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Study of the Adsorption of Heavy Metals on Clay Activated

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Abstract Presence of heavy metals in the aquatic systems has become a serious problem. As a result, there has been a great deal of attention given to new technologies for removal of heavy metal ions from contaminated waters. In this study, we carried out the elimination of the ions of cobalt, cadmium and manganese in solution by adsorption on a clay treated of the region may sour. The activation of clay is carried out by chemical way using the acid chloridric at moderate temperature. In order to optimise the operating conditions of the adsorption process, various studies on the kinetics, capacity, weight, adsorbent dosage and initial métal concentration was conducted. Experimental isotherms of adsorption equilibrium results were validated accurately by models of Langmuir and Freundlich.

Keywords corn, Adsorption, clay, heavy metals, modeling, isotherm modeling

1. Introduction

The retention of metal ions present in aqueous solutions can take place by various mechanisms such as precipitation, ion exchange, and adsorption which is considered in this work as a technique for depollution of contaminated wastewater heavy metals. In the following chapter we propose to use our clay sample treated with chloridic acid to analyze its behavior with respect to the heavy metals Cd, Co and Mn in solution as a function of the different parameters such as: the initial concentration Metal, adsorbent density, suspension pH and temperature ..., in order to evaluate its respective adsorption capacity and to define the optimum conditions for maximum adsorption.

Thus, after contacting the metal solution with the material and for a certain stirring time, we proceed to filtration using a syringe filter with a porosity of 0.45 μ m and then analysis of our Samples by atomic absorption spectroscopy for the purpose of determining the amount of adsorbed product. This quantity, expressed in mg of solute per one gram of adsorbent solid, is given by the following equation:

$$qt = V \cdot \frac{\left(C_0 - Cr\right)}{m}$$
(1)

The following parameters represent:

 q_t : Amount of adsorbate per unit mass mg / g at time t C_0 : Initial concentration mg / l.



 C_r : Residual concentration at equilibrium mg / 1 at time t

V: Volume of the adsorbate l.

m: masse de l'adsorbant g.

The calculation of the yield is obtained by the following relation:

2. Theoretical and Experimental Part

2.1. Adsorption parameters: In order to optimize process conditions for adsorption of heavy metals on clay shells, we studied the influence of some factors which may be involved in the process of this phenomenon such as concentration of adsorbate, adsorbent dosage and granulometry.

2.2. Modeling of adsorption isotherms

a) Freundlich Isotherme

Freundlich model (van Bemmelen, 1988 [1] Freundlich, 1909 [2]) is the most commonly used. We consider that it applies to many cases, especially in the case of multilayer adsorption with possible interactions between the adsorbed molecules [3]:

$qe = K_F.Ce(2)$

The most common form used is the plot in logarithmic scale variations qe according to Ce:

$Log qe = log K_F + log Ce (3)$

The constant n (adimentionelle) gives an indication of the intensity of adsorption. It is generally accepted that:

•0.1<n<0.5 characteristic of a good adsorption.

•0.5<n<1 characteristic of a moderate adsorption.

•n>1 characteristic of a weak adsorption.

b) Langmuir Isotherme

Langmuir model is based on assumptions well known. The initial assumptions are that the solid adsorbent has a limited adsorption capacity (q_m) , all active sites are identical, they can only complex solute molecule (monolayer adsorption) and there are no interactions between adsorbed molecules. This model can be expressed by equation (4):

$qe/q_m = \theta = K_L .Ce / (1 + K C) (4)$

 K_L , equilibrium constant of Langmuir, θ , recovery rate. The development of equation (4) leads to the linear form of Langmuir isotherm. The ratio $R_L = 1 / (1 + K_L C_0)$, unitless magnitude, indicates that:

• The adsorption more favorable if R_L tends to 0.

• Adsorption much worse if R_L tends to 1.

3. Results and Discussions

3.1. Détermination des conditions optimales d'adsorption

A- Adsorbate concentration effect

The application of the process for removing metal ions by clay from mays to a boulomane region on synthetic solutions at different concentrations [10, 20, 30, 40, 50 mg / 1] in a volume of 100 ml And under the optimum stirring time conditions already mentioned, allows us to study the kinetics of adsorption of each metal. (See yield evolution and determine the maximum adsorbed amount at equilibrium).

