REMOVAL OF HEAVY METALS FROM AN INDUSTRIAL EFFLUENT BY SYNTHESIZED ZEOLITE: CASE OF BOUNOURA INDUSTRIAL ZONE

Bahaz Hanane[1], Hadj Seyd Abdelkader[1,2], Moulai Kromia[3], Aggoune Mohamed Salah[1]

[1]Laboratoire de mathematiques et sciences appliquées Université de Ghardaia BP 455 Ghardaia-Algeria
[2]Faculté des Hydrocarbures Université KASDI MERBAH Ouargla BP 511 Ouargla-Algérie
[3]Faculté des Sciences et Technologies Université de Ghardaia BP 455 Ghardaia-Algeria

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ABSTRACT

Bahaz, H., Hadj Seyd, A., Moulai, K., & Aggoun, M. S. (2020). Removal of heavy metals from an industrial effluent by synthesized zeolite: Case of Bounoura industrial zone. *Lebanese Science Journal*, 21(1), 80-94.

The aim of this paper is the synthesis of a Faujasite type zeolite: $9SiO_2$: Al_2O_3: $3Na_2O$: $120H_2O$ and study its ability to remove heavy metals from an industrial effluent. Characterization of the zeolite was carried out by X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The study of the elimination of ten heavy metals on an aqueous effluent, taken from the industrial zone of Bounoua (Algeria), shows that the synthesized zeolite is able to eliminate nearly 40% of the analyzed heavy metals. the results demonstrate a removal rates of metals in a descreasing order, as following: Cd > Mn > Sn > Fe > Cr > Ni > Pb > Mg > Zn > Cu. Cadmium is the most adsorbed metal with a rate of 86.47 % and copper takes the last position with a removal rate of 19.27 %. The kinetics and isotherms study of adsorbtion of cadmium by zeolite shows that the adsorption is managed by kinetics of the pseudo-second order and the Langmuir isotherm represents better the adsorption of this metal. The study demonstrates that, besides the economy, zeolite facilitates the process of adsorbtion. Moreover, the zeolite is very efficient and reliable material to eliminate the heavy metals and to mitigate the problems of pollution of the environment caused by the industrial activities.

Keywords: heavy metals, pollution, industrial effluent, isotherms, zeolite Na-Y.

INTRODUCTION

Industrial activities are almost entirely responsible for environmental pollution, since they generate large quantities of toxic discharges in different solid, liquid and even gaseous forms. These releases present an imminent risk to human health and the environment, as long as they are characterized by a cumulative toxicity.

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Despite standards and guidelines developed to reduce the risks of polluting discharges and laws that penalize offending industrial operators, this scourge continues to increase and industrial pollution continues to accumulate in the environment in many countries around the world.

Heavy metals are among the most abundant pollutants in liquid industrial effluents; these compounds have high potential of toxicity and are highly dangerous to ecosystems and human health. Most of these heavy metals are present in polluted waters including Hg, Pb, Ag, Cu, Cd, Cr, Zn, Ni, Co and Mn (Bhuiyan et al., 2011), and it has been found that many heavy metal ions produce strong health problems and damage plants and animals (Nahar et al., 2018; Dietler et al., 2019).The dangers of pollution of some heavy metals may be acute due to their severe toxicity even at low concentrations (Christensen et al., 2000; Jarup, 2003).

The term “heavy metals” denotes the group of metals and metalloids which engenders soil and water contamination and toxicity. They are associated with elements with a density greater than 5 g/cm^3 and an atomic number greater than 20 (International Union of Pure and Applied Chemistry [IUPAC], 2002). The term heavy metals also refers to elements that are mainly present in trace amounts in the environment, such as copper, chromium, nickel, lead, zinc and cadmium. By virtue of their cumulative nature, even at low rates of concentrations, heavy metals inflict considerable harm on the organism and the environment. There are different sources for heavy metals in the environment (Ying et al., 2019). These sources can be both of natural or anthropogenic origin (Hou et al., 2017). Heavy metals are mainly introduced into groundwater by agricultural and industrial activities, land filling, mining, and transportation (Brad, 2005); and can be easily transferred to human body because they are mediated by water, air, and food (Arshid et al., 2019).

Soil and water contamination by heavy metals and metalloids has been a major concern to human health and environmental quality.

