Valorization of Moroccan clay: Application to the adsorption of cobalt ions contained in wastewater synthesized.

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Abstract

In this study, we were able to reduce the content of cobalt ions Co^{2+} contained in wastewater by the natural clay of El Oulja-Sale region Moroccan as an inorganic adsorbent. The different effects of the experimental parameters on the adsorption kinetics were studied, namely, the different masses of adsorbent, the initial concentrations of cobalt ions, the contact time, the rate of stirring and the pH of prepared solutions. The results of the studied parameters in the removal of cobalt ions have been recorded in the following values: 3 g per mass of adsorbent, 200 mg/l of the concentration of cobalt ions, 400 tr/min of speed agitation, 2 fortunes for the contact time and pH equal to 6. According to the adsorption kinetics study and according to the adsorption equations of Langmuir and Freundlich whose linear forms, it was shown that the maximum amount adsorbed of the studied ions metals have been validated by the linear models of Langmuir and Freundlich isotherms.

Keywords: Wastewaters; Naturel clay; Adsorption kinetic; Removal of cobalt; Isotherms models.
1. Introduction

The water is a vital and necessary element for life to all kinds of livings including humans. The operation of this element is in a remarkable increase in recent years because of its heavy use in everyday life and especially in irrigation and industry. Industrial activities are more diverse, among which there are the metal coating industry [1], ceramics and glass. These industries are a major source of wastewaters loaded with heavy metals namely zinc, iron, nickel, copper, lead, cadmium, mercury, arsenic and cobalt [1-3], etc. The presence of these heavy metals in industrial wastewater is a major problem for the environment because of their harmful impact on wildlife, aquatic life and therefore human health [4]. This requires their reduction according to the requirements of industrial wastewater treatment standards and environmental protection [5-7]. To handle this type of industrial wastewater, there are several treatment techniques, among which we find the processes of membrane separation [8], namely [9] ultrafiltration, nanofiltration [10, 11] and reverse osmosis [11, 12], the solvent extraction techniques [13], ions exchange techniques [9, 11], precipitation techniques, adsorption [14-24] and other. The adsorption technique for clay is often used in the removal of heavy metals because of its low operating cost, possibility of its implementation and performance in terms of reduction of heavy metals. The aim of the present study is to investigated the possibility of reducing cobalt ions contents Co\(^{2+}\) found in wastewater models prepared for the scale of our laboratory (LM2EMA), while using the technique adsorption by kaolinite-illitic clay (CKIM) levied in the region El Oulja Sale of Morocco, we have used the removal of copper ions Co\(^{2+}\) in the first part of our research about the elimination and/or reduction of existing heavy metals in wastewater [16], based on the following adsorption kinetics forms the linear model Langmuir and Freundlich [25-30].

2. Experimental

2.1. Exploited clay

The adsorbent used in this work is the kaolinite-illitic clay taken from the region El Oulja of Sale in Morocco (CKIM). The methods of preparation and characterization of this clay were already mentioned in our history of the references bellow [16].

2.2. Wastewater model loaded with cobalt ions

The wastewater model solutions used in this study were prepared by using cobalt nitrate hydrate (Co(NO\(_3\))\(_2\), 6H\(_2\)O) of molecular weight 290.9 g/mol, whose chemical structure and appearance are shown in Fig. 1 below. These solutions were obtained at a concentration of 1 g/l by separating 4.93 g of hydrated cobalt nitrate in one liter of distilled water. From these stock solutions, we have prepared other lower concentrations of solutions according to the method of dilution.