Figs. 1, 2 and 3 represent respectively the values of the adsorption histogram yields realized for the three metals. We find that the concentration value fixed in Mn by the adsorbent at equilibrium is greater for the initial solutions of concentration 30 mg / 1. The results of the tests carried out also show that the yield is variable and presents values that are quite high, which makes it possible to say that the Mn exhibits a significant affinity vis the clay. The largest calculated values are of the order of 85.25% (Figure 1). This suggests that this material has a high adsorption capacity at medium concentrations The results obtained (Figs. 2 and 3) show that the removal efficiency of Cd and Co varies with the dose of the adsorbate: a maximum efficiency after 20 minutes is obtained which is 99.95% for A dose of 10 mg / 1 in Cd and 95.87% for the same dose in Co.

We can see that the yields decrease gradually with the increase of the initial content of Cobalt and Cadmium. In the copper concentration range between 6.3 and 31.7 mg / 1, the authors (4) showed that the effectiveness of binding of



copper to goethite decreases. This result was accompanied by the decrease of the pH relative to the initial pH, associated with a release of H ⁺ protons during several fixing operations. These same authors, this decrease is related to a process of substitution between the protons of goethite and the Cu^{2+} cations according to a simplified scheme, a scheme that can be applicable for the Cobalt, Cadmium and Manganese ions:

$$-Fe - OH + Cu^{2+} \longrightarrow -Fe - O- Cu^{+} + H^{-}$$

In the experiments we carried out, we also observed a slight decrease (Table 1) in pH from the initial pH with an increase in the initial content of the three metal ions.



Figure 1: Yield as a function of the initial concentration in Optimal parameters $PH = 6.5 - \frac{1}{2} \le 6 \mu m$ - Stirring speed = 400 rpm T = 20 ° C - C (clay) = 0.2 g/1



Figure 2: Yield according to the initial concentration in Co Optimal parameters $PH = 6.5 - \frac{1}{2} \le 63 \mu m$ - Stirring speed = 400 rpm T = 20 ° C - C (clay) = 0.2 g/1





| varying initial Co, Cd and Win concentrations | | | | | | |
|---|--------|------|-----------|------|---------|------|
| ions métalliques | Cobalt | | manganèse | | cadmium | |
| Teneurs initiale (mg/l) | R% | pН | R% | pН | R% | pН |
| 10 | 95.87 | 6.3 | 69.5 | 6.25 | 99.95 | 6.25 |
| 20 | 92.5 | 6.3 | 83.79 | 6.15 | 84.43 | 6.1 |
| 30 | 91.7 | 6.1 | 85.26 | 6.11 | 64.61 | 6.05 |
| 40 | 80.67 | 6.05 | 77.56 | 5.85 | 51.61 | 6 |
| 50 | 78.31 | 5.9 | 66.3 | 5.7 | 50.8 | 5.8 |

Board 1: Evolution of the removal efficiency of metal ions Co, Cd and Mn (R (%) and pH End of treatment for varying initial Co. Cd and Mn concentrations

b) Effect of adsorbent dosage

The effect of the initial mass of activated clay was studied at pH 6.5 of the solution, at ambient temperature of 20 $^{\circ}$ C., at a stirring speed of 400 rpm and at a fixed initial concentration of 10mg / 1 of metal cations Cd and Co, and with 30 mg / 1 in Mn. With increasing concentrations of the adsorbent ranging from 0.1 to 0.5 g / 1 at a pitch of 0.1 mg / 1.

According to the results presented in figs. 4, 5 and 6, it can be seen that the elimination efficiencies of the three metal ions are variable and have doses of clay. Indeed, they have maxima of 60.62%, 95.87% and 99.95% respectively for Mn, Co and Cd at a clay dose of 0.2 mg / 1 The rate of adsorption increases markedly, when the concentration of adsorbent increases from 0.1 to 0.2 mg / 1. However, a slight decrease is observed for concentrations greater than 0.2 g/1



Figure 4: Cd adsorption efficiency as a function of the concentration of the adsorbent Optimal parameters: $pH = 6.5 - \frac{1}{2} \le 63 \mu m$ - Stirring speed = 400 rpm T = 20 ° C - C (Metal) = 10 mg