Remediation of these noxious elements has been widely investigated and multifarious technologies have been practiced for many decades (Yanyan et al., 2018), these technologies include chemical precipitation, coagulation, ion exchange, electro coagulation, nanofiltration and electrochemical oxidation (Meenakshi, 2006). However those methods have limitations in terms of high operational and maintenance cost, and generation of waste (Wang et al., 2010). The adsorptive removal of heavy metals has been considered one of the most facile, cost-effective, and eco-friendly techniques among the various removal technologies (Mohd et al., 2019; Asad et al., 2019)**.**

Adsorption has attracted much attention from researchers. Adsorption defines the property of certain materials to be fixed to their surface of molecules (gases, metal ions, organic molecules... etc.) extracted from the liquid or gaseous phase in which they are immersed. The fixing on the solid surface is done in a more or less reversible way. Adsorption processes are used for several main applications, such as refining treatments for drinking water, tertiary treatment of wastewater or industrial water (Yadav et al., 2019).

With regard to the industrial effluent treatment, the most employed adsorbents are: activated carbon; mineral adsorbents in form of alumina and various metal oxides; and organic adsorbents in the form of macromolecular resins with large specific surface area.

Zeolites are remarkable silico-aluminous minerals that have shown their effectiveness in wastewater and industrial discharges treatment; treatment of complex leachates with heavy metals, and gaseous effluents, this is due to their ability to adsorb selectively ions and polarized molecules. Zeolites are characterized by a large surface area which makes them a good absorbent. Furthermore, they are environmentally safe, eco-friendly, and low cost. Zeolites have high cation exchange capacity and are considered to be an effective material for the removal of heavy metals and very largely used in the treatment of industrial effluents (Merrikhpour et al., 2013).

In this work a Na-Y zeolite has been synthesized successfully by hydrothermal technique. In order to test the adsorbent capacity of this synthesized zeolite, tests for removal of heavy metals contained in an effluent from the largest industrial area of Bounoura of the wilaya of Ghardaïa (Algeria). The initial heavy metals concentrations (in the raw effluent) and final (after treatment) were measured and the yields were determined. Kinetics and adsorption isotherms of cadmium in contaminated solutions with this metal have also been studied.

MATERIAL AND METHODS

Presentation of the study area

The Wilaya of Ghardaïa is located in the northern part of the Sahara, 632 km from the capital Algiers. Ghardaïa is a World Heritage Site (Medejerab, 2009) and is considered a major tourist site in Algeria. The number of inhabitants is 363,598 (2008 statistics). The Wilaya's climate is a desert type dominated by heat, drought and large diurnal and annual temperature differences (Benoudj et al., 2014).

In addition to its tourist importance, the Wilaya of Ghardaïa also has an important commercial and industrial fabric; the two important industrial areas are the cities of Grara and Bounoura.

Bounoura is an industrial zone located on National Road number 1 (NR1), at geographical point 32°26'8"N, 3°42'16"E (Figure 1). Its surface area is 118 hectares and includes very important private and state industrial units such as “ALFAPIPE Company” which is a big pipeline manufacturing Company. Another important company is the company of hydrocarbon processing and distribution “NAFTAL unit”. Numerous plaster manufacturing and processing units are situated, in this industrial zone. There are also factories for the manufacture of radiators and exhaust pipes, and also factories for the manufacture of copper and luxury valves, as well as units for the manufacture of electrical components.

