RESEARCH ARTICLE   **OPEN ACCESS**

SYNTHESIS OF ORGANOPHILIC CLAY: A STUDY OF THE INFLUENCE OF pH ON CHROME ADSORPTION WITH A FOCUS ON THE TREATMENT OF CURTUM WAST

Emílio G. D. N*[1], Arno H. O. [2] and Margarete A. P.[3]

[1]Master in Nuclear Sciences and Techniques, Universidade Federal of Minas Gerais, Avenida Presidente Antônio Carlos, 6.627 - Pampulha, Belo Horizonte – MG; [2]Post Doctor in Radioisotope Application, Federal University of Minas Gerais, Avenida Presidente Antônio Carlos, 6.627 - Pampulha, Belo Horizonte – MG; [3]Master in Crustal Evolution and Natural Resources Centro Universitário Uma Rua dos Aimorés, 1451 - Lourdes - Belo Horizonte - MG CEP: 30140-071

ARTICLE INFO

ABSTRACT

The increasing strictness of environmental laws, associated with the impacts from the inadequate disposal of waste, have challenged several industries to seek more efficient ways to treat their waste. The leather manufacturing industry is constantly growing, bringing with it a large load of waste. One of the most generated solid residues in this type of industry is the so-called "splicer dust". This waste is generated in the leather finishing stage, where the leather is scraped until it reaches the thickness desired by the consumer. These scraps are generated in large quantities per day, have a high concentration of heavy metals in their composition (mainly chromium, have low specific weight, are difficult to compact, and are usually sent to industrial landfills. The adsorption of contaminants using organophilic clay as adsorbent has been gaining space as a new and potentially viable technology, mainly due to the simplicity of operation and gains in the removal of contaminants. In this work, the characterization of sodium bentonite clay was performed and then its organophilization so that it can be applied in a solution of potassium dichromate, aiming the removal of Cr (VI), the main contaminant present in tannery waste. The results of the analysis showed evidence that the organophilization of the clay occurred, given the results obtained in the chemical analysis. The results also indicated good chromium removal efficiency, especially for pH 2, where the removal was the maximum obtained.

Citation: *Emílio G. D. N, Arno H. O. and Margarete A. P.* "Synthesis of organophilic clay: a study of the influence of ph on chrome adsorption with a focus on the treatment of curtum wast", *International Journal of Development Research*, 12, (04), 55472-55477.

INTRODUCTION

Most of the environmental impacts generated by contemporary society in developed or developing countries have their genesis in the industrial sector. This sector is a major consumer of natural resources and a major producer of waste that is generally discarded in the environment - in its *natural* state or inefficiently treated [1]. The leather tanning industries are valued representatives of the extraordinary polluting potential of the industrial segment. Tanneries have always been targets of environmental control agencies, as they generate a high polluting load and release unpleasant odors that originate, mainly, in the first stage of the skin industrialization process, in addition to the pollution generated by the use of Cr (III) and Cr (VI) [3]. According to Aquim (2004), the solid waste generated by the tannery is generally sent to the municipality's landfill, without complying with the Brazilian Standard (NBR) 10004 of 2004, of the Brazilian Association of Technical Standards (ABNT), which establishes that the waste considered class I cannot be sent to

conventional landfill since they increase the risk of disease transmission to the population [3,6]. In the field of skin tanning, tanneries, in recent years, have taken great steps in the improvement of techniques and in the investment of equipment for their effluent treatment stations. In this sense, organophilic clay gains space as a possibly effective technology, due to its particular properties, and because it is economically viable [7]. The presence of clay minerals gives the clays specific physical and chemical properties, allowing their industrial application. This is due to three main factors: the small size of the particles; the morphology of the crystals (in laminae - phyllosilicates) and the isomorphic substitutions [1] that can occur in their structure. All these characteristics make the clays more visible for use in adsorptive processes [9, 10]. In this work, the characterization of sodium bentonite clay was carried out and later its organophilization so that it can be applied in a potassium dichromate solution, aiming at the removal of Cr (VI), the main contaminant present in the tannery residues. This work aims to synthesize the organophilic clay from sodium bentonite, perform the chemical analysis of sodium bentonite clay using the X-ray fluorescence spectrometry method and evaluate its efficiency in adsorption of

chromium, taking the pH of the system as a variable, aiming at the elimination of this pollutant from the tannery tailings.

