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Characterization and Application of Solid Waste in the Adsorption of Heavy metals

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Abstract
Adsorption processes are being widely used by various researchers for the removal of heavy metals from wastewater. In recent years, the need for economical and efficient methods for the elimination of heavy metals from wastewater has necessitated a research interest toward of low cost adsorbents. Therefore, there is an urgent need that all inexpensive materials and which have an adsorbent potential should be explored and their feasibility for the removal of heavy metals should be studied in detail. The main objective of this research is to study the utilization possibilities of less expensive adsorbents for the elimination of heavy metals from contaminated waters by using filtration system. Industrial waste by-products whose fly ash and bottom ash combined with sawdust and marine sand have been used for the elimination of heavy metals from wastewater of the Mghogha industrial area. The obtained results indicate that the matrix compounds with fly ash, bottom ash, sand and sawdust can be used as an efficient and low cost adsorbent for simultaneous removal of heavy metals. The resulted water respects the discharge regulations.

Keywords: fly ash, bottom ash, sand, sawdust, heavy metals, adsorption, wastewater

1. Introduction
One of the negative impacts of human activity on our planet is wastewater discharges from manufacturing industries. It is worth noting that the composition of discharged wastewater varies considerably depending on the branch of industry, technology features in an industrial enterprise, population density, climate and even cultural and social traditions in a region. This wastewater commonly includes Cu, Ni, Cr, Cd, Cr, Zn and Pb [1,2]. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms.
Several treatment methods have been used to eliminate these pollutants namely coagulation [3, 4], ion exchange, precipitation. Studies on the treatment of effluent bearing heavy metals have revealed adsorption to be a highly effective technique for the removal of heavy metals from waste stream [5, 6, 7].
The objective of this study is to contribute to the research for less expensive adsorbents and the use possibilities for various wastes, which are in many cases also pollution sources. In this spirit, we tested the performance of different matrix composed of sea sand, industrial waste (fly ash and bottom ash from thermal power plants) and waste from carpentry (sawdust) for removal of heavy metals from wastewater.

2. Sampling and methodology

2.1. Sampling of industrial waste water

Wastewater samples were collected from Mghogha industrial area. The latter is situated in approximately 8 km of the city of Tangier in Morocco on the road of Tétouan. Figure1 shows the distribution of the industries in service in the zone by sector. The drinking water consumption is about 4 000 m^3 / day. In the sense of managing water resources, our study focuses on the treatment of liquid waste from this industrial area. Wastewater samples were characterized .The parameters analyzed were: organic matter COD, BOD_5, the potential hydrogen pH, Cl^-, PO_4^{3-} [8].

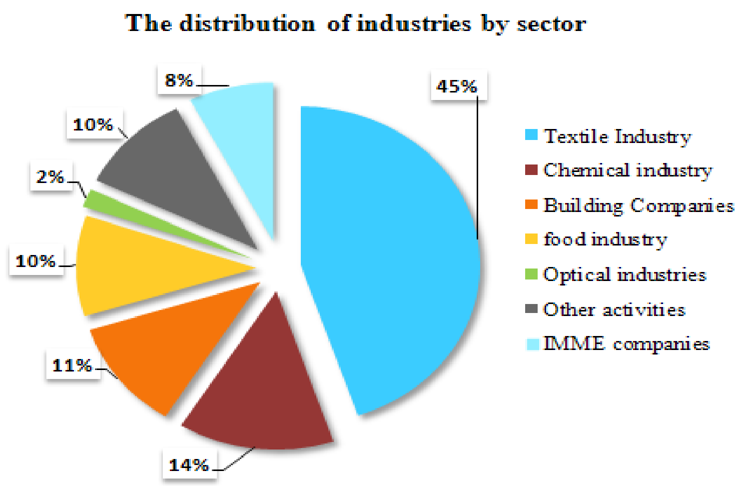


Figure 1: Distribution of industries in Mghogha industrial area

The average volume of each sample was 1 liter. Samples wastewater is collected in polyethylene bottles and kept in a cooler and transported immediately to the laboratory. These samples were analyzed by using ICP emission instrument to determine heavy metals present in this industrial wastewater.