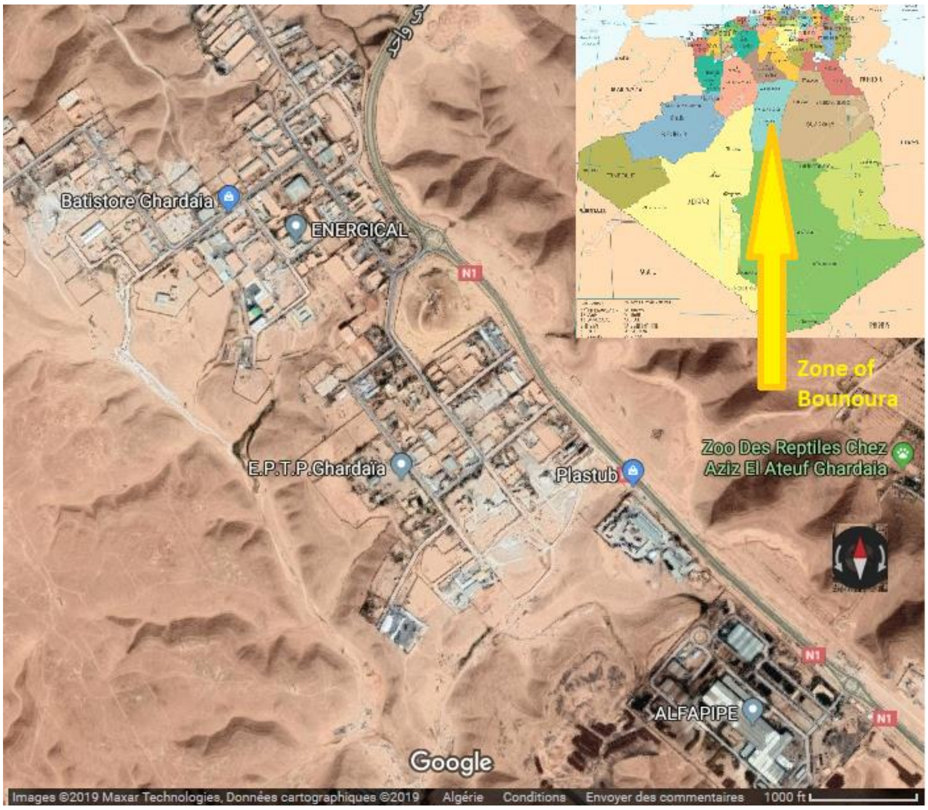

Figure 1. Satellite view of Bounoura industrial zone (Google n,d).

Bounoura area generates a large amount of wastewater in the form of liquid effluents laden with pollutants of various nature, from industrial units. Table 1, below, includes the average physicochemical characteristics of the effluent leaving the area analyzed at the main collector, for the year 2019.

Table 1. Physicochemical characteristics of the effluent leaving the industrial zone.

Parameter	**Temperature (°C)**	**pH**	**Flow (m^3/Day)**	**SM (mg/L)**	**BOD5 (mg/L)**	**COD (mg/L)**	**Conductivity (mS/cm)**
Value	17.5	5.7	25000	135	128	146	3.62

Experimental procedure

Synthesis and characterization of the zeolite

The synthesis of zeolite is carried out in four steps, shown in Figure 2 below. The reactor used is a stainless steel autoclave, with a polyethylene tetra fluoride (PTFE) of 40 mL volume. The first step consists to prepare the hydrogel by adding distilled water, NaOH soda, and a silicon source (LUDOX 25%). In the second step, curing consists in maintaining the hydrogel under strong agitation, during a period of a few ten minutes at several hours at room temperature (Nik et al., 2007; Majid, 2015).Curing allows homogenizing the reaction mixture. In the third step, the hydrogel obtained after stirring is transferred to a PTFE-coated steel reactor under autogenous pressure at a temperature of 80°C for 3 days (Holmberg et al., 2003; Aderemi, 2004). In the last step, the zeolite is finally recovered, after crystallization, separated by filtration, washed with distilled water with a vacuum pump, and dried at 50°C for one night.

Characterization of the zeolite was carried out by X-ray diffraction analysis using a Bruker MeasSrv diffractometer, Fourier transform infrared spectroscopy (BRUKERFT-IR) and scanning electron microscopy.

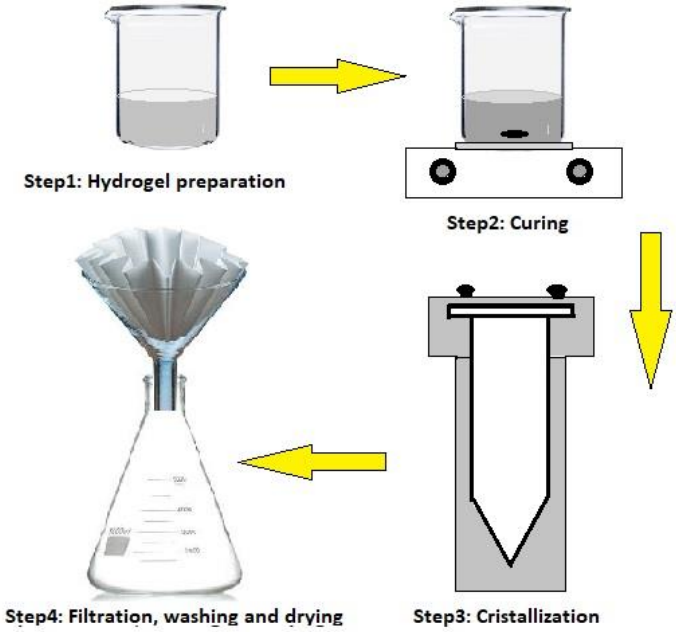

Figure 2. Zeolite synthesis steps.

Adsorption assay

Samples of the liquid industrial effluent were collected at different time intervals from the main effluent collector located at the outlet of the Bounoura industrial zone. The samples were taken during the month of March 2019, mixed and analyzed by three repetitions; the average was taken into account. The computation of the concentration of pollutants is accomplished by the standard techniques recommended by the American Public Health Association (American Public Health Association [APHA], 1998) and Algerian standards. Physicochemical parameters such as pH and temperature were taken on site using a multi-parameter analyzer (HORIBA-U 22). All other analyzes were carried out at the Mathematics and Applied Sciences Laboratory of Ghardaïa University (Algeria).