THEORETICAL FUNDAMENTALS

Clay and clay minerals: Clays are usually defined as natural, earthy, fine-grained materials that, when moistened with water, have a certain plasticity [8]. They can be originated by only one clay mineral, but the most common is to be originated by a mixture of them , with a predominance of one, for example, montmorillonite which is formed by a chemical system characterized by the high Si / Al ratio, relative abundance of Mg, Fe, Ca, Na and K e, a low concentration of H ions. In addition, they have low hardness, also of relatively low density and good cleavage in one direction [9]. The term clay minerals is used to indicate particularly phyllosilicates (silicates that form laminae), which are hydrophilic and provide the plasticity property to clays. In general, they have dimensions below 2μm and come from the decomposition of feldspar rocks. They are basically formed by hydrated aluminum silicates and exhibit a structure made up of an arrangement of two types of crystalline leaves - tetrahedral and octahedral. In the former, there are Si-O tetrahedrons, each of which shares three of its oxygen with neighboring tetrahedra, creating a structural formula of $(Si_2O_5)_n$ for the leaf. In the octahedral, there are Al^{3+} cations linked to O^{2-} and OH^- anions , composing an effective chemical formula of $AlO(OH)_2$ [10]. For a better understanding, figure 1 presents a schematic model of the basic structural layer of a smectite clay, type 2: 1.
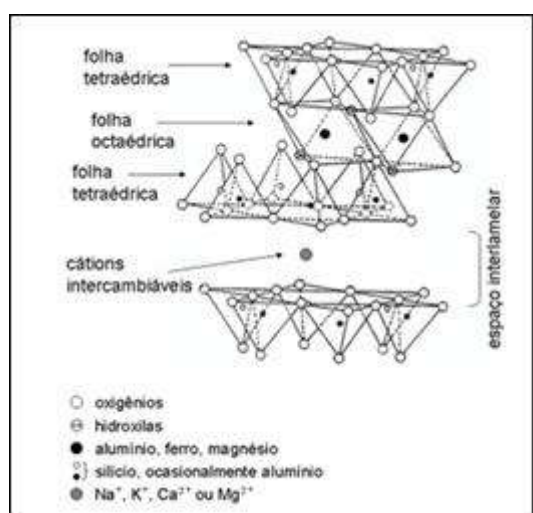
SOURCE: [13]

Figure 1. Model of the basic structural layer of a smectite clay, 2: 1

Some studies also show the efficiency of clays in adsorptive and catalytic processes, since the clays most commonly used in adsorption studies belong to the smectite group, mainly montmorillonite [15]. The adsorbent property of this group of clays is related to the active sites present, in the clay minerals, on its surface and also on its edges. Such sites are conceived by two phenomena: isomorphic substitutions and edge interactions. The isomorphic substitution happens as follows: Si^{+4} atoms are replaced by Al^{+3} atoms in the tetrahedral sheet and in the octahedral sheet Al^{+3} atoms are replaced by Mg^{+2} (e or Fe^{+2} or Fe^{+3}) , causing a deficit of positive charges on the clay surface. The interactions at the edges, on the other hand, come from the protonation or deprotonation processes, a fact that causes the valences located in the atoms to be partially saturated or not, and have a tendency to adsorb organic or inorganic compounds [16]. Because of this, a good part of the ionic exchanges and the colloidal behavior of clay minerals is due to the behavior of the edges [17].

Properties of clay minerals: The type of application of clay minerals is linked to its properties such as: cation exchange capacity, plasticity and swelling [18].

