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[Bellarbi* 4(10): October, 2017] ISSN 2349-4506
Impact Factor: 2.785

Global Journal of Engineering Science and Research Management

VALORIZATION OF BOTTOM ASH GENERATED BY A THERMAL POWER PLANT IN THE TREATMENT OF CARDBOARD MANUFACTURING WASTEWATER

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DOI: 10.5281/zenodo.1007135

KEYWORDS: Percolation - Infiltration - Bottom ash – Wastewater- Cardboard.

ABSTRACT
The aim of this study is to valorize the bottom ash generated by the thermal power plant in the cardboard manufacturing wastewater treatment by infiltration percolation process and to study the purifying effect of the crushed bottom ashes used instead of the fly ash which is already recycled in the cement industry.

For this purpose, different coastal sands of the area of the city of El Jadida, combined with bottom ash (by-products of a local power plant), are used to filter wastewater from a cardboard manufacturing plant. The chemical and mineralogical composition of bottom ash are produced respectively by X-ray fluorescence and X-ray diffraction. The wastewater samples were collected during a complete cycle of production of the cardboard. The heavy metals content before and after filtration was obtained by atomic emission spectrometry, with inductively coupled plasma (ICP-AES).

The main parameters analyzed were: total suspended solids (TSS), organic matter COD, BOD5, the potential hydrogen pH and heavy metals (iron, zinc and arsenic). The results are very conclusive and respect the essence of control required by Moroccan regulations (law 1606-06) related to discharges from the papermaking and cardboard industry.

INTRODUCTION
The problems of environment protection in Morocco, just like in the whole world, are becoming more and more relevant. The impact made by the companies upon the environment also influences their economic situation. Large expenses occur not only due legal strict requirements related to the environment protection but also due to the expenses incurred that seem to have nothing in common with the environment protection. This encourages researchers to look for new process of environment protection.

The waste management is a major challenge for all countries. To prevent its abundance in nature, it is recommended to store these by-products in landfills [1-2]. However, this storage raises two problems: the first is economic like the management and development of landfills, the second is environmental: Presence of the risk of contamination of water and soil in case of infiltration of harmful elements such as heavy metals (Arsenic, cadmium, lead, iron, zinc ...)

The Local thermal power generates a large amounts of ash (fly / bottom ash) which amounts to more than 800 000 T/ year [3-4]. If fly ash is totally valorised in the cement manufacturing plant, the bottom ash is stored in a landfill.

The cardboard manufacturing plant rejects on average 40m3 of wastewater / ton of cardboard produced. Our main objectives is to valorize the bottom ash generated by the thermal power plant in the treatment of cardboard manufacturing wastewater by infiltration percolation process.

The infiltration percolation process remains the method of choice not only in rural areas but also in many industrialized countries [6]. Our contribution in this study is the combination use of natural porous materials (sand) with industrial waste (bottom ash from thermal power plants) [7].

MATERIAL AND METHODS

2.1 Origin of waste

As shown in the figure 1, the origin of wastewater object of our study is the cardboard manufacturing process and the origin of bottom ash is a coal burning in the thermal power plant.

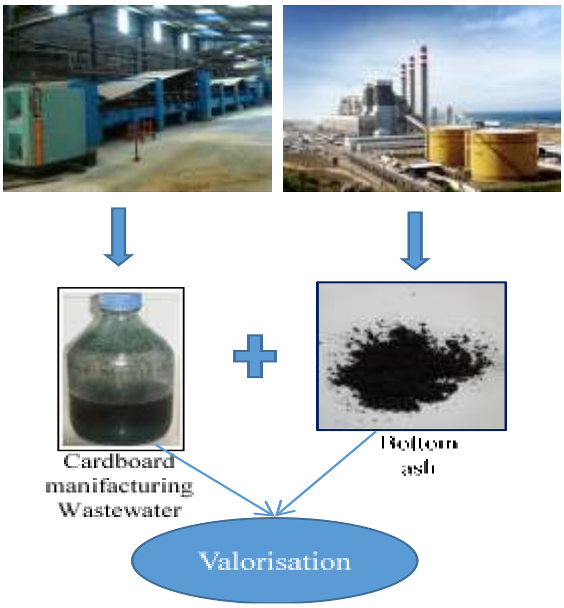
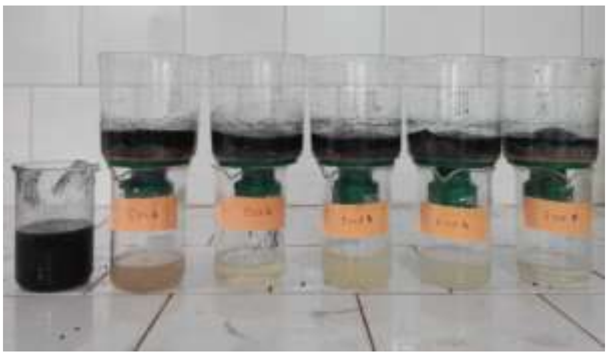