2.2. Sampling of solid waste

2.2.1. Bottom ash

Bottom ash used in our experiments as adsorbing arise from the thermal power plant of Jorf Lasfar " JLEC " situated at a distance of 17 km from the city of El Jadida on the road which leads to El Oualidia. Other researches are oriented to use bottom ash in cement industry [9]. They are in the form of porous dark grains of grey color. Their color and their shape depend on the origin of the coal and on the conditions of combustion. The chemical composition of bottom ash is obtained by fluorescence X technique and crystalline structure was evaluated by XRD.

Figure 2: Visual aspect of bottom ash

2.2.2. Fly ash

Fly ash were also collected from the thermal power plant Jorf lasfer " JLEC ". The mineralogical composition of fly ash was analyzed by X-Ray Diffractometer. Fly ash has been chemically characterized using the technique of spectroscopy flame atomic absorption (ICP). Although the chemical composition of fly ash and bottom ash are similar, fly ash has a much higher reactivity because of its finely divided particle size. Fly ash is a fine powdery material composed of predominantly spherical particles. It's typically pale grey to dark grey in colour. Fly ash is often described as pozzolanic material. A pozzolanic is defined by the ASTM as a silica-rich. Their composition is in connection with the various types of present incombustible materials in the coal. Generally the present elements in fly ash are: the silicon, the aluminum, the iron, the calcium and the magnesium [10].

Figure 3: Visual aspect of Fly ash

Fly ash is one of the most known waste and it is being used as raw material in many industries such as cement industry [11], but its negative effect on the environment cannot be completely neutralized by doing this, so reusing it as an adsorbent in removal of different types of pollutants from wastewater solves two problems: water quality and waste management [12].

2.2.3. Sawdust

Sawdust used in our experiments as adsorbent material arises from carpentry. It is produced in large quantities at sawmills as a solid waste. Sawdust contains primarily lignin and cellulose. Cellulose is the most important constituent of the sawdust. The percentage varies between 40 and 45% by dry weight [13]. Its structure is characterized by hydroxyl groups in the equatorial position, and since the cellulose is a linear polymer, it becomes then easy to understand why the hydrogen bonds promote the adsorption capacity of the sawdust.

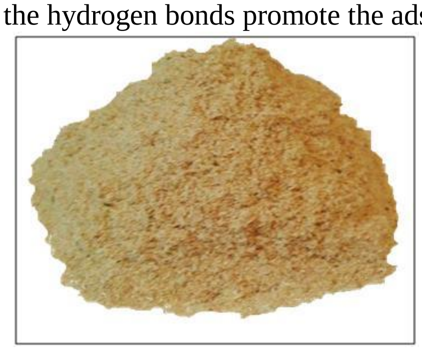


Figure 4: Visual aspect of Sawdust

2.2.4. Marine sand

Samples of sand used in our study were collected from 86 km of coastline of El Jadida between El Oualidia and sidi Bouzid [8]. These samples were carefully washed and dried at 40 ° C in stove, then screened to determine the different sizes. Table 1 summarizes the different sands samples used in our study.

The mineralogical characterization was studied by (ICP). The results of physical and chemical analysis of sand samples are given in Table 4.