Figure 5: Mn adsorption efficiency as a function of the concentration of the adsorbent Optimal parameters: $pH = 6.5 - \frac{1}{2} \leq 63 \ \mu m$ - Stirring speed = 400 rpm $T = 20 \ ^{\circ}C - C \ (Metal) = 10 \ mg \ / l$





Figure 6: Rendement de l'adsorption de Co en fonction de la concentration de l'adsorbant Paramètres optimales : $pH = 6.5 - \frac{1}{2} \le 63 \mu m$ – Vitesse d'agitation = 400 trs/min T = 20°C – C(Métal) = 10 mg/

According to figs. 7, 8 and 9, there is a decrease in the adsorption density when the concentration increases. These results can be explained by the fact that, in the presence of a low dose of adsorbent material, all the adsorption sites can be occupied by the metal But if the adsorbent dose increases (increase in active sites), with the same ion concentration and therefore the adsorption capacity decreases. Same behavior has been observed by several authors Thus, an adsorption study of metal ions such as copper and cadmium on an adsorbent matrix (rhssoulite) revealed that an increase in the concentration of adsorbent leads to a decrease in the adsorption capacity (5). A similar study of the effect of the liquid solid ratio on the adsorption of pb^{2+} by bentonite and activated carbon shows that the adsorption capacity for both adsorbents decreases according to the solid / liquid ratio (6) huang et al (7) Have found that as the concentration of the adsorbent carrier increases, The adsorption density of the Zn ion becomes significantly low. On the other hand, a reverse behavior has been observed by several authors. The use of a large dose of adsorbent material increases the available sites and therefore promotes adsorption. This means that the percentage of adsorption increases as the amount of adsorbent increases. Amirouche L, following a study of the sorption power of copper, zinc and polyphenols by bentonites under the effect of microwave irradiations Was able to show that the fixation of the two metal cations is generally also favored by the increase of the mass of clay, whatever the value of the pH and the initial metal cation concentration (8). Se Dire et al (9) demonstrated that an increase in the mass of coal from 0.1 to 1.2 g results in a more or less significant variation in the residual concentration Indeed, the rate of fixation of the element studied goes from about 53% for a mass of 0.1 g to a rate of about 93% for a mass of 0.7 g. Beyond this mass, the adsorption rate became stable. Beyond this mass, the adsorption rate became stable. In fact, the adsorption capacity increases with the mass of the adsorbent, even though the activated carbon reaches saturation at an optimum mass of 0.7 g. The same result was observed when treating a synthetic solution of distilled water initially containing 5 mg / l Zn and varying the dose of Mostaganem bentonite (bentonite calcium) from 0.1 to 8 g / 1 (10) (Larakeb et al, 2014). According to Zhang et al. (2011), zinc removal efficiency and adsorption capacity increased with increasing bentonite dose (0.2 to 2 g/1)(11).



Figure 7 : Evolution of the adsorption density of the Cd ion as a function of the concentration of clay





Figure 8: Evolution of the adsorption density of the Mn ion as a function of the concentration of clay



Figure 9: Evolution of the adsorption density of the Co ion as a function of the clay concentration

c) Adsorbent particle size effect

Il est très bien connu que la granulométrie du solide joue un rôle prépondérant sur la vitesse du transfert du cation, de la solution vers l'adsorbant (**12-13**). De ce fait nous avons procédé dans cette étape en variant le diamètre du grain de l'argile en deux intervalles. Les diamètres choisis sont : $\varphi < 63 \mu$ m, 63μ m $\leq \varphi \leq 80 \mu$ m et $\varphi > 80 \mu$ m. Les résultats expérimentaux montrent que la sorption maximale est obtenue pour une granulométrie de diamètre di diamètre du gran de l'argile en deux intervalles. Les diamètres choisis sont : $\varphi < 63 \mu$ m, 63μ m $\leq \varphi \leq 80 \mu$ m et $\varphi > 80 \mu$ m.

inférieure 63 μ m, (Fig. 10), avec un rendement égale à 84.4 % (Fig. 11) et une concentration résiduelle égale à 4,68 mg/l.