![Chemical structure and form of cobalt nitrate](image)

(a) (b)

**Figure 1:** The chemical structure (a) and form (b) of the cobalt of nitrate.
2.3. **Wastewater model loaded with cobalt ions**

The wastewater model solutions used in this study were prepared by using cobalt nitrate hydrate \((\text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O})\) of molecular weight 290.9 g/mol, whose chemical structure and appearance are shown in **Fig. 1** below. These solutions were obtained at a concentration of 1 g/l by separating 4.93 g of hydrated cobalt nitrate in one liter of distilled water. From these stock solutions, we have prepared other lower concentrations of solutions according to the method of dilution.

\[
Q_e = \frac{(C_i - C_e) \times V}{m}
\]

\[
\% R = \frac{C_i - C_e}{C_i} \times 100
\]

2.4. **Adsorption process**

We have prepared ions concentration of cobalt solutions in the range of 100-300 ppm from a stock solution of \(\text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\). The pH was adjusted with 0.1 M of NaOH or HCl and the quantities of 1g; 2g; 3g; 4g; 5g of clay was added to 60 ml of Co(II) solution [16]. The dispersions were filtered and the cobalt concentration was determined by atomic absorption spectrophotometer (analytical Jena brand, model Navaa 350). The amounts of cobalt ions adsorbed in the Qe equilibrium (mg/g) were calculated according to the following expression. The effectiveness of the cobalt removal (% R) contained in the treated solutions is given by the following equation. Whereas: \(C_i\) and \(C_e\); are respectively the initial concentration and balance of the ions Co\(^{2+}\) in solution (ppm); \(Q_e\): the amount of adsorbed metal (mg/g) \(V\): is the volume of the used solution (ml) \(m\): is the mass of the used adsorbent (g) For the adsorption capacity of cobalt ions, it was based on the adsorption kinetics of heavy metals, exploiting adsorption isotherms according to the models of Langmuir and Freundlich.

3. **Results and discussion**

3.1. **Effect of amount of adsorbent**

The removal of Co\(^{2+}\) ions by CKIM was examined at different amounts of the adsorbent (1; 2; 3; 4; 5 (g/60ml)) with a cobalt ions concentration fixed in the value of 100 mg/l, stirring speed of 200 rev/min and a contact time of 60 min.
The Fig. 2 shows the variation of reduction of performance values of Co$^{2+}$ ions (R %) and the adsorption amount of these ions from the masses of emerald CKIM. From the above figure, it is shown that there is an increase in clay masses, and a gradual increase in the abatement rate of ions Co$^{2+}$ and a subsequent decrease in the amount of adsorption. This can be explained by the large number of the selective sites found at the surface area of the adsorbent by the addition of the latter. In this study, we took the optimum adsorbent mass in the value of 3 g/60ml, because from this value, the adsorption curve is the first beginning to stabilize, and the second, the residual content Co$^{2+}$ ions is less than that indicated by the World Health Organization (WHO) standard (2 ppm) [16].

3.2. Effect of the contact time on the adsorption of Co$^{2+}$ ions

The effect of adsorption contact time of cobalt ions by CKIM clay was investigated for the time intervals of 10; 20; 40; 60; 80; 100; 120; 140; 160; 180 min. The Fig. 3 shows the variation of the effect of contact time on the adsorption of cobalt ions in each time interval. Seeing the adsorption curves and the retention of cobalt ions, it is shown that these curves are divided into two phases in which one is gradually increasing and the other is stationary. In the first stage, the adsorption rate is high between 10 and 100 minutes, which are due to the specific surface which is charged negatively leading to the rapid electrostatic adsorption of the cationic molecules of cobalt ions contained in the prepared solutions. During the second phase, the curves are remedied, which may indicate that the number of free active sites decreases gradually. This allowed us to take 120 min as the optimum time of agitation required for maximum adsorption performance of Co$^{2+}$ ions [31].

3.3. Isotherm adsorption

The isotherm adsorptions are used to indicated the contents of cobalt ions which are distributed between the liquid phase and the solid phase when the adsorption processes lead to balance [32]. They are used, in this case, to establish the maximum capacity for the adsorption of the adsorbate and the adsorbent which is expressed in terms of the content of cobalt ions adsorbed per unit mass of the used adsorbent. The Table 1 includes the sizes of linear and nonlinear models of Freundlich and Langmuir isotherms.
Table 1: Forms linear and nonlinear of Freundlich and Langmuir isotherms.

