Cr>Cu. Fe, Zn and Ba recorded high value in all samples and exceed the norms of FANOR. The concentration varied respectively 497 to 544mg/kg and 3000 to 9000mg/kg.

The high concentration of Ba shows that the soil samples were moderately or highly contaminated by barite. This pollution is due to the irrational extraction of the substance because 25% of the part is rejected with the processing waste [7], occupying thousands of hectares of the territory of Ain Mimoune; this waste presents a crucial problem for the environment and the habitat (Table 3).

Figure 5 shows the results of principal component analysis (PCA) which was applied to better understand the possible origins of metal contamination in surface waters [8]. The two axes considered to describe the correlations between the variables related to the spatial structure holds alone 64% for axis 1 and 21.55% for axis 2. Axis 1 is expressed towards its positive poles influenced mainly by the metallic elements Ba, Zn Cd Cu Hg and the polluting elements NH_4^+, NO_2^-which present the good correlation between them. This factor could indicate the signature of the industrial and agricultural origin of this pollution, essentially by the barium. While axis 2 is defined by the elements Pb, NO_3^- towards its positive pole and the pH towards its negative pole. This factor probably is a secondary contamination and related to the erosion of the discharges of Ain Mimoune. The main factor 3 advocates about 15% of the total variance influenced only to the conductivity which indicates that the latter is not related to mining discharges but only to geological formations of the Cretaceous.

Table 3. Correlation between variables and factors.

	F1	F2	F3	F4	F5
pH	-0,689	0,430	-0,522	0,139	0,217
Conductivity (ppm)	0,337	-0,626	0,680	0,039	0,156
NH4+ (mg/l)	0,995	-0,046	-0,042	-0,038	0,036
NO3- (mg/l)	0,612	0,648	0,310	0,302	-0,077
NO2 (mg/l)	0,995	-0,007	-0,064	-0,051	0,044
Ba (mg/l)	0,993	0,069	-0,025	-0,031	0,085
Pb (mg/l)	0,618	0,739	0,193	0,070	0,027
Zn (mg/l)	0,757	-0,520	-0,369	0,130	-0,046
Cd (mg/l)	0,747	0,571	-0,160	-0,261	-0,014
Cu (mg/l)	0,752	-0,472	-0,433	0,143	-0,034
Hg (mg/l)	0,995	-0,041	-0,042	-0,037	0,036
Own value	6,996	2,371	1,226	0,229	0,093
Variability (%)	63,597	21,556	11,144	2,079	0,847
% cumulative	63,597	85,153	96,297	98,375	99,222

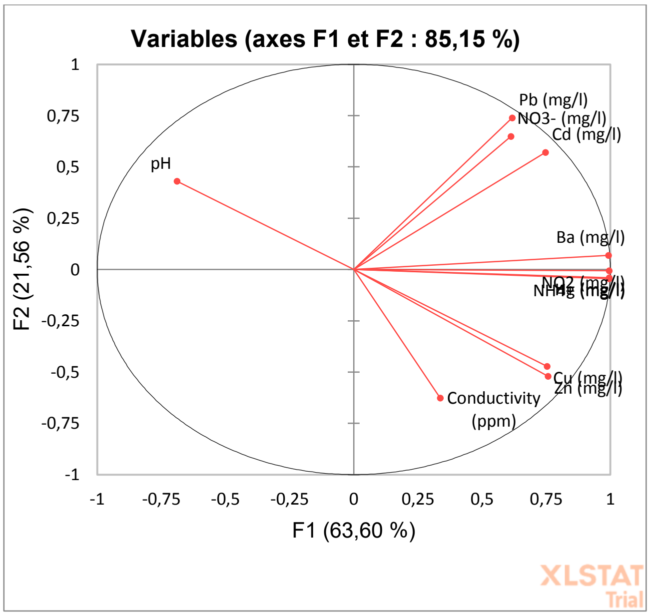

Figure 5. PCA applied to chemical elements

In the circle of correlation, the 1st component (F1) contributing to 64% and defined by the parameters of industrial and agricultural pollution, namely NH_4^+ (0.989), NO_2^- (0.99), Ba (0.985), Zn (0.573), Cd (0.559), Cu (0.566) and Hg (0.99) with the inertia of 21.55% of the second component F2 is defined by the parameters NO_3^-(0.42), Pb (0.546) and pH (0.475). The examination of the correlation matrix between variables reveals the presence of a first set of variables made up of variables that are well correlated with each other [9]:

pH: with parameters of conductivity, ammonium, Nitrate, Nitrogen dioxide, Barium, Lead, Zinc Cadmium, Copper and Mercury.
Ammonium: with Nitrate, Nitrogen dioxide, Barium, Lead, Zinc, Cadmium, Copper, mercury.
Nitrate: with Nitrogen dioxide, Barium, Lead, Zinc, Cadmium, Copper, mercury.
Nitrogen dioxide: with Barium, Lead, Zinc, Cadmium, Copper, mercury.
Barium: with Lead, Zinc, Cadmium, Copper, mercury.
Lead: with Zinc, Cadmium, Copper, mercury.
Zinc: with Cadmium, Copper, mercury.
Cadmium: with copper; mercury.

CONCLUSIONS AND RECOMMENDATIONS

This study showed that the mining centre of Ain Mimoune, in the eastern part of the Auras, has a high potential of pollution of industrial origin by Ba and that of agricultural origin by ammonium, Nitrate. The environmental impact of the mining activity in the region is confirmed. The mining centre has an effect not only on the environmental aesthetics of the area, but also on the surface waters and soils in the vicinity of the mine, contaminated by toxic trace metal elements. High levels of trace elements Ba have been recorded in surface water (2.34 mg/l to 124.66 mg/l) and soil sample (3000 mg/kg to 9000 mg/kg). We propose that the processing water of the mine be purified before it is released into the wadi Ain Mimoune in order to preserve the water table and protect surface waters against pollution by heavy metals. It is even for the solid waste which must be tries then stokes tries very far from the points of water.

REFERENCES

[1] Batouche T et al (2019): Mineralogical and physico-chemical characterization of barite wastes from Ain Mimoun deposit (Khenchela, Algeria). Article in Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu. Juin 2019. 29-35 p.

[2] Baladah F (2012) : Revalorisation des rejets Barytiques issues des jigs et impact enviremantal: cas de la mine Ain Minoune. Thèse de magister. Université d'Annaba.91p.
[3] Laffite R (1939): Etude géologique de l'aurés. Publ. Serv. Carte Algérie, Alger,2éme série. Bull. N°15.
[4] Koriche R (2018): Impact des rejets miniers de la mine d'Ain Mimoune sur l'environnement. Mémoire de Master. Université de Constantine.
[5] Zouaoui H, Roummani A (2017): Etude d'influences des impuretés sur la qualité de la baryte, cas de la mine d'Ain Mimoune. Mémoire de Master. Université de Tabassa.
[6] Rodier J (2009): L'analyse d'eaux. Paris- Dunod. 9 Edition P1579
[7] Batouche F et al (2018). Caractérisation des rejets barytiques en vue de leurs volarisation et impact enviremental. Fourth International Conference on Energy, Materials, Applied Energetics and Pollution.
[8] Ayayi J (2012): Impact d'un site minier abandonné sur l'environnement: Cas de la mine de khanguet kef ettout. Colloque international en évaluation enviremental. Juin 2012. 41-47 p.
[9] Chaouki I (2014): Application de l'analyse en composantes principales pour l'évaluation de la qualité des eaux usées industrielle de Salam Gaz. J. Mater. Environ.Sci. 6(2) (2015). 445-464 p.