Retention of heavy metals (Pb, Cd, Cr and Zn) by a sand area of Agadir: Equilibrium and kinetic

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Abstract. Because of the increasingly importance of industrial and agricultural activities, many pollutants reach aquifers that deplete groundwater quality and rivers with organic and inorganic pollutants such as heavy metals. These latter are huge nuisance to public health and cause serious problems because of their stability and low biodegradability by natural processes. In this study, we tried to develop an abundant raw material from the sand dunes of M'zar (Agadir region) by cleansing them through adsorption wastewater containing heavy metals (Pb, Cd, Cr and Zn). The results are comparable to other media such as kaolinite, Cotton fibers and sawdust.

1. INTRODUCTION

Nowadays the problem of heavy metals from wastewater has become increasingly worrisome. A common feature of industrial effluents is the fact that they almost always contain harmful heavy metals [1,2]. To protect the environment, the maximun level of these metals must be limited. Several treatment methods have been used to eliminate these pollutants [3].

This study's main object is the promotion of a abundant raw material in Morocco's sand dunes of M'zar (Agadir region). This will cleanse them through adsorption wastewater containing heavy metals such as cd, Pb, Cr and Zn.

2. MATERIALS AND METHODS

2.1. Dosage of heavy metals

In nature, some metals exist in their raw or free form. But generally, they are known as minerals and they are most often insoluble in bonds with oxygen, silicates, carbonates, sulfides, phosphates, etc. [4].

The studies were conducted by contacting of a mass of sand with 50 ml of metal solution to a given concentration prepared from a salt. The pH of the solution was adjusted to 4.5 by using dilute nitric acid to obtain a stable solution while avoiding the precipitation of metals.

The metal cations were prepared from the following salts: for lead $Pb(NO_3)_2$, $Cd(NO_3)_2$ were used. $4H_2O$ for cadmium, $CrCl_3.6H_2O$ for chromium and $ZnCl_2$ for zinc. The Concentration prepared for each element is 1 g / l.

Metals in suspensions were measured by atomic absorption spectrometry (AAS) using an atomic absorbtion apparatus of flame and Varian furnace controlled by computer [5].

2.2. Characteristics of the sand

Sand used is from sand dune of M'zar (Agadir region) was chosen because it is thin and rich in silica and carbonates.

Table 1. The basic parameters of M'zar sand.

D_{10} (mm)	D_{60} (mm)	$C_u = D_{60}/D_{10}$
0.15	0.22	1.46

* D_{10}: The effective diameter E_D, corresponds to the size of the mesh of the sieve which passes 10% of particles.
* D_{60}: corresponds to the size of the mesh of the sieve which passes 60% of the particles.
* $C_u = D_{60}/D_{10}$: the coefficient of uniformity.

Table 2. The weight parameters of M'zar sand.

Water content	relative density	Porosity	unit mass (g/cm^3)	Permeability (cm/s)

It has a good adsorption rate compared to other types of sand that have a large enough size. This finding has been demonstrated by other researchers [6].

Sand is sifted through a sieve with a diameter of 1 mm to remove coarse particles and then dried in an oven at 105 °C for 4 h. From the grading curve of M'zar's sand, we can calculate the basic parameters of the sand used (Table 1):

The weight parameters are also calculated, Table 2 summarizes the results [7]

So this is sandy, slightly moist and dense enough.