Figure 1: The origin of waste and wastewater

2.2 Infiltration percolation process

The five filters used consist of three layers: crushed bottom ash (CBA) / Bottom ash (BA) / sand.
On the other filter what changed was only the sand samples following sites as indicated on Figures 2 and 3.



1: Bottom ash crushed + bottom ash + (sand) I ;

(i=1,…5)

Figure 2: Visual aspect of different matrices filtrates

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Fig. 3: Matrix filter

2.3 Physico-chemical characterization of wastewater
2.3.1 Sampling
Samples of analyzed wastewater were carefully removed in order to obtain the most representative sample possible; we conducted sampling for 24 h (sampling every 2 h). The average volume of each sample was 1 liter. The samples were collected in glass bottles, stored in a cooler, and transported immediately to the laboratory.

2.3.2 Physico-chemical analysis
The physicochemical parameters to be analyzed were chosen following the regulatory requirements with respect to Moroccan discharge limits for paper and cardboard industry (= law 1606-06 laying down specific limit values for wastewater discharge of the pulp, paper and cardboard manufacturing plant) [8] .
We limited our study to the following parameters:
-Temperature, pH, COD, BOD5 and TSS
-Heavy metals: Arsenic (As); Zinc (Zn) and Iron (Fe).
All physico-chemical parameters of wastewater were determined by the wastewater analytical standard methods [7].
The content of suspended solids (TSS) was determined by the filtration method.
The Chemical Oxygen Demand (COD) was analyzed using a COD meter thermo-type reactor Behr TRS 300 and biological oxygen demand (BOD5) was measured using an Oximeter 538 (WTW) / BODmèter: TS606 / 2. Heavy metals were determined by atomic emission spectrometry with Inductively coupled plasma (ICP-AES).
2.4 Requirements of the Moroccan regulations
Table below shows the limit values for discharges of cardboard paper industry as required by the regulations in Morocco:

Table 1: Release limit values of the paper and cardboard manufacturing in Morocco [8]

Parameters	Moroccan Regulation
Temperature (°C)	Do not exceed 10 ° C the temperature of the receiving environment
PH	5.5-8.5
COD (mg O_2 / l)	900

BOD_5 (mg O_2 / l)	200
TSS (mg / l)	400
Arsenic (mg/l)	0,1
Iron (mg/l)	3
Zinc (mg/l)	2

The table 1 present the requirements of the Moroccan regulations on discharges from the paper and cardboard industry in Morocco.

2.5 Structures and morphologies of adsorbents used
2.5.1 Bottom ash
The bottom ash used in our percolating infiltration experiments are produced in the Jorf Lasfar thermal power plant located at a distance of 24 Km from El Jadida city on the cost road to Safi. They appear as porous dark grains more or less gray; our samples of bottom ash are black with a highly variable particle size. Figure 4 gives the visual aspect [5].

Figure 4: visual aspect of bottom ash

The Bottom ash is removed from the combustion of coal. Each sample was obtained by quartering from several samples of 5 kg. The quartering is to divide the sample into four equal parts. Two opposite parts are recovered and homogenized. One of these latter two parts is subject to a new quartering. The operation can be repeated three or four times in order to obtain a representative sample [11].

The sampled bottom ash had been previously sifted and crushed.
We chose to work with a particle size of the bottom ash that is less than 1 mm, this increases the contact surface of the bottom ash grains with substances from the wastewater and improve the adsorption.
The chemical composition of bottom ash is obtained by fluorescence X technique.
This is a non-destructive elemental analysis technique which allows multiple dosing of basic materials compounds.
The mineralogical composition bottom ash is obtained by X ray diffraction technique.