Cation exchange capacity (CTC): The cation exchange capacity (CTC) can be defined as the amount of ions, mainly cations, that the clay can adsorb and exchange. Due to the greater number of negative than positive charges of these colloids, adsorption is mainly of cations. However, there are some sites in these colloids with positive charges that can attract anions (mainly in iron and aluminum oxides). Exchangeable ions can be organic or inorganic in nature [18]. In the case of smectites, as they have large isomorphic substitutions in both their tetrahedral and octahedral leaves, they have a high cation exchange capacity. Table 1 shows the CTC values of some aluminosilicates determined using the direct saturation method with ammonium cation [19].

Table 1. Cation exchange capacity and specific surface area

| Mineral	CTC (meq/100g of clay)	Specific surface area ($m^2 g^{-1}$)
Kaolinite	3-15	15-50
Haloisite $4H_2O$	10-40	60
Haloisite $2H_2O$	05-10	-
Illita	10-40	50-100
Montmorillonite	80-150	75-150
Vermiculite	100-150	100-150
Sepiolite-atapulgite	20-35	-

SOURCE: [20].

In montmorillonites, the cation exchange capacity is mainly associated with isomorphic substitutions of the tetrahedral leaf. In illites and chlorites, CTC is due to broken bonds and the exchange of K^+ ions on the edges of illites or Mg^{2+} ions on the surface of chlorites [21].

Plasticity: This property is defined as the deformation capacity of a system through the application of a determined force and to maintain that deformation once that force is removed. This property in clay minerals is important, for example, in the brick extrusion process [21]. In clays, this property is the result of attractive forces that occur between clay mineral particles and also due to the lubricating action exerted by water between lamellar anisometric particles (with unequal sizes) [22].

Swelling: This property happens due to the intercalation of water that occurs in the interlamellar spaces, solvating the typically exchangeable cations that are between the layers. After solvation, cations no longer balance negative charges from isomorphic substitutions. As a result, the clay layers are negatively charged, which generates a mutual repulsion between the lamellae, thus causing the clay to disperse in the aqueous medium. The degree of swelling is dependent on a number of conditions, such as, for example, the charge of the clay particles, the nature of the counter-ion, the hydration energies involved, the ionic strength of the medium and the total water contained. It is also related to the charge density of the clay [20].
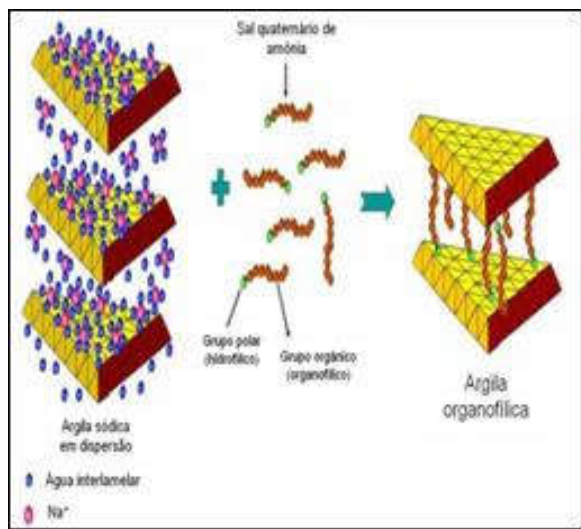
Organophilic clays: Organophilic clays are basically clays that have organic molecules interspersed between the structural layers. The main clays used for the preparation of organophilic clays are smectite clays, mainly due to the size of their crystals, their high CTC and the swelling capacity in water that make the intercalation of organic compounds used in the synthesis quick. and efficient . However, other clays can also be used in the synthesis of organophilic clays, such as hectorite [18]. Among the organic compounds most used in the synthesis of organophilic clays are the quaternary ammonium salts of long chains. The final state in the alkylation of nitrogen amines is represented by these salts. This represents the state where four organic groups are covalently linked to the nitrogen atom and the positive charge of this atom is neutralized by an anion, usually a halogen, as shown in Figure 2 [18]. During the process of synthesis of organophilic clay, these salts are added to the aqueous dispersions of bentonites. Thereafter, organic cations replace sodium cations (in the case of sodium bentonites). Thus, the cations of the quaternary ammonium salts, with their long chains of free hydrocarbons, are

introduced between the 2: 1 layers of the mineral clay making it then organophilic [20]. Figure 3 presents a simplified scheme of this process.