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Linear form</th>
<th>Nonlinear form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>$Q = \frac{K_f q_m C}{1 + b C}$</td>
<td>$1 \log Q = \frac{1}{n} \log K_f + \frac{1}{n} \log C_e$</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$Q = q_m + q_m \times b C$</td>
<td></td>
</tr>
</tbody>
</table>

Whereas: $q_m$: adsorbed amount of heavy metals to the saturation (mg/g) which corresponds to the formation of a monolayer on the solid surface and $K_f$, n, b are constants of the adsorption [33]. Based on the linear forms of the isotherms above in the models, we grouped the parameters exploited in these models in Table 2:

Table 2: Settings isotherms Freundlich and Langmuir models.

<table>
<thead>
<tr>
<th>Model</th>
<th>$N$</th>
<th>$K_f$</th>
<th>$R^2$ (%)</th>
<th>$q_m$(mg/g)</th>
<th>b (l/mg)</th>
<th>$R^2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>0,16</td>
<td>17,90</td>
<td>0,92</td>
<td>0,29</td>
<td>1,6</td>
<td>0,90</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From this table, it is shown that these two models are applicable and the cobalt removal efficiency varies in the same direction as in the two items and an adsorption is better than cobalt ions. The results are similar to those obtained in other studies [16].

3.4. Effect of the stirring speed

The stirring speed effect was assessed by varying the stirring speed of 100 to 700 tr/min with an initial concentration of cobalt ions of about 100 ppm and maximum mass of adsorbate about 3 g, and the time of optimum contact of 2 hours. The Fig. 4 shows the variation in the adsorption of $\text{Co}^{2+}$ ions on CKIM following the increase of the stirring rate.

Figure 4: Freundlich isotherms (a) and Langmuir (b) of adsorption of ions $\text{Co}^{2+}$

In the two curves we see a linear growth up with 200 tr/min and from this speed the two curves are quite remedied to the optimal speed indicated in the value 400 tr/min. This can be explained by the fact that when increasing the speed of agitation, all particles are held in suspension, which increases the contact surface of the solid torque/liquid while the transfer of $\text{Co}^{2+}$ ions on adsorbent surface will be favorable [34].
3.5. Effect of the concentration of cobalt
The effect of the concentration of the copper used in this work is carried out by ions Co\(^{2+}\) initial levels which are varied between 20 and 240 ppm with a stirring speed of 400 tr/min, an adsorbent mass of 3 g and the contact time of 2 hours. The Fig. 5 (a) and (b) shows the variations of the adsorption performance and the adsorbed amount of cobalt ions (mg/g). The curves in this figure progressively increase to the concentration of 160 ppm. After that the curves are remedied. This allowed us to identify the optimal concentration in the value of 200 ppm/100 ml.

Figure 5: Effect of initial concentrations (a) and the agitation rate (b) on the adsorption of ions Co\(^{2+}\).

3.6. Effect of pH on the adsorption capacity
In this study, the effect of pH parameter was studied for the adsorption of ions Co\(^{2+}\) on CKIM at room temperature, with a Co\(^{2+}\) ions content of 200 ppm. The pH range of the solution is adjusted between 2 and 7 with NaOH and HCl solutions (0.1 M).

Figure 7: Effect of pH on the adsorption of ions Co\(^{2+}\).

The Fig. 6 shows the variation of the adsorption capacity following the increase in pH. The variation in the removal of Co\(^{2+}\) ions in relation to the pH may be explained by the activation of the surface area of the exploited clay. In this figure, we find that the ions removal efficiency of cobalt increases and the residual concentration decreases depending on the pH. Hence, the adsorption of cobalt by the studied clay depends mainly on the pH

4. Conclusion
In the light of this study, we showed that the results of the adsorption of heavy metals like cobalt ions by kaolinite Illitic clay in the region El Oulja Sale of Morocco are satisfactory. This was done according to the kinetic study of the
adsorption of isotherms of Langmuir and Freundlich models after optimizing the effects of physical and chemical adsorption of such mass absorber settings, contact time, stirring speed, content Co\textsuperscript{2+} ions and pH.

References