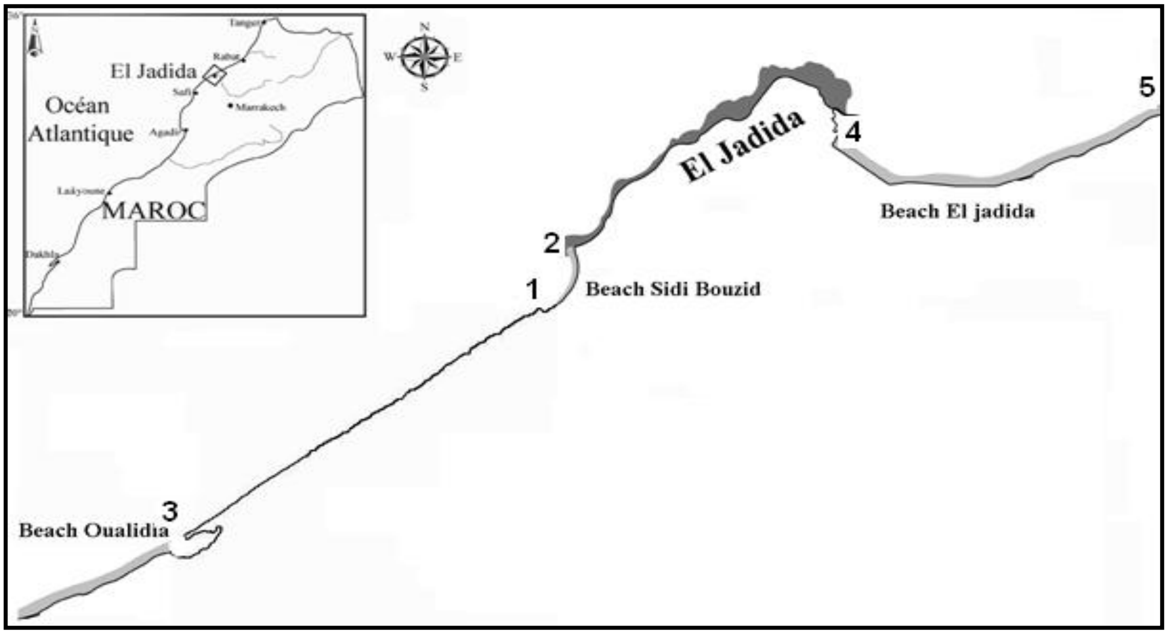


Figure 5: Map shows the location of sample sites.1: sand 1, 2: sand 2, 3: sand 3, 4: sand 4, 5: sand 5

Table 1: Locations of studied sands

Sand	Situation	coordinates (X,Y)
Sand 1	Sidi bouzid Beach near the complex ONE	33°13'13.2"N 8°33'36.8"W
Sand 2	Sidi Bouzid Beach (8 km from El Jadida on the coastal road to Safi)	33°13'42.0"N 8°33'16.1"W
Sand 3	Oualidia Beach from 80 km of El Jadida	32°44'14.9"N 9°02'34.3"W
Sand 4	El Jadida Beach near the Ibis hotel	33°14'47.8"N 8°29'42.7"W
Sand 5	El Jadida Beach	33°14'40.1"N 8°28'59.5"W

2.3. The experimental setup

Figure 6 reveals the experimental setup used during filtration percolation of our samples. Column dimensions are R = 100 mm and H = 120 mm where R and H are respectively the diameter and height of the column. The matrix is composed of two to three layers of adsorbents materials with the exception of matrix A composed by one adsorbent. The mass of each layer of absorbent is 50 g. Let V=150ml the volume of wastewater to be filtered. Table 2 provide in detail the various matrix used and the position of each substrate. The choice of this layout takes into account the granulometry of the materials to prevent their clogging [14]. Percolating filtration tests were repeated five times.

Figure 6: Filtration columns used in our experiments

Table 2: The matrix used as adsorbent

Matrix A	Sawdust
Matrix B	Sawdust+ Fly ash
Matrix C	Sawdust + Bottom ash
Matrix D	Sawdust + Fly ash + Bottom ash
Matrix 1	Sand 1+ Fly ash + Bottom ash
Matrix 2	Sand 2+ Fly ash + Bottom ash
Matrix 3	Sand 3+ Fly ash + Bottom ash
Matrix 4	Sand 4+ Fly ash + Bottom ash
Matrix 5	Sand 5+ Fly ash + Bottom ash

3. Results and discussion

3.1. Chemical Analysis of bottom ash and Fly Ash

Table 3 summarizes the medium values expressed at an oxide percentage of different elements contained in fly ash and in bottom ash. The major part includes SiO_2, Al_2O_3, CaO and Fe_2O_3 in both types of ashes.

