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 maximum 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(NO₃)₂, Cd(NO₃)₂ were used, 4H₂O for cadmium, CrCl₃, 6H₂O for chromium and ZnCl₂ 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.

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):

| D₁₀ (mm) | D₆₀ (mm) | Cᵤ = D₆₀/D₁₀ |
|---------|---------|-------------|
| 0.15    | 0.22    | 1.46        |

* D₁₀: The effective diameter EN, corresponds to the size of the mesh of the sieve which passes 10% of particles.

* D₆₀: corresponds to the size of the mesh of the sieve which passes 60% of the particles.

* Cᵤ = D₆₀/D₁₀: the coefficient of uniformity.

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

| Water content | relative density | Porosity | unit mass (g/cm³) | Permeability (cm/s) |
|---------------|------------------|----------|-------------------|---------------------|

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.
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 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 3. Sufficient amount of the mass of sand to eliminate Qms almost 100% of the metal. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Qms en g | Zinc  | Chromium | Lead | Cadmium |
|---------|-------|---------|------|---------|
| 0.550  | 6  | 20.0 | 362  | 1.161  | 0.023  |

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| Rate in% | Adsorption kinetics of zinc |
|----------|-----------------------------|
| 0        | 20                          | 60                          | 100                         |
| 2        |                             |                             |                             |

| Rate in% | Adsorption kinetics of chromium |
|----------|-------------------------------|
| 0        | 20                            | 60                          | 100                         |
| 2        |                               |                             |                             |

| Rate in% | Adsorption kinetics of lead |
|----------|-----------------------------|
| 0        | 20                           | 60                          | 100                         |
| 2        |                              |                             |                             |
Table 4. Values of Langmuir and Freundlich parameters for the adsorption of heavy metals studied on sand M’zar

| Metal | Equilibration time (H) | Range Conc. (mg/l) | Quantity of sand (g) | \( Q_m \) | \( K_L \) | \( R^2 \) | \( K_F \) | \( n \) | \( R^2 \) |
|-------|------------------------|---------------------|----------------------|--------|--------|--------|--------|--------|--------|
| Zn    | 1                      | 0.1 - 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.

\( 0 < K_L < 1 \): 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.

References

[1] Daniel R. Thevenot, Michel Meybeck et Laurence Lestel, Bilans métaux lourds, CNRS, février 2002.
[2] André Picot, Intoxication de l’organisme par les métaux lourds et autre toxiques, novembre 2003.
[3] M. Ghaoouch, Détermination des métaux lourds dans les eaux usées, épuration par des polymères d’originenaturelles et test sur végétaux, DEA, Paris, 1998.
[4] M. Verloo, les métaux lourds dans les denrées alimentaires, origines et évolution des teneurs (2003).
[5] Ecole des mines de Saint-Étienne, Méthodes spérométriques d’analyse et de caractérisation, spectrométrie d’absorption atomique.
[6] Benguella B., Benaissa H., Cadmium removal from aqueous solutions by chitin, Kinetic and equilibrium studies. Water Res. 36 2463–2474 (2002).
[7] V. Ferber, Sensibilité des sols fins compactés à l’humidification Apport d’un modèle de Microstructure, Thèse 2005.
[8] Shaa M., Chergui H., Melhaoui M., Bouali A., Test d’adsorption des métaux lourds (Cd, Cu, Ni, Pb, Zn) sur des substrats organiques et minérales, Ville d’Oujda (2000).
[9] Bryant P.S., Petersen J.N., Lee J.M., Brouns T.M., Sorption of heavy metals by untreated red fir sawdust. App. Biotechnol., 34/35.

[10] Khangan V.W., Dara S.S., Effectiveness of Terminalia Bellirica bark for scavenging Zinc ions. Chem. Environ. Res., 1, 87–94.

[11] I. Langmuir, J Am Chem Soc, 40 (1918) 1361–1403

[12] H. Freundlich, Colloid and Cappillary Chemistry, Ed. Methuen, London, (1926) 883.

[13] D. Ghosh, K.G. Battacharyya, Applied Clay Science 20 (2002) 295–300.

[14] M. Ez-zahery et al, Phys. Chem. News 58 (2011) 06–11.