$$R$$
$$R: \ddot{N}: R+X^-$$
$$R$$
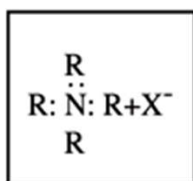
Where R = organic radical, X = halogen
SOURCE: [19]

Figure 2. Structural formula for quaternary ammonium salt

SOURCE: [21]

Figure 3: Organophilization scheme

Many studies have shown the potential use of organophilic clays in adsorption and retention of organic contaminants, which indicates the potential use of these clays in the retention of chemical pollutants that are discarded together with industrial waste [19].

Chromium in tannery residues: According to Jones (1979), to tan the skin through the typical tanning process, more than 2/3 of the chromium does not reach the final product. About 10 to 40% of the chromium remains in the liquid residue, depending on the amount of chromium used and the use of various additives. The other part, (1/3) of the chromium, is in the solid residues in the form of chips. This leather residue usually contains 3 to 4% of chromium [23.24]. NBR 10004, from ABNT, classifies chromium as class I waste. According to this classification, it needs specific treatment and disposal before dumping in rivers and springs [6]. In view of the problems caused by chrome tanning, according to Jones (1979), many tanning research groups have been making new proposals to replace and also save chrome, but unfortunately, nothing that has yet been accepted in practice. Everything that has been done leads to the conclusion that, as a tanning agent, nothing is better than chromium [23]. In the case of tannery residues, only trivalent chromium is present, but due to its oxidation to Cr (VI) and its high toxicity, it is important to study the possibility of this oxidation. The oxidation of Cr (III) is viable at a pH below 4. At pH between 5 and 12, chromium hydroxide precipitates and because of its low solubility product ($2.9x10^{-29}$) there is no Cr (III) available and thus no oxidation of chromium will occur. At pH values greater than 12, the soluble chromate ion is formed, and if manganese is present, oxidation of chromium to the hexavalent state may occur. One of the major problems is that manganese is easily found in many types of soil, so if the tailings containing chromium are discarded without proper treatment, oxidation to its hexavalent state may occur [23, 26]. This information, combined with the fact that many tanneries practice the clandestine disposal of their waste,

makes the study of alternative and cheaper ways to treat this waste [20]. Chrome-tanned leather, which represents 90% of the world's leather, is called *wet blue* and has a fast tanning process and good resistance and malleability. Another process used is vegetable tanning based on natural tannins, which is a very common element in nature, and can be found in different parts of some types of vegetables such as oak and mimosa bark. However, the leather from this process is less resistant and demands a longer stabilization time, when compared to the chrome tanning process. The great advantage of vegetable tanning is that, because it is a natural organic material, it becomes easy to handle with regard to pollution. [20].

Treatment and destination of waste: It is necessary that the industrial effluents that have chromium are treated in a specific way before their final destination, aiming at not contaminating the water, soil or even the air, when these effluents are discarded in any way and without a previous treatment. These treatments reduce the damage that effluents can cause to the environment. A significant percentage removal occurs in the treatment of heavy metals present in water [6]. Chemical precipitation, adsorption, electrodeposition and ion exchange are some processes used for the treatment of effluents, each with advantages and disadvantages depending on the effluent and its contaminants. Within the aforementioned processes, adsorption stands out as a promising method for this purpose [44].

MATERIALS AND METHODS

Experimental Part: The experimental part of the present work was carried out in the organic chemistry laboratory of Centro Universitário Una and in the Nuclear Technology Development Center.