Table 3: Chemical Composition of bottom ash and Fly Ash

Percent of chemical element	Fly ash	Bottom ash
SiO_2	57	52,07
Al_2O_3	34	8,86
Fe_2O_3	3,4	23,34
CaO	10	1,92
MgO	0,02	1,09
SO_3	0,5	1,87
K2O	1,2	1,9
$\sum SiO_2 + Al_2O_3+Fe_2O_3$	94,4	84,27
Na_2O		0,4
free CaO		0,29

3.2. Mineralogical analysis of bottom ash and Fly Ash

The chemical crystallites of all fly ash samples have been determined by XRD. The XRD pattern of fly ash and bottom ash are given in Fig.7. These samples present similar XRD patterns.

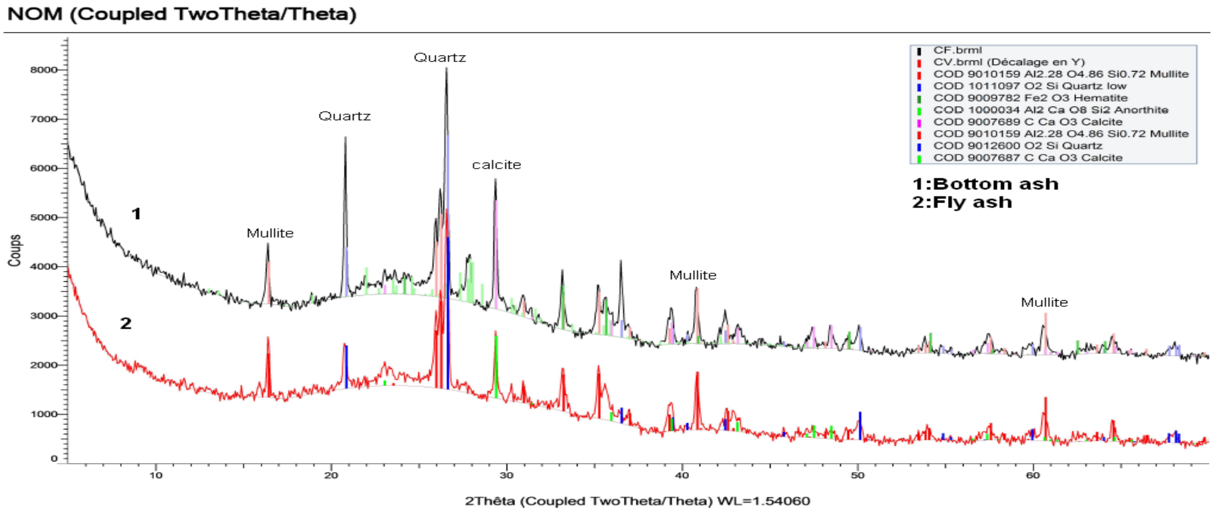


Figure 7:X-Ray Diffraction Pattern of bottom ash (1) and Fly ash (2)

The mineralogical composition of fly ash was analyzed by X-Ray Diffractometer. It was found from the diffraction peaks that bottom ash consisted mainly of crystalline phases such as Quartz (SiO_2) and Mullite. This result is explained by the mineralogy of the coal used, which generally consists of crystalline silica as quartz and clays phyllitheux group minerals (shale). During combustion these minerals change structure and give rise to a low crystallized portion in the form of Mullite and quartz and an amorphous portion. Likewise Mineralogical spectrum of fly ash reveals the same result of bottom ash.

