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"Retention of nickel and zinc from raw and intercalated FeSb clay materials "

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Résumé :

" Dans cet article, un matériau Argileux intercalé a été préparé par l'insertion de fer pour éliminer le Zn (II) et le Ni (II) des solutions aqueuses. Pour caractériser les propriétés d'adsorption du matériau argileux produit, la surface spécifique, la composition minéralogique du matériau argileux et les changements d'espace basale de l'échantillon préparé ont été identifiés.
Les effets du pH, de la concentration initiale en ions métalliques et de la température sur l'efficacité d'adsorption du matériau argileux intercalé FeSb pour les ions Zn (II) et Ni (II) ont été examinés en mode batch. Les données d'équilibre d'adsorption ont été analysées par les isothermes de Langmuir et Freundlich. Nous avons conclu que la capacité maximale d'adsorption du zinc et du nickel calculée à partir du modèle de Langmuir était de 9977 mg/g et 2161 mg/g respectivement."

Abstract

In this paper, intercalated clay material was prepared with insertion of iron to remove Zn (II) and Ni (II) from aqueous solutions. To characterize the adsorptive properties of the produced clay material, surface area, mineralogical composition of the clay material and the changes of interlayer spacing of the prepared sample were identified.
The effects of pH, initial metal ion concentration and temperature on the adsorption performance of intercalated clay material FeSb for Zn (II) and Ni (II) ions were examined by batch method. The adsorption equilibrium data were analyzed by Langmuir and Freundlich isotherm models. We concluded that maximum adsorption capacity of zinc and nickel calculated from Langmuir isotherm was respectively around 9977mg/g and 2161mg/g.

Keywords: Adsorption; intercalated clay; heavy metals; isotherms

1. Introduction

Pollution of water and soil, accidentally or deliberately, by certain industrial chemicals (hydrocarbons, phenols, dyes, etc.) or agricultural chemicals (pesticides, fertilizers, etc.) creates a source of environmental degradation and causes an international current interest. Water contamination by heavy metals arising from mining operations, metal plating and textile industries tannery is a serious environmental problem [1, 2]. Heavy metals may have an extreme toxicity as well as with low concentrations. Due to their presence in industrial effluent, problems of heavy metals have become more and more worrying. Nickel and zinc are hazardous; they are among the commonly encountered metals [3]. These metals released into natural water from metal plating, mining, pigments and alloy industries. They may spread into the environment through soils and water streams, and they may bring a chief threat to the human health [4].
Several treatment processes make it possible to limit the concentrations of these pollutants include oxidation, reduction, precipitation, membrane filtration, ion exchange, electrochemical operation, biological treatment, and adsorption. Among these techniques, adsorption has shown this evidence in the depollution of industrial waste water for the removal of certain heavy metals. Several solids such as biomass, activated carbon, zeolites, and clays [5–7] have been used for the removal of heavy metals. Several studies have shown the effectiveness of clays for the retention of heavy metals.
The objective of our work is to valorize a local clay material and to study its power for the decontamination of effluents containing heavy metals.

2. Materials

The clay used in this work was taken from Jbel Sbih in the region of Skhira (Sfax) in the south of Tunisia. The natural clay was first purified by dispersion in water, decantation, and extraction of the fraction with a particle size smaller than 2µm. The resulting solid was dried at 60°C, ground to 80 mesh, and kept in a sealed vessel. Intercalated clay was prepared by insertion of iron Fe(NO3)3,9H2O, HCl. The intercalating Fe(III) solution was prepared by adding 0.75mol L-1 NaOH solution into 0.4mol L-1 Fe(NO3)3 solution at a flow rate of 1mL min-1. The reaction medium was maintained under stirring while the NaOH solution was pumped, providing a 2:1 molar ratio of [OH-]:[Fe(III)]. The solution was maintained at 50°C for 24h. The clay suspension was heated to 50°C and the intercalating solution was added at a flow rate of 1mL min-1 under strong stirring, providing 10mmol of Fe (III) per gram of clay. The suspension was left to rest for 7 days at room temperature [8, 9]. The resulting suspensions of clay/intercalating solution were centrifuged at 1000rpm for 10min and the solid phase was washed five times with deionized water. The modified clay mineral was crushed, dried in an oven at 100°C for 24h, heated at 350°C under a stream of air for 3h, and stored in desiccators. The modified clay prepared with [OH-]:[Fe(III)] molar ratios 2:1 was identified as FeSb.
The aqueous solutions of Zn (II) and Ni (II) were prepared in double distilled water. A stock solution of heavy metals containing 2000mg L−1 was prepared by dissolving the required amount of heavy metals in double distilled water. Solutions for adsorption experiments were made from the stock solution by appropriate dilution.