In order to study the removal performance of heavy metals by the synthesized zeolite, 500 mL of raw wastewater was shacked for one hour in 0.5 g of zeolite, at constant temperature (25 °C). After agitation and filtration employing Whatman 42 filter paper, the filtrate was analysed in order to determine the concentration of heavy metals by atomic absorption spectrometry (AAS).The heavy metal removal efficiency were calculated using the formula (1) below (Shamsan et al., 2018):

$$\text{Removal rate (\%)} = \frac{C_i - C_f}{C_i} \text{x} 100 \tag{1}$$

With:
C_i: initial concentration of the metal in mg/L at the raw effluent.
C_f: final concentration of the metal in mg/L in the treated effluent.

Kinetic study

One characteristic with overarching importance that defines the absorption efficiency is the absorption kinetics. In this work, cadmium was chosen to study adsorption kinetics. Cd (SO_4), $8H_2O$ (Merck analytical products) was used as a source for Cd (II) ions, then a stock solution (1g/ L) was prepared from the obtained concentrated solution. The working solutions were prepared by means of dilution of stock solution. A series of adsorption essay, for different initial concentrations of Cd(II), ranging from25 to 100 mg / L, by measuring in each the adsorbed quantity Q_t at time t (t = 30, 60 , 90, 120 and 150 min) and to carry log $(Q_e\text{-}Q_t)$ and t/Q_tin function of time, kinetics of the pseudo first order and pseudo 2nd order are represented by the following models in equations (2) and (3), respectively (Elwakeel et al. 2017):

$$\ln(Q_e - Q_t) = \mathrm{Ln}(Q_e) - K_1.t \qquad (2)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \qquad (3)$$

K_1 and K_2 are, respectively, the first and second order rate constants.
V: volume of the solution and m mass of the adsorbent (zeolite).
Q_e and Q_t are, respectively, the adsorbed amount of Cd at equilibrium and at time t. These entities are given by the following expressions:

$$Q_e(\mathrm{mg/g}) = \frac{C_0 - C_e}{m}.V \qquad (4)$$

$$Q_t(\mathrm{mg/g}) = \frac{C_0 - C_t}{m}.V \qquad (5)$$

Adsorption isotherms

Adsorption isotherms relate the equilibrium mass of adsorbed material in the adsorbate phase (Q_e) to its equilibrium concentration in the solution phase C_e. Langmuir and Freundlich isotherms of absorption were used to fit the data in the experimentation.

Langmuir's isotherm hypothesizes that the absorption is of monolayer type on a uniform surface, provided that the sites of absorption are of a finite number. Once a site is filled, no further sorption can occur place at that site (Hardiljeet et al., 2011)

The Langmuir equation can be written in the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m.K_L} + \frac{C_e}{Q_m} \qquad (6)$$

Where:
C_e denotes the concentration of adsorbate at equilibrium (mg. g^{-1}).
Q_m is the maximum adsorption capacity (mg. g^{-1}).
K_L is Langmuir constant which refers to adsorption capacity (mg. g^{-1}), which can be correlated with the variation of the suitable area and porosity of the adsorbent.

In contrast to Langmuir's isotherm, the isotherm of Freundlich may represent monolayer absorption (chemisorption) and multilayer absorption referred to as physisorption. The assumption of which this model is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent (Hardiljeet et al., 2011)

The linear form of the Freundlich isotherm is as follows:

$$\log Q_e = \log K_F + \frac{1}{n}.\log C_e \qquad (7)$$

K_F and 1/n are the parameters of the Freundlich equation.

RESULTS AND DISCUSSION

Zeolite characterization

A Faujasite zeolite with a high SiO_2/Al_2O_3 ratio its formula: $9SiO_2$: Al_2O_3: $3Na_2O$: $120H_2O$, was successfully synthesized, (Holmberg et al. 2004, Wang et al. 2003). The structural characterization of zeolites is essential owing to their properties, namely, size and configuration of the cavities or channels that make up the zeolite pores. Thus, the first characterization was carried out by X-ray diffraction. The X-ray difractogram in the 2θ range, from 5° to 100°, in figure 3, clearly indicates the good crystallinity of the synthesized zeolite. Intense peaks located at 2θ at 21.8°, 28.1° and 33°. The diffraction lines are displaced towards the large angles 2θ, this means that the material is rich in silica. For this zeolite, the Si/Al ratio is around 4.5.