The study of the morphology of the fly ash and bottom ash was performed by an electronic microscope of scanning type Philips XL 30 ESEM. Figure 8 illustrate the morphological structure of the studied adsorbents. Fly ash presents in the form of the spherical particles, of the small size as shown in figure 8(X). However bottom ash present a different structure compared with the morphology of fly ash. It appears in the form of the bigger particles and irregular as shown in figure 8(Y).

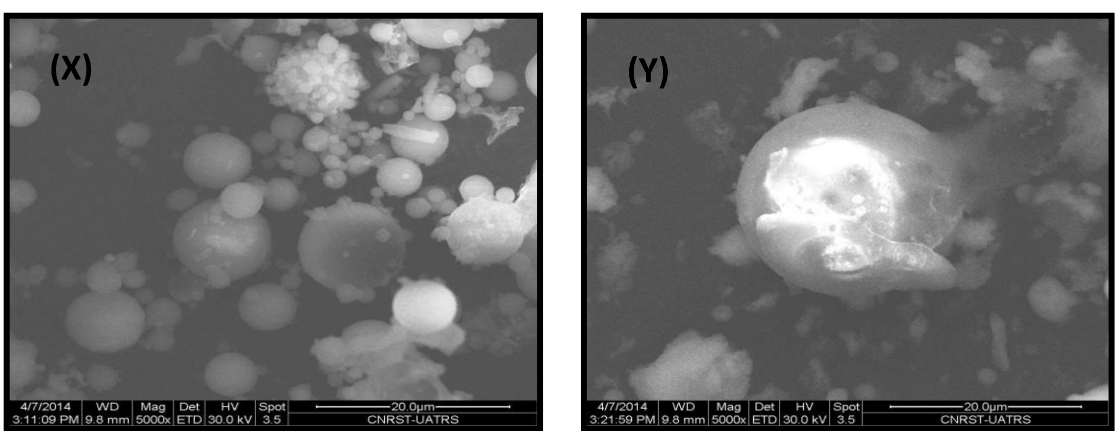


Figure 8: Morphology of fly ash (X) and bottom ash (Y)

3.3. Chemical Analysis of sand samples

To determine the chemical characteristics of the natural sand, chemical analyses were performed by atomic emission spectrometry with inductively coupled plasma (ICP-AES).The major element oxides present in marine sand samples were determined. The chemical compositions of the sand samples are given in table 4.

Table 4: Percentages of major element oxide of the sands

	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	K_2O%	MnO %	TiO_2 %
Sand 1	61.14	5.16	3.37	19.27	3.81	1	0.06	0.45
Sand 2	50.17	4.56	5.2	22.4	6.37	0.81	0.08	1.04
Sand 3	46.54	3.98	3.22	24.19	5.01	0.84	0.06	0.49
Sand 4	31.69	1.73	1.55	36.04	4.55	0.4	0.04	0.28
Sand 5	51.54	10.77	9.13	23.3	4.74	0.28	0.03	0.03

3.4. Analysis Results of Heavy Metals in wastewater before treatment

Table 5 shows the result of the analysis of wastewater by (ICP-AES). We observe that this wastewater is charged with heavy metals (Cr, Cd, Zn, Cu, Fe, As and Mn). Each value is the medium obtained after tree sampling campaigns. The results obtained show that the concentration of iron and cadmium present in the water are well above the required standard respectively (3 mg/l and 0.1 mg/l). We note that the Chromium is the metal element present in the water with a value of 11.98 mg/l, is well above the regulation (2 mg/l).
Chromium, copper and cadmium concentration can be source of dyeing, bleaching and printing of textile industry since the latter represents 45% of industrial area of Tangier city. Regarding the last two heavy metals, we found a concentration of 0.092 mg/l for arsenic and 0.976 mg/l for manganese, values which perfectly respect the standard respectively 0.1 mg/l and 1 mg/l.