Synthesis of orgonophilic clay: For the organophilization stage, natural sodium bentonite ($O_2 Al_{34} SiO_2 H_2 O$) was used, with 98% purity, of a light cream color, supplied in powder form, by Bentonisa do Nordeste, located in the municipality of Boa Vista / PB and cetyltrimethylammonium bromide (Cetremide) - $CH_3 (CH_2)_{15} N$ (Br) $(CH_3)_3$ - content of 98%, from the Neon brand using the methodology adapted [20]. Initially, 1600 mL of distilled water was heated to approximately 80 ± 5 ºC in a Biomixer 7811W-1 heater. Then, 32 g of clay and 9.8 g of quaternary ammonium salt (Cetremide) were added to the water in a Jar Test ethik 218-LDB with a constant stirrer rotation of 200 RPM, which was maintained for 90 minutes after addition of inputs. After the process, the system remained at rest for 48 hours at room temperature, being then filtered in a Buchner funnel and washed with approximately 2000 mL of distilled water, in order to remove all excess salt. The agglomerates obtained were dried in an oven, initially at a temperature of 50 ± 5ºC and, after 48 hours, at a temperature of 70 ± 5 ºC, for another 6 hours. Finally, the clay was broken up in a mortar and passed through an ABNT 270 sieve, with a diameter equivalent to 0.053 mm. Finally, the clay was stored in a place without the presence of moisture.

Characterization of clay: Chemical analysis of the samples was carried out using the X-ray fluorescence spectrometry (FRX) method on a Panalytical Axios Max X-ray spectrometer, with a rhodium tube. The sample was prepared through the process of fusing a pearl with lithium tetraborate so that it could later be read on the equipment. The clay samples were prepared using lithium tetraborate, in dilutions 1: 4, 1: 6 and 1: 8 (g of sample: g of flux). To perform the process, an automatic fusion machine model Eagon 2 from Panalytical was used at a working temperature of 1050 ºC. Possible contamination by Pb, Cd, Zn, Cr and As was detected using a flame atomic absorption spectrometer (Thermo Scientific, ICE 3000), with the sample preparation following the normal pattern of the clay mineral opening procedure [71] . The mineralogical composition was also analyzed, using X-ray diffraction (XRD) in a Shimadzu diffractometer, XRD-6000 through CuKα radiation, with 2θ ranging from 3 ° to 80 ° under the following conditions: 25.0 kV potential, current 25.0 mA, scanning speed of 2 ° / min and reading step of 0.02 °.

Preparation of the standard solution: The standard solution of potassium dichromate ($K_2Cr_2O_7$) 1000 mg.L^{-1}, was prepared by dissolving 2.8290 g of $K_2Cr_2O_7$ in deionized water using a 1000 mL volumetric flask. 4 L of the standard solution was prepared. The choice of potassium dichromate for the preparation of the standard solution was due to the fact of the presence of chromium VI in its composition. The solution with a concentration of 5 mg.L^{-1} of potassium dichromate was prepared by dilution.

Application of organophilic clay: The adsorption studies using organophilic clay as an adsorbent for the removal of chromium were carried out using the batch adsorption process. Distilled water was used throughout the process. After dilution of the standard solution, a 5 mg.L^{-1} potassium dichromate solution was obtained. The choice of the concentration value of the standard solution was due to the fact that the analysis was performed on a spectrophotometer (UV / VIS), and thus the equipment was able to carry out the readings without problems. 4 aliquots of 1 L each of this solution were separated, and each one was added to a specific Jar Test vessel. A 0.5 mg organophilic clay mass was fixed to be used as an adsorbent in each of the Jar Test vessels. The choice of the clay mass value was due to previous tests involving different mass values, where the 0.5 mg mass resulted in the largest chromium removal [25]. After adding the clay to the pots containing the potassium dichromate solution, Jar Tes was started with a constant stirrer rotation of 200 RPM, which stirred the best adsorption result in previous tests with different rotation gradients. For the tests of the pH influence, sodium hydroxide solutions (0.1 M NaOH) and hydrochloric acid (0.1 M HCl) and a previously calibrated pH meter Lutron model PH-221 were used to adjust the pH. The pH adjustments were already made in the Jar Test vessels. Four pH values were determined in order to cover the acid and alkaline range: 2, 4, 6, 8 and 10.