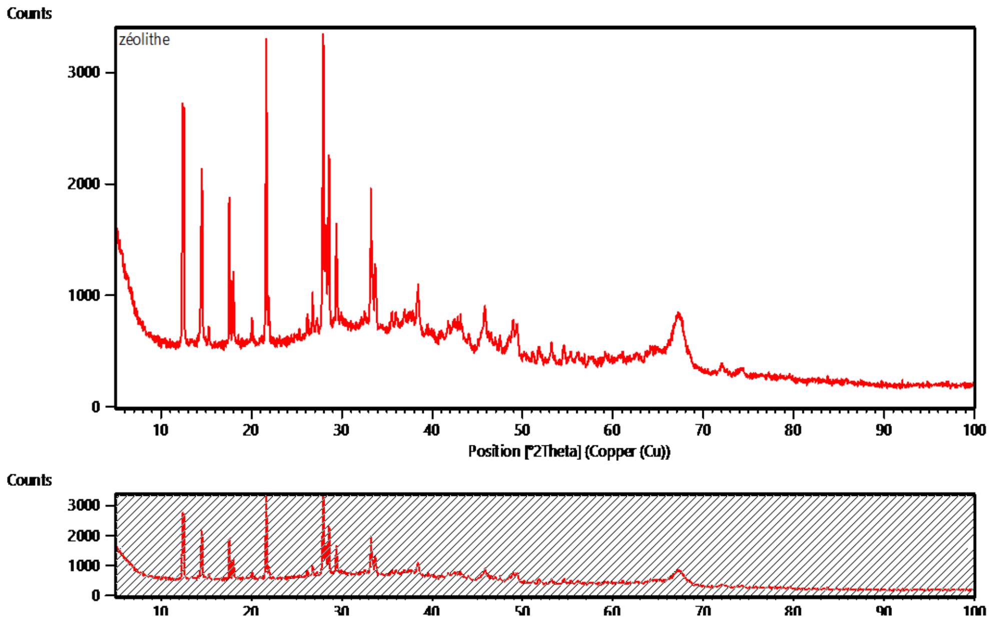

Figure 3. X-ray difractogram of synthetic Zeolite Y.

This structure is confirmed by the SEM images (Figures 4 and 5) which clearly shows that the crystals have sharp edges and large size. On the other hand, the FTIR spectra also assert the structure of zeolite, characterized by the presence of intense bands at 477 - 509 cm^{-1} that characterize the TO_4 tetrhedral site (T=Al, T=Si). A 609 cm^{-1} peak characteristic of the outside of the double ring and bands at 738-680 cm^{-1} and 591-427 cm^{-1} attributed to the symmetrical elongation and bending vibrations of TO atoms respectively (Utami et al., 2019). The 1466-1476 cm^{-1} bands are assigned to the internal vibrations of the T-O-T tetrahedron and finally a 1638 cm^{-1} band characterizing the O-H bond of the water.

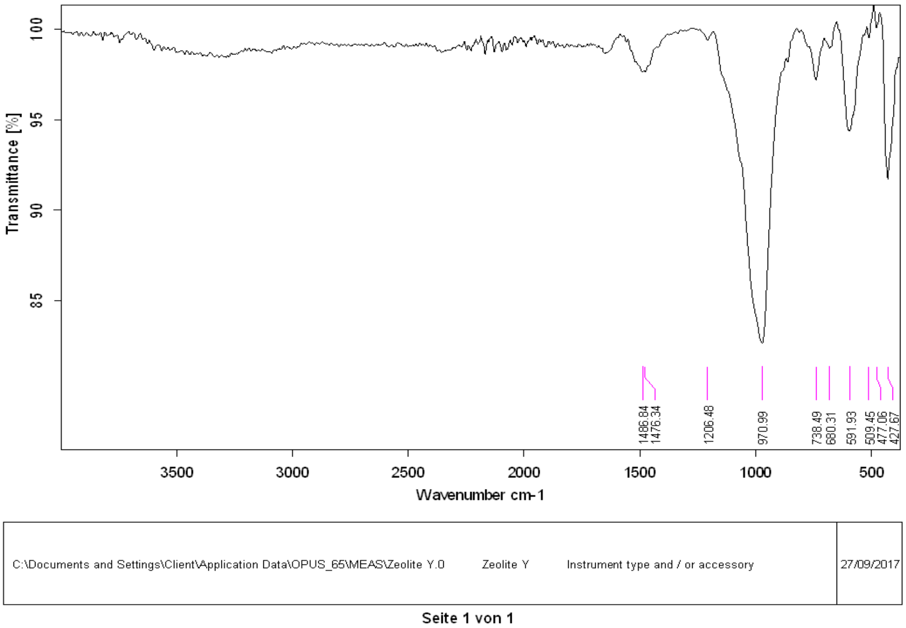

Figure 4. FTIR analysis of synthetic Zeolite Y.