Table 5: Concentration of heavy metals in raw wastewater (mg/l)

Zn	Fe	Cr	Cu	Cd	Mn	As
14.78	6.224	11.98	2.35	3.1	0.976	0.092

3.5. Analysis Results of Heavy Metals in wastewater after treatment

Many kinds of methods have been applied to remove heavy metal ions and they have their own advantages and disadvantages. Among them, adsorption by low-cost adsorbents is recognized as an effective and economic for the removal of heavy metals from wastewater. Many low-cost adsorbents have been developed and tested to remove heavy metal ions. However, the adsorption efficiency depends on the type of adsorbents.
The aim of our work is to develop a filter by a combination of two to three adsorbents material to remove heavy metal ions. Figure 9 to figure 11 shows the evolution of concentrations of heavy metals in the filtered water after treatment by using different combination of absorbent.

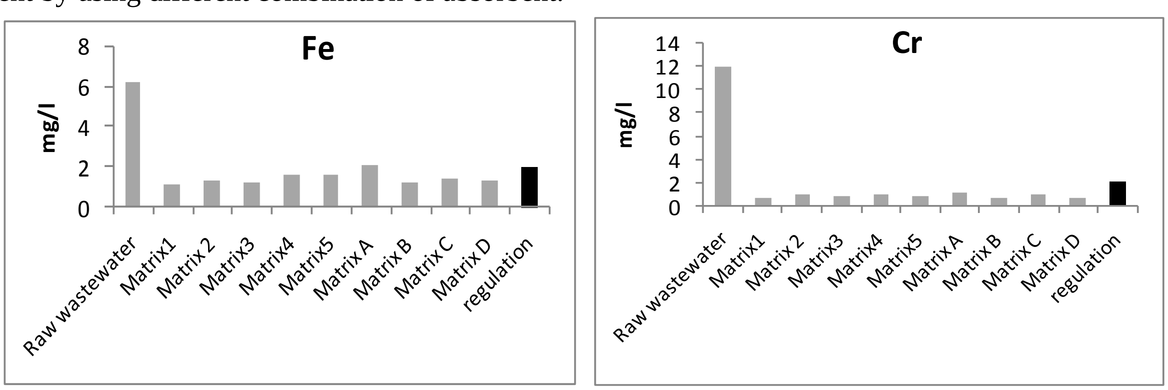
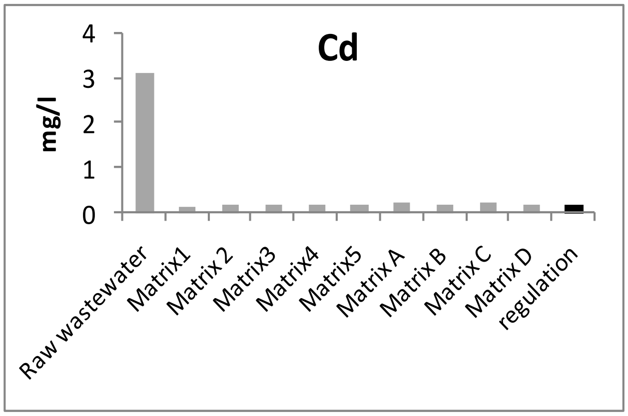