The agitation in the Jar Test was maintained for 1.5 hours. Previous tests with different stirring times have shown that stirring times greater than 1.5 hours did not alter% removal and chromium [73]. After this procedure, the pots were kept at rest for 12 hours in order to decant the clay. 100 ml aliquots were removed from each of the Jar Test vessels. The solutions were filtered through a Buchner funnel and packaged so that they could later be analyzed by the absorption spectrophotometer (UV / VIS). The samples were analyzed for chromium content through absorption spectrophotometry (UV / VIS), in a spectrophotometer (UV / VIS) of the brand Biospectro, model SP-220, at a wavelength of 357.9 nm, operating in the organic chemistry laboratory at Centro Universitário Una. To determine the chromium concentration, absorbance analyzes were used. Calibration was performed with 7 standards with different concentrations of the standard solution (including the blank). Subsequently, the samples were read in duplicate. For this, 5 ml of the samples treated in different pH ranges were collected and, then, the absorbance reading was performed in quartz cuvettes. From the calibration curve, it was possible to determine the oil concentration in the samples. The removal (R) of chromium was calculated using Equation 1:

$$R = \frac{C_i - C_f}{C_f} \cdot 100$$

(1)

Where Ci represents the initial concentration of chromium in the solution and Cf represents the final concentration.

RESULTS AND DISCUSSIONS

Chromium removal analysis: The results of the chromium removal analysis carried out through the UV / VIS spectrophotometer showed that the application of the organophilic clay was able to remove chromium (VI) from the solution. Table 2 shows the results obtained for each pH value. It is important to note that each point represents the average of the duplicate of tests where the error was less than 5% and the standard deviation of 0.50.

Tabela 2. Effect of pH on chromium removal

pH	Final concentration (mg.L^{-1}) (n=2)	%Removal
2	0,00	100
4	3,80	24
6	4,00	20
8	4,30	14

Initial concentration: 5 mg.L^{-1}. Detection limit = 0.19 mg / L

Table 2 shows the decrease in chromium removal as the pH of the system increases. It is also seen that when pH = 2 the removal was maximum. This happened due to the presence of anions that favor adsorption on the surface of the organophilic clay. According to (JUNG et *al.,* 2013) this event is attributed to the fact that the adsorbent surface is positively charged, thus attracting anions and repelling cations or other cationic particles present in the solution. For hexavalent chromium, hydrogen chromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{-2}$), are the predominant ions in acidic solutions, while chromate (CrO_4^{-2}) prevails under alkaline conditions, depending on the oxidation state. and the concentration and respective pH of the system. Another hypothesis for which the removal did not happen efficiently when the pH was alkaline is the presence of SiO_2 in the clay structure. When in alkaline pH, there is a change in the Si structure, becoming amorphous, which interferes with the adsorption process. Figure 4 presents a graph where it is possible to visualize the removal variation according to pH, according to the data contained in Table 2.
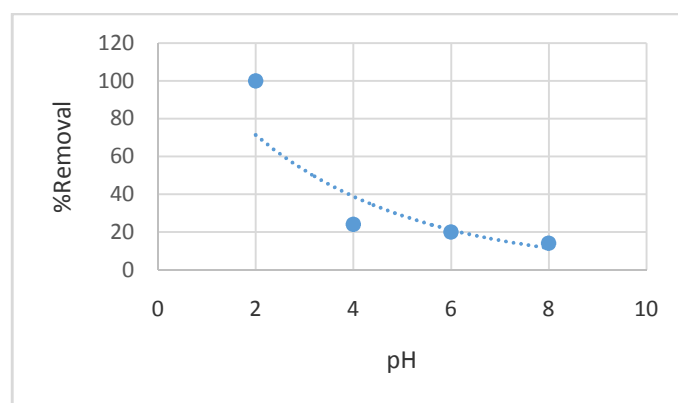