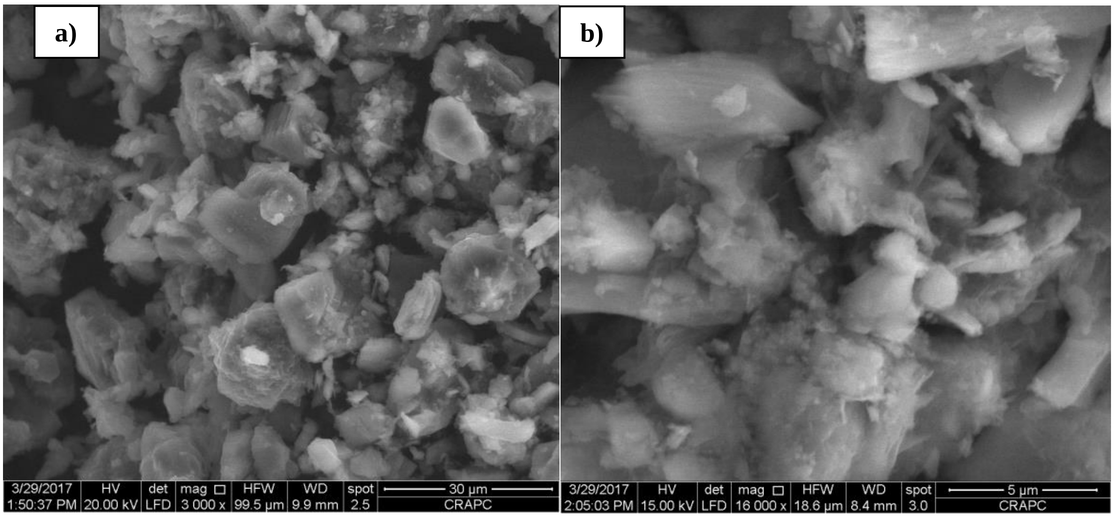

Figure 5. SEM analysis of synthetic zeolite Y (a: image at 3000X magnification, b: image at 16000X magnification).

Removal of heavy metals

The below Table 2 summarizes the results of the treatment of the industrial effluent of the Bounoura industrial zone with zeolite Y. The first and second columns contain respectively the values of the initial C_i and final concentrations C_f of heavy metals before and after treatment. The third column shows the heavy metals removal rates by the zeolite. The last column includes the tolerable concentrations of heavy metals C_{Max} required by the Algerian standards, in accordance with Executive Decree 09-209 of 11/06/2009, fixing the terms and conditions for granting the authorization to waste water discharge other than in a public network sanitation or in a station of purification (JORA, 2009).

Table 2. Heavy metals removal rates from industrial effluent, by Na-Y zeolite.

Metal	C_i (mg/L)	C_f (mg/L)	Rate %	C_{Max}(mg/L)
Fe^{2+}	4.543	1.157	74.541	1.00
Cu^{2+}	4.377	3.533	19.269	1.00
Zn^{2+}	0.917	0.643	29.818	2.00
Mn^{2+}	11.733	2.767	76.420	-
Ni^{2+}	21.520	13.150	38.894	2.00
Sn^{2+}	0.533	0.130	75.625	0.10
Mg^{2+}	239.067	154.707	35.287	300.00
Pb^{2+}	0.573	0.370	35.465	0.50
Cd^{2+}	0.397	0.054	86.471	0.10
Cr^{2+}	0.782	0.214	72.665	2.00
Hg^{2+}	0.000	0.000	-	0.01
As^{3+}	0.000	0.000	-	0.01
Total	**284.442**	**176.724**	**37.870**	-

The results show that raw wastewater from the studies industrial site is overloaded with metals which causes numerous risks on the organism and the environment.

Most metal concentrations exceed the limits tolerated by the Algerian standards for industrial water discharges (JORA, 2009).

It highlights a very high concentration for iron (5.9 mg/l), nickel (4.26 mg/l) and tin (0.5 mg/l). Concentrations are just within the required limits for magnesium (228.8 mg/l) and lead (0.52 mg/l) and are tolerable for the remaining metals. Mercury and arsenic are practically absent in the effluent. Their contents have been detected in traces.

The total initial concentration of heavy metals, analyzed in the effluent, is of the order of 284.4 mg / L, after treatment and agitation of the effluent with the zeolite, the total final concentration is reduced to 176.7mg / L, with a removal rate of the order of 38%.

The zeolite is able to eliminate nearly 40% of the ten heavy metals analyzed. This result is satisfactory since the effluent contains, in addition to metals, other pollutants and organic materials, such as: nitrates, nitrites and others, for example, COD, BOD5 and suspended matter have been reduced to the respective percentages: 55.4, 64.07 and 71.32%.

The adsorption rates by zeolite Y in the effluent studied are low compared to those found by Parag et al., (2010) in the treatment of an effluent from a metallurgical industry, with zeolite A, iron was eliminated with 99.23%, copper 97.37% and zinc with 94.68%. But our results are clearly better than those found by Sabry M. S. et al. (Sabry et al., 2012) in their study of the elimination of some heavy metals by a natural zeolite (clinoptilolite), in which the elimination rates of copper, cadmium and nickel were valued at 47%, 22% and 29% respectively.