3. RESULTS AND DISCUSSION

3.1. Effect of the amount of M'zar sand on the removal of heavy metals

This study determines the mass of sand which gives a maximum retention of these metals. For this we chose a given concentration of metal from which we take a volume of 50 ml and varying the mass of sand. After agitation for one hour followed by one night of rest, we shall analyze the residual metal from the supernatant by atomic absorption spectrophotometer.
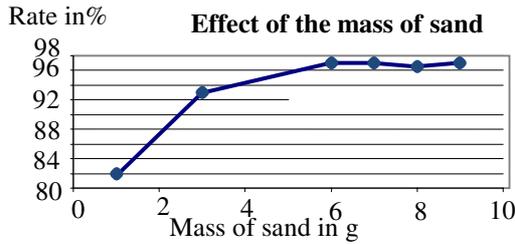
Figure 1. Variation of the retention rate of zinc in terms of the mass of M'zar sand (C_i = 0.5 mg/l; pH = 4.5 et T = 25 C°).
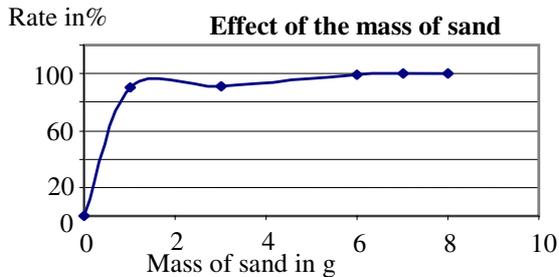
**Figure 2.** Variation of retention rate of chromium based on the mass of M'zar sand (C_i = 0.2 mg/l; pH = 4.80 et T = 25 C°).
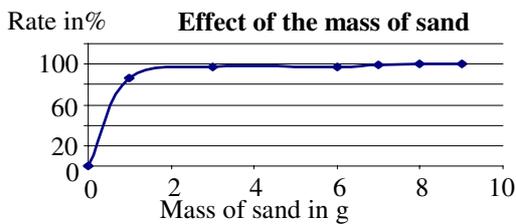
**Figure 3.** Variation of the retention rate of lead according to the mass of M'zar sand (C_i = 0.2 mg/l; pH = 4.60 et T = 25 C°).
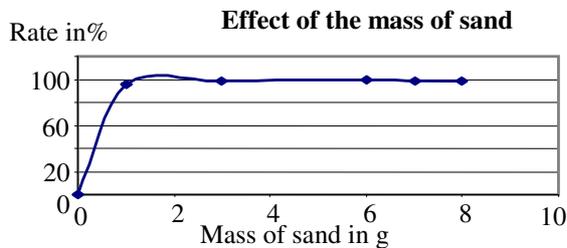
**Figure 4.** Variation of the retention rate of cadmium in terms of the mass of M'zar sand (C_i = 0.2 mg/l; pH = 4.50 et T = 25 C°).

Changes in the rate of metal retention depending on the mass of sand are shown in Figures 1,2,3 and 4.

From these curves, the amount of metal adsorbed increases with the mass of sand placed in solution to stabilize at values close to 4 to 6 g depending on the metal studied. Table 3 shows the values of sufficient amount of the mass of Qms sand to be used to follow the adsorption kinetics.

3.2. Kinetics of the adsorption

This kinetic study of heavy metal removal is considered important in determining the time of contact between sand

Table 3. Sufficient amount of the mass of sand to eliminate Qms almost 100% of the metal.

	Zinc	Chromium	Lead	Cadmium
Qm$_s$ en g	6	5	4	4
0.550	1.820	0.362	1.161	0.023
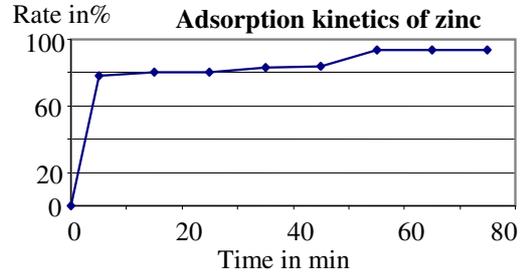
Figure 5. Zinc retention rate based on time for the M'zar sand (C_i = 0.5 mg/l; pH = 4.5; ms = 6g et T = 25 C°).
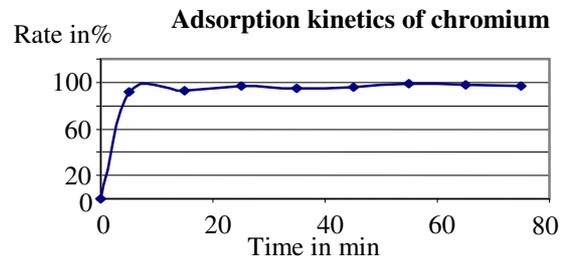
Figure 6. Chromium retention in terms of time for the M'zar sand (C_i = 0.2mg/l; pH = 4.8; ms = 5 g et T = 25 C°).
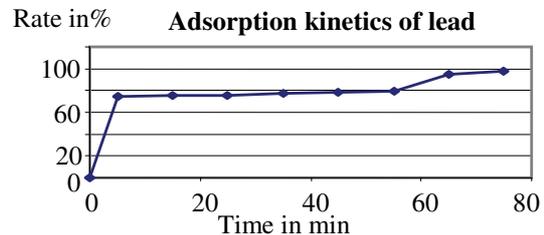
Figure 7. Retention of lead depending on time for the M'zar sand (C_i = 0.2 mg/l; pH = 4.6; ms = 4g et T = 25 C°).

and the solution (adsorbate / adsorbent) to clean containing the metal in necessary question to reach adsorption equilibrium. It depends on the pH of the medium [8], the initial concentration of heavy metals and the temperature of the medium [9,10].