Figure 10: Residual Cobalt concentration as a function of time Optimal parameters: PH = 6.5 - Stirring speed = 400 rpm T = 20 ° C - C (Metal) = 10 mg / l



Figure 11: Yield of cobalt adsorption as a function of grain size

3.2. Modelling of adsorption isotherms

To study the isotherms of adsorption of the three metal ions by activated clay, of volumes of 100 ml of concentrations different from each ion going from (10 à50 mg/l) are put in contact with an amount of 0.2 g/l for adsorbent, at a temperature of 20°C. The determination of the quantity of ion fixed corresponding to the balance of adsorption, allowed the establishment of the isotherms of adsorption for each adsorbate. The knowledge of the latter is essential for the calculation of the maximum capacity of adsorption and for the identification of the type of adsorption which can occur into mono or multi-layer.

Discussions

The experimental isotherms of adsorption equilibrium and maximum adsorption capacity (Fig 12,13, 14) have been validated in detail by the Langmuir and Freundlich model (Fig.15,16, 17). The isotherms obtained were L-type according to the classification of Giles [14], which promotes a monolayer adsorption and the interaction between the adsorbate and the adsorbent is important. We notice, that the metal capacity of adsorption of the ions on activated clay, increases remarkably with the increase in the concentration to balance. Even result was got Lords of a study of the adsorption of the copper ions by the clay of Algerian south-western Tiout-Naama [15]. The computed values of R_L to various concentrations (going from 10 jusqu ` to 50 mg/L), are given in table 2. We note that the argillaceous matrix used has a good capacity of adsorption for the three metal cations etles values R_L range between 0 and 1 which indicates that favorable sorption destrois cations métalliquesest. Let us recall that this presentation is carried out in the optimal operating conditions.



Figure 12: Cobalt ion adsorption isotherm for an activated clay agitation time: 20min; PH: 6.5; Dose of clay: 0.2g / l; Ambient temperature = 20 \circ C



Figure 13: Isotherm of adsorption of the ions Manganese for an activated clay agitation time: 20min; PH: 6.5; Dose of clay: 0.2g / l; Ambient temperature = 20 ° C





Figure 14: Cadmium ion adsorption isotherm for an activated clay agitation time: 20min; PH: 6.5; Dose of clay: 0.2g / l; Ambient temperature = 20 ° C

3.3. Isotherm of Adsorption

Thanks to an adjustment by the method of least squares, we obtain for each studied law and each metal ion of the right-hand sides with coefficients of correlation. The various constants deduced from the line equations obtained are gathered in table 3:

3.3.1. Langmuir Isotherme and Freundlich Isotherme

The layout of the isotherm of adsorption of the ion cobalt shows that Co expresses an important homogeneity with respect to clay. This affinity is stronger than that expressed with respect to other mineral adsorbents such as Algerian bentonite (16). For a concentration with Ce=10.84mg/l balance, the density of adsorption can reach 19,593 mg/g and remains almost constant. The figures 15,16et 17 show the representation of these isotherms in their alineatized forms:

According to table (3), the capacity of maximum adsorption calculated according to the model of Langmuir (20mg/g) is higher than that determined by the model of Freundlich. Consequently, it is close to that found in experiments which is of 19.533mg/g. One can thus deduce according to these results which the model of Langmuir is more adapted to this sorption. For manganese, isotherm traces it experimental watch that clay used expresses an affinity with respect to mn. This affinity will be important during the adsorption of the ions mn on the kaolin (17). The density of adsorption Qe (ads) varies from 3.47 respectively has 16,556 mg/g for a concentration with the balance from 3.05 to 16.88 mg/l. (see figure)

According to table (3), the capacity of maximum adsorption evaluated with 24.39mg/g, according to the model of Langmuir, is higher than that obtained by the model of Freundlich (6,353 mg/g), but remains always lower has that found by [4] which is about 35.21 mg/g.