In this study, the results demonstrate a decreasing order of the removal rates of metals as follows: Cd>Mn>Sn>Fe>Cr >Ni>Pb>Mg>Zn>Cu. Cadmium is the most adsorbed metal with a rate of 86.47 % and copper takes the last position with a rate of removal of 19.27 %.

Lead is better adsorbed than zinc and copper by zeolite, this is probably due to the adsorption selectivity of zeolite vis-a-vis these metals. This is confirmed by the results found by Kesraouiouki et al., (1994) and Caputo and Pepe (Caputo and Pepe, 2007) in their studies of the removal of heavy metals by zeolites.

Kinetic study

Parameters of linear forms of kinetic models for pseudo-first-order and pseudo-second-order are given in figures 6 and 7 below, and summarized in table 3. The correlation coefficients associated to the linear fits was used to evaluate the best model to describe the metal ions adsorption data. Results demonstrate that the pseudo-second-order model is the most appropriate to represent cadmium removal kinetics by synthetized zeolite.

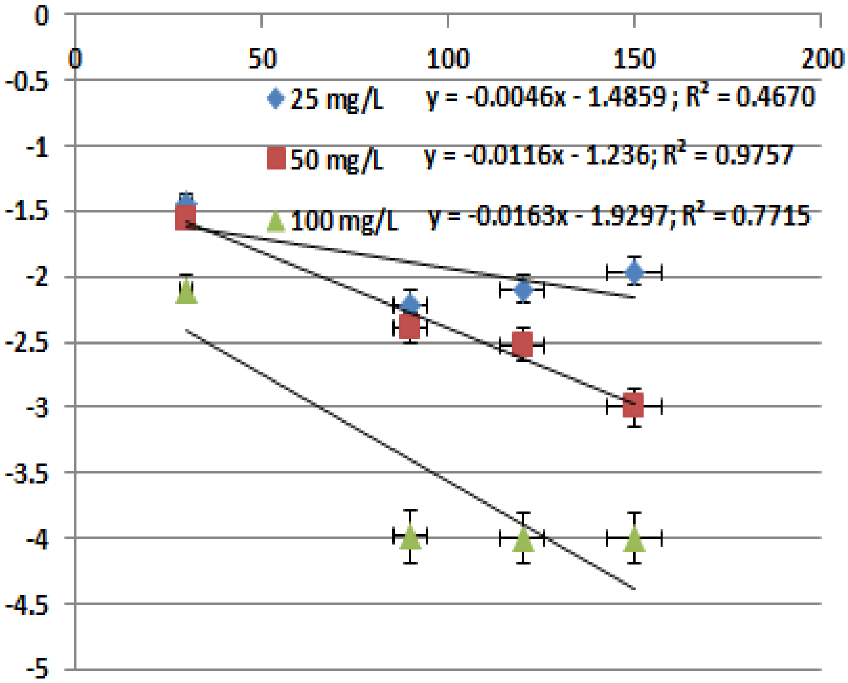

Figure 6. 1st order kinetic model.

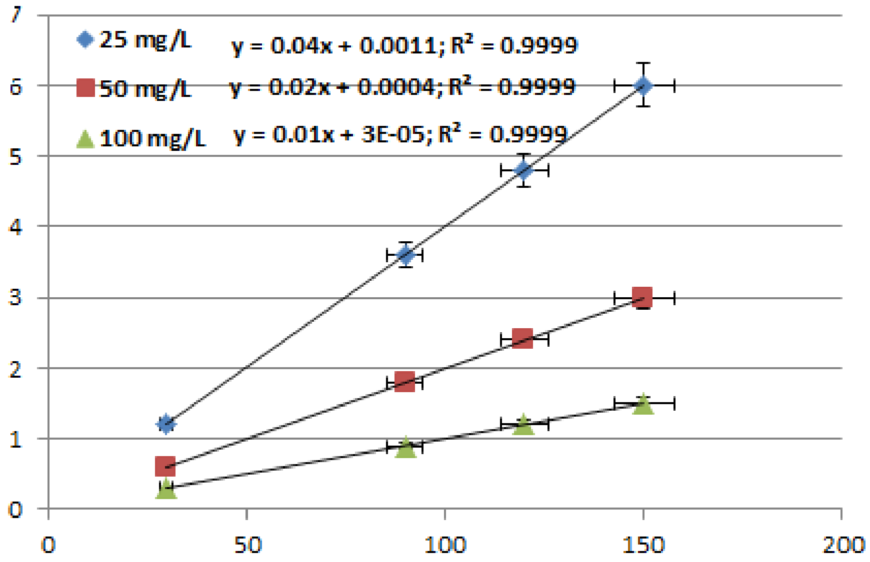

Figure 7. 2nd order kinetic model.