Figure 4. Chromium removal as a function of pH in the application of organophilic clay

The data show a decrease in removal efficiency and an increase in the residual chromium concentration of the aqueous solution with an increase in pH. It is possible to verify that the adsorption in acidic medium is more effective when in alkaline medium, since the% of removal is decreased when the pH increases. As the pH of the leather tanners' waste has an alkaline character, it would be necessary to carry out a pH adjustment, making it acidic, which should be tested in order to confirm the stability of the effluent after such adjustment. It is also of great importance to emphasize the competitiveness between the elements when they are adsorbed. Since the composition of the tailings in tanneries has other elements, even if in quantities much lower than chromium, the presence of these elements can interfere with the removal efficiency presented in this work [26]. Importantly above tests the pontaram for better agitation and better weather air mass gila be used. Table 3 presents the results obtained through the UV / VIS spectrophotometer. Different masses of organophilic clay were used, at a constant temperature of 70 ° C. The analyzes were performed in triplicate, the error was less than 5% and the standard deviation was 0.61 mg.L^{-1}. Through these results it was possible to observe the greater removal of chromium (VI) when the mass of organophilic clay was 0.5 mg, thus justifying its choice for application in this work. When the mass was 0.6 mg, the removal showed a decrease, which shows that, possibly, for the concentration of potassium dichromate used, this mass showed a saturation state of the contaminant adsorption process. Other tests, with masses greater than 5 mg, should be done to confirm this information.

Tabela 3. Concentration Chromium (VI) after application of different masses organophilic clay (n = 3)

Clay mass (mg)	Chromium (VI) concentration (mg.L^{-1})
0,2	4,51
0,3	4,02
0,4	3,78
0,5	3,50
0,6	3,65

Initial concentration: 5 mg / L [22]

Tests were also carried out in order to find a better stirring time at JarTest. 4 samples were subjected to agitation at different times in JarTest: 60 minutes, 90 minutes, 120 minutes and 150 minutes. The clay mass used was fixed at 0.5 mg. Table 4 shows the results presented. The analyzes were performed using a UV / VIS spectrometer, in triplicate, with an error less than 5% and standard deviation of 0.45 mg.L^{-1}.

Table 4. Application of organophilic clay at different times of agitation in JarTest (n = 3)

Shaking time (min)	Chromium (VI) concentration (mg.L)
60	3,85
90	3,05
120	3,14
150	3,20

Initial concentration: 5 mg.L^{-1}. [22]

From the results presented, it is seen that times greater than 90 minutes of agitation did not bring significant results for the removal of Cr (VI), therefore the agitation time of 90 minutes was chosen for this work.

Chemical analysis: The result of the chemical analysis of sodium bentonite and organophilic clay, carried out using the X-ray fluorescence (FRX) method , can be seen in table 5 . The standard deviation is 0.60 (mass%) and the error is less than 5%.

Table 5. Chemical analysis (% by mass) of sodium bentonite and organophilic clay using the X-ray fluorescence (FRX) method

Oxide	% found in sodium bentonite	% found in organophilized bentonite
Red loss	18,03	29,77
MgO	3,40	3,20
Al$_2$O$_3$	19,04	16,60
Fe$_2$O$_3$	4,90	3,20
K$_2$O$_3$	0,40	0,45
Na$_2$O	2,50	-
Br	-	1,06
SiO$_2$	50,70	43,40

n = 3. Detection Limit = 0.58 (mass%)