3. Results and discussions

The X-ray diffraction mineralogy (Figure1) shows that the raw clay is mainly composed of smectite by the *appearance of peak at 14,13Å and kaolinite (K) by the appearance of peak at 7,01Å in addition to the Quartz 3.33Å and calcite (C) at 3.04Å. Hence, the clay material contains mainly clay minerals of the smectite and kaolinite type [10].*

The intercalated clay shows an increase in the basal space. Indeed, this distance goes from 14 to 19.36Å. The appearance of the adsorption / desorption isotherms obtained for the raw and intercalated clay (Figure 2) shows that these isotherms are of type II of the B.E.T classification and are characterized by a multilayer adsorption. It is noted that the specific surface area still increases from 67 to 112.76m2/g. Hence the interest of the intercalation of clay to improve the porous texture of clay materials, as well as their adsorption capacity.

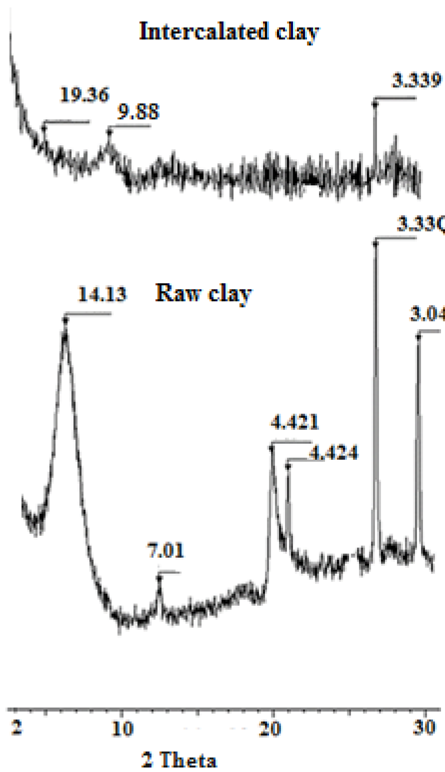

Figure 1. X-ray diffraction pattern of raw and intercalated clay materials

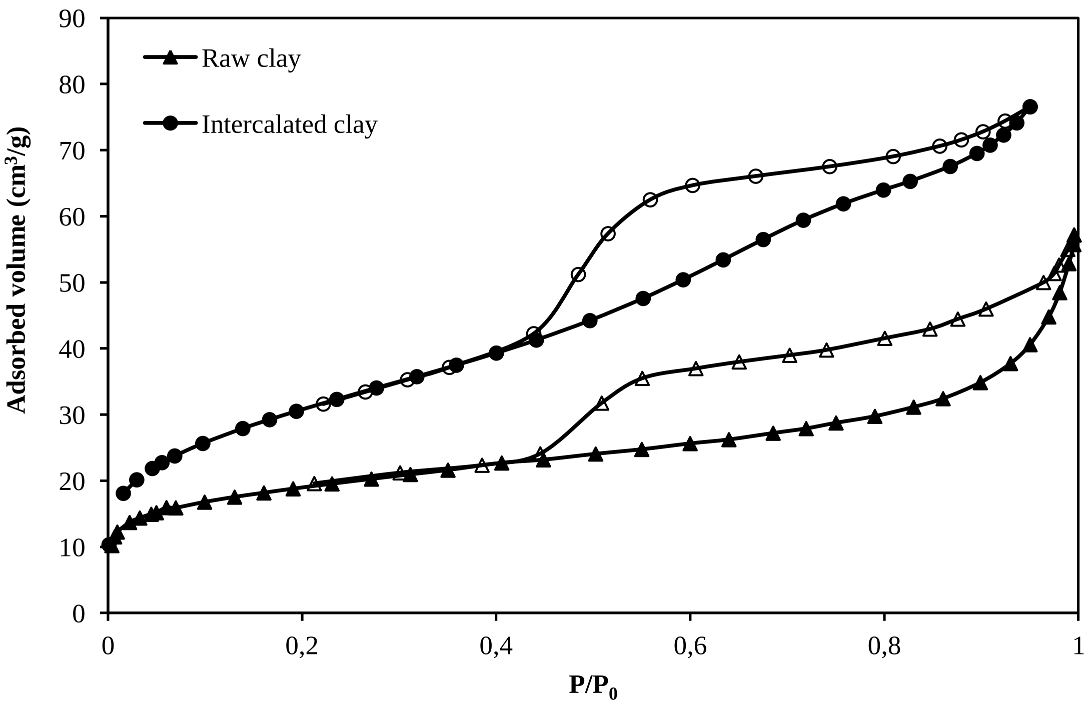

Figure 2. Adsorption / desorption isotherm of Nitrogen on intercalated clay materials