Figure 9: Abatement of iron and chromium after treatment in used matrix



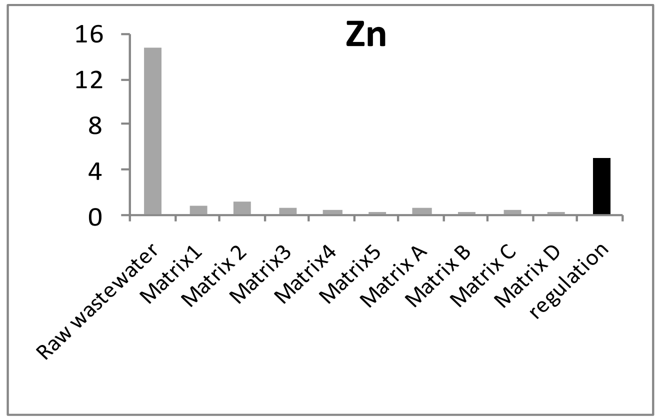


Figure 10: Abatement of cadmium and Zinc after treatment in used matrix

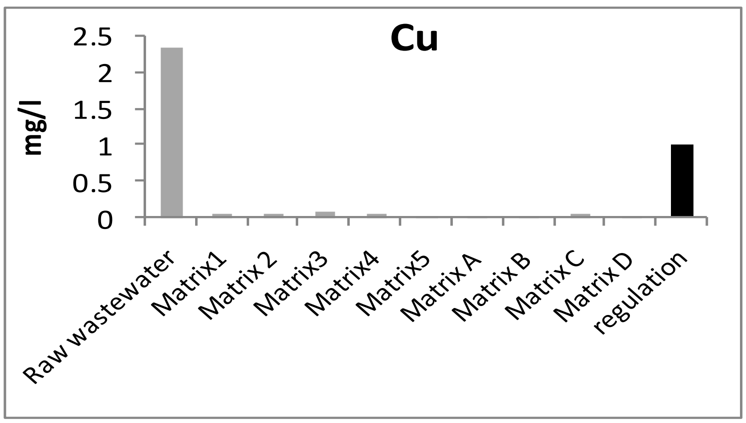


Figure 11: Abatement of copper after treatment in used matrix

The abatement of heavy metals after treatment using the different matrix is given in table 6.

Table 6: Abatement of heavy metals after treatment using the different matrix

	Zn	Cr	Cd	Fe	Cu
Matrix1	94.65	94.25	95.81	81.75	97.87
Matrix 2	92.56	92.15	93.39	78.57	98.09
Matrix3	96.21	93.40	94.35	79.51	96.60
Matrix4	98.17	92.90	93.23	74.33	97.15
Matrix5	98.44	93.82	93.90	73.97	98.51
Matrix A	96.83	91.32	92.26	66.42	98.34
Matrix B	98.85	95.06	94.13	80.24	98.72
Matrix C	97.77	92.06	92.74	76.88	97.45
Matrix D	98.71	94.91	93.87	79.29	98.70

The effectiveness of fly ash and bottom ash filter in the context of removal of heavy metals has been demonstrated by other researchers (combination of sand/fly ash filter [15,16] and combination of Sand/bottom ash filter [16]). Our contribution is the addition of bottom ash into the matrix and also the combination between wood sawdust and the matrix fly ash/bottom ash. These matrixes in this study give interesting results.

For iron, we observe a significant reduction in the concentration of iron as shown in figure 8 with abatement of 81.75% and a minimum concentration of 1,136 mg/l strongly less than the norm (3 mg/l).This finding can be explained by the reaction between CaO present in fly ash and SiO_2 present in the sands to form calcium silicate hydrates C-S-H. This latter can incorporate iron by substitution [17].

Figure 9 shows that chromium concentration record the highest concentration of 11.98 mg/l in raw wastewater, is strongly reduced after treatment with the high reduction rate of 95.06 % and a concentration 0,592 mg/l which perfectly respect the norm (2 mg/l). As regards cadmium, figure 10 shows that the different matrix used have enabled us to achieve a high abatement. However, we note that matrix 1 provide the best performance for the removal of this element with an abatement of 95.81% as shown in table 6.This result is due to the richness in silica of sand 1, the surface hydroxyl groups are formed by hydration which allows the adsorption of metallic cations [18].

Figure 10 shows a significant reduction in different filters used, before treatment we recorded a concentration of 14.87mg/l of zinc. The matrix 5 conducted an abatement rate 98.44 % with a concentration of 0.23 mg/l. A value strongly less than the regulation (5 mg/l).this reduction of zinc ion can be explained by the adsorption capacity of the bottom ash and fly ash. So it can be incorporated in the interlayer spaces of the C-S-H.