Table 3. Parameters of 1st and 2nd order kinetic models.

C_0 (mg/L)	pseudo-first-order			pseudo-second-order		
	K_1 (min^{-1})	Q_e ($mg.g^{-1}$)	R^2	K_2 ($g.mg^{-1}.min^{-1}$)	Q_e ($mg.g^{-1}$)	R^2
25	0.004	0.227	0.467	1.455	25	0.999
50	1.236	0.989	0.975	1.000	50	0.999
100	0.016	0.145	0.771	3.333	100	0.999

Adsorption isotherms

Adsorption isotherms provide some information on how an adsorption system proceeds, and indicate how molecules of adsorbate interact with adsorbent. Figures 8 and 9 below, represent the Langmuir and Freundlich isotherms for the adsorption of cadmium by the zeolite, the parameters of their linear equations are summarized in Table 4 below.

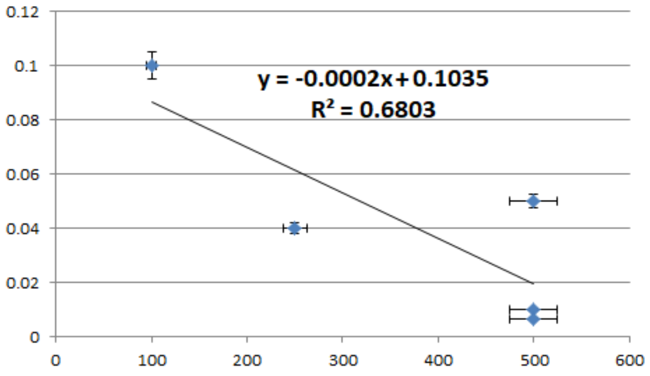

Figure 8. Langmuir adsorption isotherm.

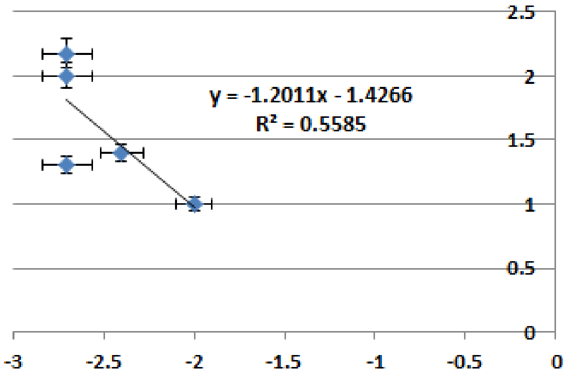

Figure 9. Freundlich adsorption isotherm.

Table 4. Parameters of the models for adsorption isotherms.

Langmuir model			**Freundlich model**		
Q_m (mg.g^{-1})	K_L (L.g^{-1})	R^2	1/n	K_F	R^2
96.618	0.517	0.680	-1.201	0.240	0.558

Based on R-squared values, Langmuir isotherm model signifies the best correspondence with the experimental data. The maximum adsorption capacity Q_m is 96.62 mg/g. This isotherm is associated to a monolayer adsorption involving homogeneous interactions with the solute.

The adsorption of cadmium is weakly represented by the Freundlich isotherm with an R-squared value of the order of 0.558. This isotherm defines the surface heterogeneity and the exponential distribution of active sites and their energies. The parameters of the linear model of this isotherm for K_F and 1/n are 0.240 and -1.201, respectively.

CONCLUSION

In this study, due to the use of hydrothermal method, zeolite Na-Y was successfully synthesized. Many techniques were used to characterize the zeolite and to confirm its structure, such us: X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

In order to test the effectiveness of the zeolite in reducing the concentration of pollutants contained in an industrial effluent, samples of wastewater were taken from an effluent from a very important industrial area of southeastern Algeria (Bounoura Industrial zone, Wilaya of Ghardaïa). The analysis of ten heavy metals in the effluent shows that it contains eccessive heavy metal rates, whose concentrations exceed the Algerian standards required.

Tests for removal of these metals by agitation in the synthesized zeolite show that it is an effective adsorbent capable of reducing up to 37.87% of the heavy metals contained in the effluent. The reduction is in decreasing order of: Cd > Mn > Sn > Fe > Cr > Ni > Pb > Mg > Zn > Cu. Cadmium is the most adsorbed metal with a rate of 86.47 % and copper takes the last position with a rate of removal of 19.27%.

Cadmium removal kinetics by synthesized zeolite is successfully modeled by the pseudo-second order rate equation; nonetheless, the Langmuir isotherms fit well the adsorption of this metal.

The study also shows the effectiveness of synthetic zeolite and its great ability to reduce pollutant levels of industrial effluents that can harm the environment and threaten the life of living beings.

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