2.5.2 The Sands
Samples of sand that we used in our experiments percolation filtration were collected from 86 km of coastline of El Jadida between El Oualidia and El Haouzia.

Table 2 presents details of the sites of our samples of sand. As shown in figure 5 these were in a first step, carefully washed with distilled water then dried at 40 °C in a stove [12-13]. They were then sifted to determine the various sizes.

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Figure 5: Sand treatment protocol

Table 2: Situation of sand sampling sites

Sand 1	El Jadida Beach
Sand 2	Sidi Bouzid Beach (8 km from El Jadida on the coastal road to Safi)
Sand 3	El Haouzia Beach (20 km from El Jadida on the coastal road to Casablanca)
Sand 4	Sidi Abed Beach (31 km from El Jadida on the coastal road to Safi)
Sand 5	El Oualidia Beach (78 km from El Jadida on the coastal road to Safi)

We conducted a detailed analysis of particle size of 5 types of sands [11] on a column of 12 sieves (standard method NF P 18-560) [7]: this involved passing a quantity of 100 grams of sand through the 12 sieves, they were ranked in descending order (AFNOR standard) and to which we applied a mechanical vibratory movement for 30 minutes.
The chemical composition of sand is obtained by fluorescence X technique.

RESULTS AND DISCUSSION

3.1. Physico-chemical composition of wastewater
As shown in Table 3 below, the wastewater of cardboard is characterized by a very high COD, BOD_5, TSS, and some metals such as iron and zinc with values that exceed the specific limit discharges values applicable to discharges from paper and cardboard industries in public sanitation.

Table 3: Physical and chemical analyzes of the studied wastewater

Température (°C)	27
PH	6.03
COD (mg O_2/l)	17606
BOD_5 (mg O_2/l)	4053
TSS (mg/l)	4232
Arsenic (mg/l)	0.014
Iron(mg/l)	15.8
Zinc (mg/l)	2.51

3.2. Chemical and mineralogical composition of bottom ash
The results of analysis of the chemical composition of bottom ash are supplied in Table 4.
We note that over 80% of the chemical composition of bottom ash consists of elements SiO_2, Al_2O_3 and Fe_2O_3, for lime, it hardly exceeds 2%.

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The bottom ash mineralogical composition is obtained by ray diffraction technique. This study reveals the existence of two peaks.

The first quartz (SiO_2) and the second corresponds to mullite (Figure 6).
This result is explained by the mineralogy of the coal used, which generally consists of crystalline silica form of quartz and clay minerals phyllitheux group (shale).

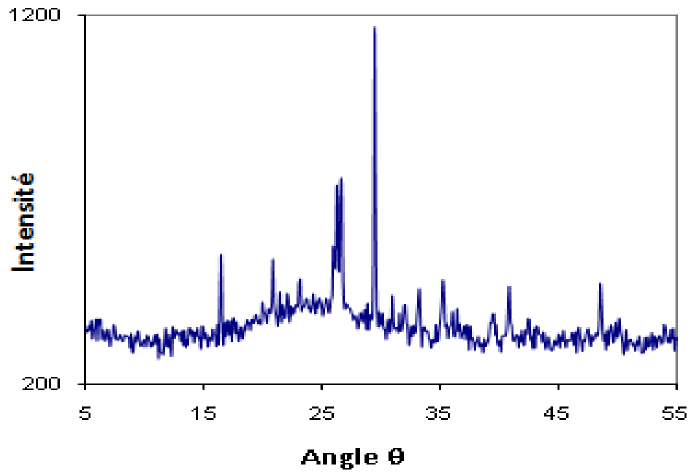

Figure 6: mineralogical spectrum of bottom ash

Table 4: Analysis of the chemical composition of bottom ash (%)

Na_2O	ZnO	PbO	SO_3	MgO
0,4	0,01	0,01	1,87	1,09
CaO	SiO_2	Fe_2O_3	Al_2O_3	K_2O
1,92	52,07	8,86	23,34	1,9

3.3 Sands particle size analyzes

The chemical composition of sands is obtained by fluorescence X technique.