According to the two models, the coefficients of correlation obtained are satisfactory in this case of study Then, it is important to announce that under the selected optimal conditions neither the model of Freundlich nor the model of Langmuir do not make it possible to correctly present the isotherm D experimental adsorption of mn on activated clay. This report is justified by the difference between the values of the adsorbed quantities obtained in experiments (16.556ùg/g), and of the quantities adsorb theoretically calculated in the two models (24.39mg/g calculated starting from the model of Langmuir and 6,353 mg/g obtained by the model of Freundlich). The follow-up of the quantity of the absorbed Cd ion as a function of the residual concentration was studied by several authors (18; 19; 20; 21). The appearance of the isotherm of the Cd from FIG. 14 shows that the clay shows an important affinity with respect to this metal ion. This characteristic was also observed during the adsorption of Cd on Smectite calcium [18], kaolinite-illite [19], again on nude bentonite from Mostaganem (20) and montmorillonite sodium [21]. The adsorption density of Cd on the clay increases markedly and reaches a value of 4.975 mg / g for a concentration Ce = 0.005 mg / 1 However, for the concentration Ce = 24.69 mg / l, the adsorbed amount reaches a maximum of 12.651 mg / g. The adsorption of Cd on the activated clay perfectly supports the Freundlich model. In this case, the correlation is very good, (R being greater than 0.9). However, this model is based on the assumption of the heterogeneity of the surface energy.

According to the Langmuir model, the adsorption capacity of Cd is higher than that determined by the Freundlich model (see Table 3). Such remarks have been observed by other works (19; 21: 22), contrary to demonstrated the



reverse in a study of the adsorption of Cd ions on a Marghnia clay. The domain of validity of Freundlich's constant1 / n is [0-1] However, all the values obtained for the Cobalt, Manganese and Cadmium, respectively: 0.431.0.367 and 0.096 belong to this domain and indicate that the elimination Of the metal ions on the activated clay is favorable and increases with the increase of adsorbent.



Figure 15: Linear form of the Freundlich and Langmuir adsorption model of Mn (II)by activated clay



Figure 16: Linear model of the Freundlich and Langmuir adsorption models of Co (II) By activated clay



Figure 17: Linear form of the model of Freundlich and Langmuir of adsorption of Cd (II) by activated clay

| Table 2. KL fails as a function of mittal concentration of metal fors | | | | | | |
|---|---------------------------|----------------|----------------|--|--|--|
| C initiale (mg/l) | Со | Mn | Cd | | | |
| | \mathbf{R}_{L} | R _L | R _L | | | |
| 10 | 0.11 | 0.35 | 0.10 | | | |
| 20 | 0.06 | 0.21 | 0.057 | | | |
| 30 | 0.04 | 0.15 | 0.038 | | | |
| 40 | 0.03 | 0.12 | 0.029 | | | |
| 50 | 0.02 | 0.09 | 0.023 | | | |

 Table 2: R_L ratio as a function of initial concentration of metal ions



| - | Freundlich | | | Langmuir | | |
|----|------------|-------|----------------|----------|--------|----------------|
| - | Kf | 1/n | \mathbf{R}^2 | Q0 | b | \mathbf{R}^2 |
| Co | 7.583 | 0.434 | 0.961 | 20 | 0.757 | 0.988 |
| Mn | 6.353 | 0.367 | 0.781 | 24.39 | 0.1838 | 0.860 |
| Cd | 8.10 | 0.096 | 0.944 | 11.628 | 0.827 | 0.752 |

Table 3: Parameter of the adsorption isotherms of the Freundlich and Langmuir models

Conclusion

In this study, we removed cobalt, cadmium and manganese ions in solution by adsorption on a clay in the activated state of the maysour region.

The activation of the clay is carried out chemically with the aid of chloridic acid at moderate temperature. Several parameters were studied, such as the effect of the dose and the size of the activated clay

Our results showed that the equilibrium is reached during a contact time of 20 min.

Good adsorption efficiency is obtained at low doses of 10 mg / 1 successively in Cobalt and Cadmium ion. But for manganese, a good rate is achieved at a dose of 30 mg / 1.

The isothermal study of the adsorption of the metal ions Co, Cd, and Mn on the clay showed that the latter exhibits an important affinity with respect to these ions.

The application of the linearized forms of the Freundlich and Langmuir equations allowed us to calculate the fixing capacities and to verify whether these two models are applicable.

The Freundlich model was the most plausible for the Cadmium ions. On the other hand, the Langmuir model is reliable for the retention of Cobalt ions.

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