Batch experiments were carried on in order to investigate the efficacy of adsorption processes on the efficiency of heavy metal (Zn (II) and Ni (II)) removal. For this, the initial heavy metal concentration, adsorbent amount and contact time were adjusted to 1000 mg/L, 0.5 g/L and 60 min, respectively. The efficiency of adsorption on natural clay was obtained to be 82.5 to 100%. Furthermore, the results mark that removal of Zn (II) are faster than removal of Ni (II). The efficiency of Zn (II) removal increases quickly and reaches a maximum beyond 17 minutes. This maximum value of the adsorption capacity corresponds to the ultimate experimental adsorption capacity which represents a total overlap of the surface of the clay material.
The adsorption of Ni (II) and Zn (II) onto the raw clay as a function of Temperature and concentration is shown in Figure 3. The temperature was varied from 20 to 50°C at pH 5.5, contact time of 1 h and ion concentrations was varied from 0 to 1g/L. According to Figure 3, with increased temperature the adsorption capacity of nickel ions decreased and the heavy metal retention reaches its maximum at 20°C.confirming that the process was exothermic. The same effect was observed with zinc ions [11, 12].
It can be seen that for low concentrations, the isotherms are almost linear and as the concentration increases, the isotherms tend towards a horizontal asymptote. This marks the saturation of clay by heavy metals. From figure 3 (a) and (b) it can be seen that the maximum adsorbed amount of nickel is about 900mg/g whereas for zinc we find 1600mg/g. This result suggests that the affinity of Zn (II) for raw clay material surface were higher compared to Ni (II) which appeared to have a lower affinity for the clay surface.

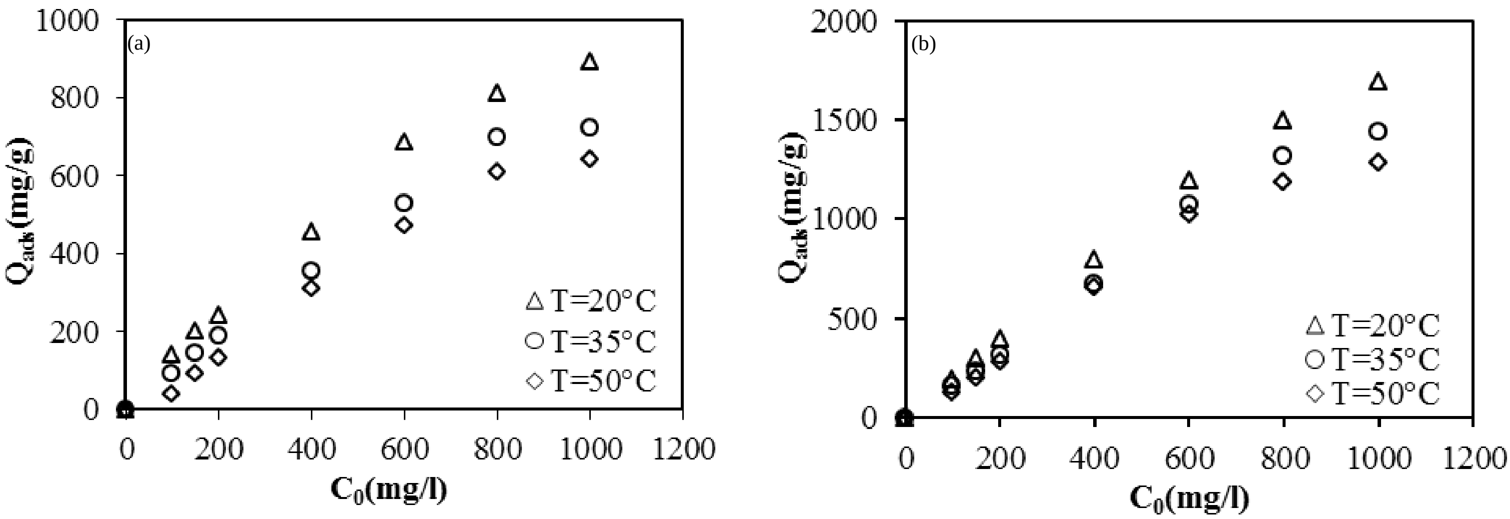

Figure 3. Adsorption isotherms of nickel (a) and zinc (b) on raw and intercalated clay materials at 20, 35 and 50°C