Table 5: chemical composition (in %) of the sands of the city of el Jadida

	SiO_2 %	AL_2O_3 %	Fe_2O_3 %	CaO %	MgO %	K_2O %	TiO_2 %
Sand 1	61,14	5,16	3,37	19,27	3,81	1	0,45
Sand 2	50,17	4,56	5,2	22,4	6,37	0,81	1,04
Sand 3	46,54	3,98	3,22	24,19	5,01	0,84	0,49
Sand 4	31,69	1,73	1,55	36,04	4,55	0,4	0,28
Sand 5	46,54	3,98	3,22	24,19	5,01	0,84	0,49

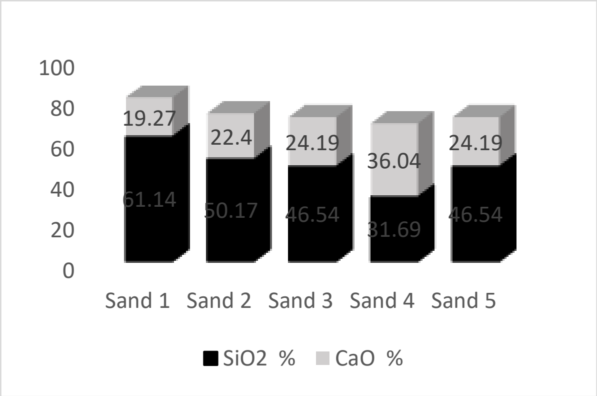

Figure 7: Results of X-ray fluorescence analysis of sand samples

From the above particle size distribution curves for 5 sands, it reaches 80% of cumulative undersize passing through mesh screen between 400 and 500 microns, we can conclude that the predominant size of the studied sands is between 400 microns and 500 microns, which attributed it to the class of fine sand [14-15]. The small particle size of the latter facilitating the fixation of the organic material to the surface of adsorbent material which is generally more important when the particle size of the material is low.

In our filtration tests of wastewater from the cardboard, we used a sample of each type of sand we have used fractions ≤ 600µm.

Relating to chemical analysis, it is noted that the silica and calcite content is very important for the analyzed sands.

3.4 Results of wastewater infiltration percolation tests

The five filters used consist of three layers: Crushed bottom ash (CBA) / Bottom ash (BA) / sand. On the other filter what changed was only the sand samples following sites as indicated on Table 2.

Previous studies have shown the effectiveness of the sand / Fly Ash/ Bottom ash filter in the context of synthetic discoloration [18]. The instead the fly ash by the crushed bottom ash in this case gives interesting results.

3.4.1 Abatement of COD

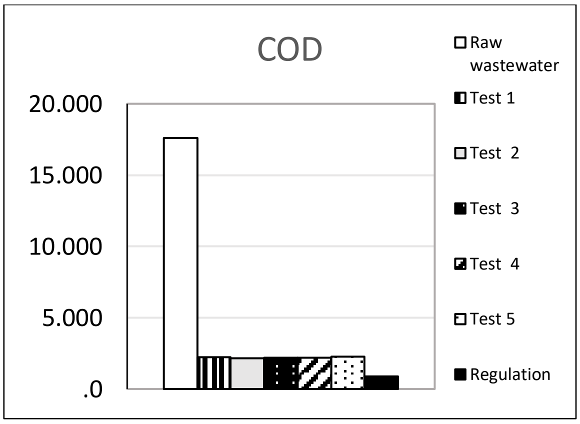

Figure 8 : Abatement of COD

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3.4.2 Abatement of suspended matter

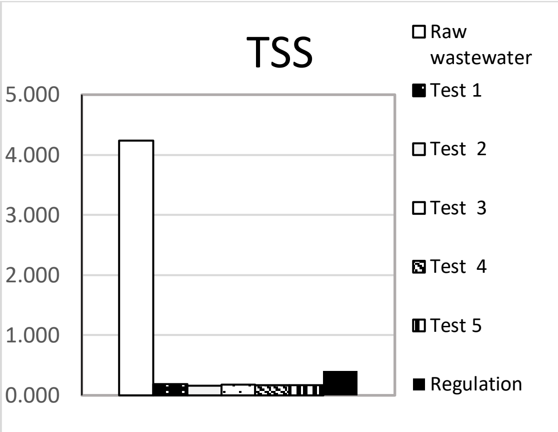

Figure 9 : Abatement of suspended matter

Analysis of the suspended matter enables us to identify the amount of undissolved material (colloid), whether organic or inorganic, present in the sample. Wastewater studied is highly charged with suspended matter 4232 mg / l.