The results of the binding kinetics of heavy metals studied by sand (Figures 5, 6, 7 and 8) show that the phenomenon of binding of these metals is very fast, especially for chromium. The duration of 5 minutes is sufficient to achieve a superior removal rate of 91% for this latter.

3.3. Adsorption isotherm of heavy metals by sand M'zar

The isotherms represent the variation of the amount of the adsorbed per unit weight of the adsorbent or unit area

Table 4. Values of Langmuir and Freundlich parameters for the adsorption of heavy metals studied on sand M'zar

Terms of adsorptions				Isotherms					
				Langmuir			Freundlich		
Métal	Equilibration time (H)	Range Conc. (mg/l)	Quantity of sand (g)	Q_m	K_L	R^2	K_F	n	R^2
Zn	1	0.2 -3.5	6	0.10	0.90	0.9938	0.053	0.8136	0.8985
Cd	1	0.1 - 3.50	4	0.20	0.33	0.9687	0.061	0.9411	0.9089
Pb	1	0.4 - 4.00	4	0.60	0.082	0.9839	0.048	0.9820	0.9673
Cr	1	0.4 - 4.00	5	0.099	0.77	0.9244	0.033	0.6260	0.8540

Q_m: maximum quantity of adsorbate (mg/g).

K_L: constant relating to the adsorption energy (L/g).

K_F: Freundlich constant (mg/g).

n: factor relating to the intensity of adsorption, also called heterogeneity factor.
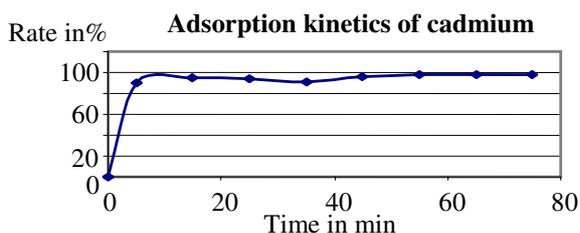
Figure 8. Cadmium retention rate based on time for the M'zar sand ($C_i = 0.2$ mg/l; pH = 4.5; ms = 4g et T = 25 C°).

in terms of the activity of the adsorbate, in the liquid or gas phase in equilibrium under conditions of pressure and temperature. This change allows us to characterize the type of adsorption isotherm which defines the metal studied at the material surface.

To describe the results of equilibrium sorption of heavy metals by the sand M'zar, using two simple models and commonly we use in the literature the Langmuir model [11] and Freundlich model [12]. The curves giving the adsorbed amounts, for a temperature of 25 °C, depending on the amount of adsorbate in the balance allowed us to determine the constants of Langmuir and Freundlich adsorption for the adsorption of heavy metals studied on sand M'zar (Table 4).

The results presented in the table above show that:

- The application of the laws of linearized forms of Langmuir and Freundlich adsorption on metals studied has verified that these two models were applicable, and the removal efficiencies of metals studied (Cd, Pb, Cr and Zn) vary in the same direction with these two models.

- $0 < K_L < 1$: the adsorption process is favorable

- n <1: the conditions are favorable for the adsorption and the system adsorbent / adsorbate is profitable.

The adsorption of heavy metals is influenced by the pH of the medium (it is high in acid compared to alkaline) and increases with the temperature of the medium and the initial concentration. This result is comparable with other media such as Kaolinite, Cotton fiber and sawdust [13]

and the adsorption of methylene blue on the sand M'zar [14].

4. CONCLUSION

The study of the adsorption of heavy metals by M'zar sand showed good performance of this latter and that the adsorption kinetics shows that the binding is done in a very rapidly (within minutes). The adsorption of heavy metals in an acid medium is high relative to the alkaline medium and increases with the initial concentration and the temperature of the medium. The results of the modeling of the adsorption of metals studied (Cd, Pb, Cr and Zn) in the sand M'zar showed a correlation of experimental data with models of Langmuir and Freundlich.

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