The figure 11 reveals an important reduction of copper concentration after filtration especially in matrix B with an abatement of 98.72 %. This elimination of copper ion is due to the adsorption capacity of the sawdust [19].

The rate of elimination of heavy metals is important due to:

- The adsorption properties of the fly ash and bottom ash. They are rich in silica and metal oxides ($\sum SiO_2 + Al_2O_3+Fe_2O_3$= 94, 4 % in fly ash and $\sum SiO_2 + Al_2O_3+Fe_2O_3$=84% in bottom ash), which gives them a high surface reactivity [20].
- An important adsorbent has a high electrical polarity and nutrients in particular ferrous ions (Fe^{3+}) which contribute to the neutralization of negative charges contained in the wastewater.
- Trapped in organic material layers stacked.
- Mechanical trapping: the metallic contaminants can react as nucleation center and remain trapped in the hydrate thus formed.
- Adsorption: calcium silicate hydrates CSH have a good adsorption capacity [21].
- The adsorption capacity of the sawdust.

Since the abatement is almost similar in the first fives matrices composed by the combination sand + Fly ash+ bottom ash, we had recourse to another parameter that is the residence time. It has a very important parameter study in large scale seen its role to avoid clogging and in the performance of installation.

Poured V = 150 ml of the wastewater, first we note t_0 the time corresponding to the descent of the first drop of water. Then we leave all of the volume V and we note the time t_f.

Table 7: The residence time of every matrix

	t_0	t_f
Matrix 1	6s	5min 45
Matrix 2	5s	5min 33
Matrix 3	4s	5min 37
Matrix 4	4s	5min 48
Matrix 5	3s	5min 20
Matrix A	2s	1min
Matrix B	10s	4min 11
Matrix C	4s	2min
Matrix D	12s	4min 40

Comparing the residence time of the first fives matrix composed of the combination of sand, fly ash and bottom ash. In the first fives matrix, we varied the type of sand of a matrix to another. We note that the maximum stay time is 5min 48 and the minimal time is 5min 20. Since the matrix 1, 2, 3, 4, 5 have similar reductions of heavy metals. However, the matrix 5 presents the optimal residence time. This latter is an important parameter in driving the process.
From the obtained results, we observe that the matrix 5 and matrix B can be a highly excellent adsorbent to remove heavy metal ions because it allows us to achieve good removing efficiencies compared the others.
Thus the treatment proceeded during this study allows on one hand the management of solids waste by applying as an adsorbent and the other hand it proposes a economical treatment seen the exploitation of raw solid waste without development. Because the cost must be considered to reduce the treatment fees whether the developed adsorbent is appropriate to be implemented in large scale. About the resulting sludge, it will be valued in civil infrastructures in an upcoming work Seen the pozzolanic properties of fly ash that resemble a cement powder [22.23]. This work is a preliminary study designed to test the possibility of using the combination developed from solid waste. The results of this preliminary study encouraged us to investigate the ability of these adsorbents via a system on a pilot scale and a kinetic study will be accompanied to judge the performance of the proposed method (work in progress). We think that the environmental interest to this kind of work is extremely significant in industrial fields as well as scientific fields.

Conclusion

Industrial wastewater of the city of Tangier is a source of nuisance that is added to the many problems of environmental contamination if they are not treated before discharge. The heavy metals in this water must retain great attention because it is difficult to prevent the spread and dissemination of this pollution in soils and into groundwater.
The results of this study proved the feasibility of removing heavy metals by using two efficient matrixes:

- The first matrix is a combination between three adsorbents (marine sand-fly ash and bottom ash).
- The second matrix is a combination between fly ash and sawdust.

So the use of these materials has double benefits to the environment: these materials are converted into high added value adsorbents, whereas these adsorbents are suitable for wastewater purification. From the obtained results, the conducted study is an economical method for the treatment of discharges from industrial plants specially the Mghogha area.

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