This treatment has allowed us to achieve an average reduction rate of 96.2% with a minimum TSS content of 164 mg / l value that complies with current regulations (400 mg / l). (figure 9)

3.4.3 Abatement of BOD5

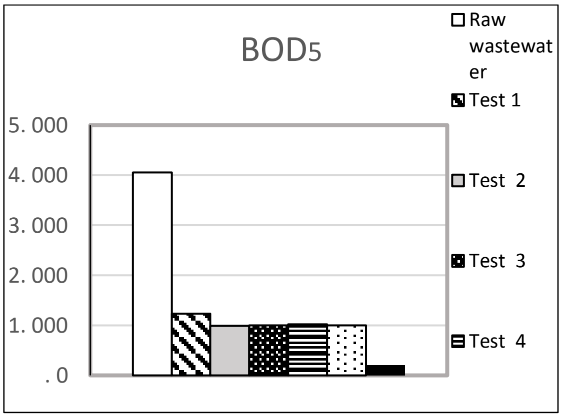

Figure 10: Abatement of BOD_5

The wastewater treated by the filter beds 1-2-3-4-5 test shows a reduction of organic pollution in terms of BOD_5 with an average reduction rate of 76% with a minimum content of 987 mg BOD_5/l value that not complies with current regulations (200 mg / l).The initial BOD_5 of the sample before treatment was 4053 mg / l.(figure 10)

3.4.4 pH evolution

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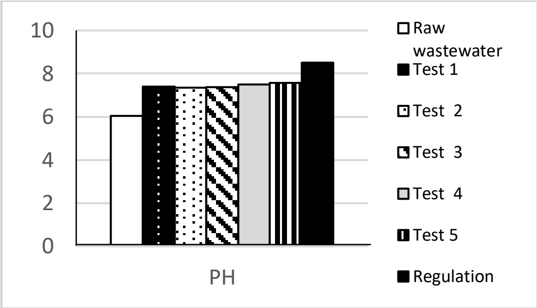

Figure 11 : pH Neutralization

Wastewater treated by the test filter beds 1-2-3-4-5 shows a pH neutralization (figure 11). The studied wastewater has a pH of 6, while all the tests helped neutralize discharges (pH between 7.3 and 7.5).These pH values meet the regulations in force (pH between 5.5 and 8.5).