For a better valorisation of the clays, we compare adsorption capacity of prepared FeSb clay with that of activated carbon AC (Figure 4 (a) and (b)), it is equal to 3 times the adsorbent capacity of the raw clay and 2 times of the modified clay. The adsorption capacity of the AC exceeded that FeSb. Thus, activated carbon showed a distinctly higher sorption capacity, which can reach 4000mg/g for nickel and 20000mg/g for zinc due to the large specific surface area, which can reach 1500m2/g [2]. In contrast, the activated carbon regeneration is difficult and usually quite expensive compared to clay materials that are low cost and good competitive adsorbent for the adsorption of heavy metals.

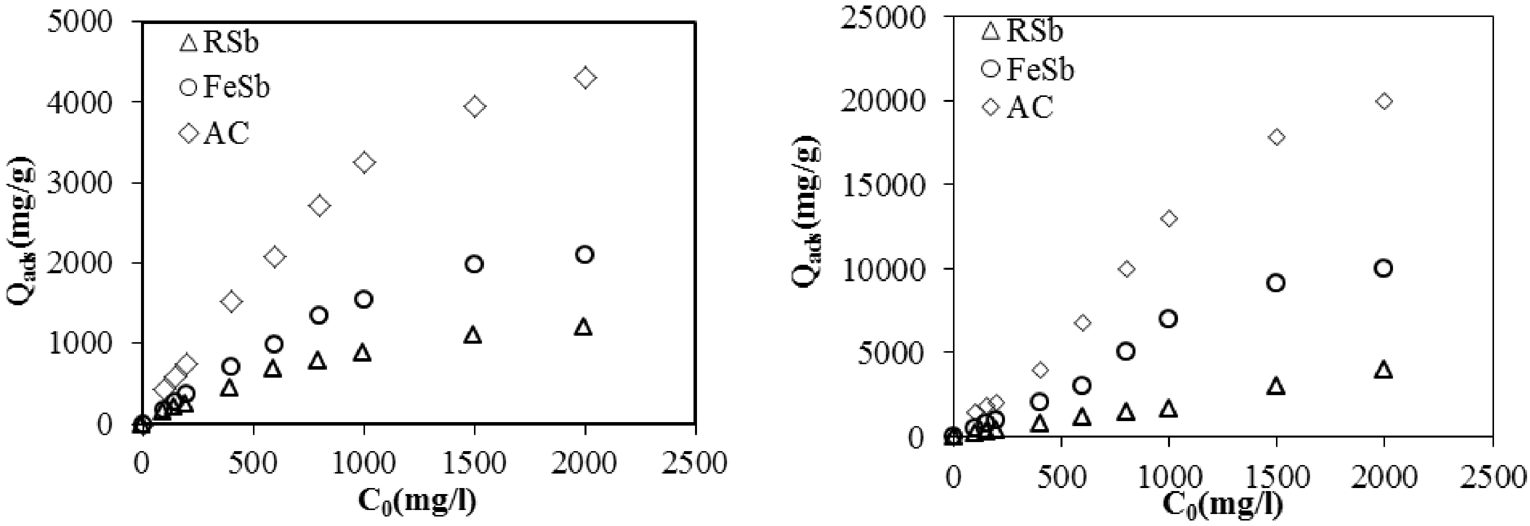

Figure 4. Nickel (a) and zinc (b) adsorption isotherm on raw clay, intercalated clay and activated carbon at 20°C

4. Conclusion

The main objective of this work was to study the application of raw and intercalated Tunisian clays for the treatment of industrial liquid effluents loaded with heavy metals.

The mineralogical characterization of the intercalated material showed an improvement of the basal space as well as the specific surface with respect to the raw clay.

As a result, the intercalated clay has a greater adsorbent capacity, this is subsequently confirmed by the adsorption tests which have proved an improvement in the maximum adsorption capacity.

Hence the interest of using raw and intercalated clay materials as adsorbents of heavy metals due to their high performance and low cost.

5. Bibliographie

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