3.4.5 Abatement of heavy metals: Zinc, Iron, and Arsenic

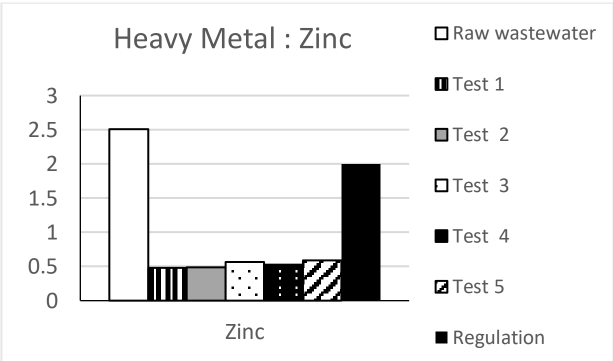

Figure 12 : Abatement of Zinc

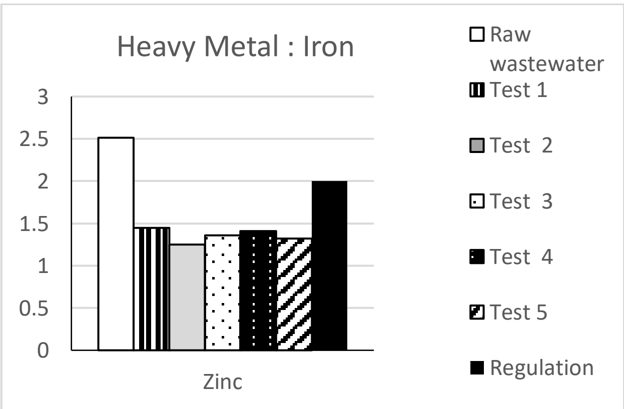

Figure 13: Abatement of Iron

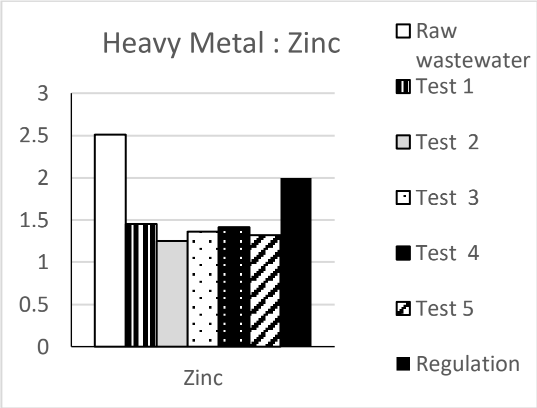

Figure 14: Abatement of Arsenic

The cardboard wastewater treatment by the sand, fly ash and bottom ash bed filtration has enabled us to achieve a zinc abatement rate of 50% and a reduction rate of 80% iron with minimum values of 1.25 mg / l and 2.92 mg / l respectively that meet current regulations.

These high values of iron and zinc in the wastewater can have as a source the printing inks used (figures 12, 13 and 14).

For arsenic analysis of rejection has allowed us to identify the very low concentration of arsenic and that respects the current regulations.

3.5 Results analysis

The polluting effect of wastewater results from the use of cleaning water of equipment and of adhesive and printing machines and spills of adhesives and inks etc...

Environmental monitoring of wastewater from the cardboard during a complete production cycle (24 h: start lines, normal cycle of production, stopping, end of the day and cleaning), shows that the concentrations of COD and BOD_5 increase in the end of day: a time of cleaning. The ratio COD / BOD_5 being about 4.34 (> 3), which makes this hardly biodegradable water.

The optimal treatment is the separation of water to pollutant, and determining a way of treatment or valorization of this pollutant.

A remarkable discoloration is obtained using the sand-Crushed bottom ash- bottom ash matrix.
The best discoloration is observed for test 5 and test 2, test 4, test 3 and the less degree discoloration is observed with test 1.

Sands used in test 1 will be taken as the starting optimization in sand- Crushed bottom ash - bottom ash filter.
The high abatement rates of organic matter (COD, BOD_5, TSS) is explained by the composition of bottom ash used that is rich in SiO_2 elements [10] Al_2O_3, and Fe_2O_3 more than 80% of its compositions [16], The iron and aluminum oxides are the essential raw materials for the manufacture of water and wastewater treatment coagulants [17].

As regards heavy metals, the rate of elimination is remarkable due to the adsorption properties of bottom ash: containing a high content of silica, an important adsorbent having a high electrical polarity and nutrients in particular ferrous ions (Fe^{3+}), they contribute to the neutralization of negative charges contained in the wastewater. The replacement of fly ash by crushed bottom ash is linked to the fact that fly ash is totally recycled in cement while thousands tons of bottom ash are still stored in landfills.

CONCLUSION

This study aimed to characterize the cardboard manufacturing wastewater and demonstrate that natural adsorbents like sand or some industrial wastes such as bottom ash could be used as filtration support for treatment of wastewater from the paper and cardboard industry.

The results obtained showed that:

1. Studied wastewater does not meet the standards of Moroccan and International releases of the paper and cardboard industry for physicochemical parameters studied.
2. Filtering through the matrix (marine sand /Crushed bottom ash /bottom ash) enables effective reduction of organic and inorganic pollutant charge. The results of the tests have allowed us to reach an abatement rate of 75% COD, BOD_5 76% of the TSS 97%. They also allowed a significant reduction in heavy metals such as zinc and iron (respectively abatement rate 79% and 81%). The results obtained are compared successfully with International [9] and Moroccan standards.
3. The origin of the sand 5, the object of the better results (purifying effect) is the Oualidia area remote from all sources of pollution.
4. In perspective, we will focus on the valorization of sludge obtained in civil engineering and building materials.
5. For this, the balance between the three constituents used (sand / Crushed bottom ash / bottom ash) will be optimized in the filtration to obtain sludges that are easy to modify and treat.

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