The red loss constitutes the loss of interspersed water, the loss of hydroxyl water from clay minerals, organic matter and carbonates. For the samples under study, the red loss levels present values of 18.03% for the sodium bentonite clay and 29.77 for the organophilized clay with Cetremide. The greatest red loss exhibited by the organophilized clays points to indirect evidence that the quaternary ammonium salt was added to the structure of the clays and, therefore, that the organophilic clays were obtained. The highest value was organophilized clay, which shows that this clay has higher humidity and a greater amount of volatile components, such as hydroxyls, organic matter or even carbonates. Table 5 shows the presence of specific elements of smectitic clay, such as silica (SiO$_2$), which presented 50.70% of the composition before oganophilization and 43.40 after, and alumina (Al$_2$O$_3$) , which presented 19.04 of the composition before oganophilization and 16.60% after, which with the addition of organic salts on the clay surface showed different levels. For the organophilized clay with Cetremide, there is the absence of sodium (Na$_2$O) present in sodium bentonite clay (2.50%) and the presence of bromine (1.06%), showing the cation exchange. However, it can be attributed to the amount of Bromine still found in the organophilized clay with cetremide to an ineffective process of washing the clay. It was also possible to observe the presence of characteristic elements of clay from the smectite group, represented by iron oxides (Fe$_2$O$_3$) composing 4.90% before oganophilization and 3.20% after and potassium (K$_2$O), composing 0.40% before oganophilization and 0.45% after.

CONCLUSIONS

The data obtained in the present study showed that pH is crucial to evaluate the ability of organophilic clay to adsorb Cr (VI) in aqueous solutions. For the tested conditions of stirring time of 90 minutes, initial concentration of 5 mg.L^{-1} of Cr (VI) and mass of organophilic clay of 0.5 mg, the best result was obtained at pH = 2, where the removal achieved its maximum efficiency value. It is concluded that this technique is interesting for application in the treatment of electroplating effluents, since the effluents generated in this type of process are acidic, so it would not require large expenses with chemical products to adjust the pH. In the case of leather tannery effluents, where the tailings pH is in the alkaline range, the process is also interesting, since the costs for pH correction would not be large. Economically speaking, the technique presented has a lower cost of operation than other techniques used, such as chemical precipitation, electrodeposition and ion exchange. In order to reduce the environmental liabilities generated by industries that generate effluents contaminated with chromium, adsorption appears as a promising alternative to the processes conventionally applied to the treatment of effluents. This new alternative has the advantage of less residence time to the process, lower operating cost and greater ease of operation, combined with satisfactory chromium removal rates [26]. The tests carried out to check the chemical composition of sodium bentonite clay were important for a better understanding of the mineral chosen and used as an adsorbent in the process.

REFERENCES

AQUIM, P. M. de; GUTTERRES, M.; TESSARO, I. C. Análise dos efluentes gerados no processo de ribeira e curtimento da indústria do couro. In: Programa de Pós-Graduação em Engenharia Química, 2004. Disponível em: <http://www.ppgeq.ufrgs.br/projetos/curtumes/Arqs/Analiseefluentes.pdf>. Acesso em: 01/10/2018.

BRANCO, P. M.. Dicionário de Mineralogia e Gemologia. São Paulo: Oficina de Textos, 2008. 608 p. il.

BRINDLEY, G. W. 198. Order-Disorder in Clay Mineral Structures, Chapter2. In:Brindley G.W. and Brown, G. Crystal Structure of Clay Minerals and their X-ray Identification. Mineralogical Society, p.125 - 195. London, 1994.

COSTA. J. M. - Desenvolvimento de nanoestruturas adsorvente de argilas para tratamento de efluentes contendo compostos orgânicos do tipo betx – Faculdade Tecnológica SENAI CIMATEC – Salvador 2012.

CUNHA, R. S. S.; MOTA, J. D.; RODRIGUES, M.G.F. Síntese, caracterização estrutural e aplicação de argila organofílica na remoção de óleo lubrificante e óleo diesel no processo de adsorção em sistema de banho finito. X Encontro Brasileiro sobre Adsorção. São Paulo: Guarujá, 27 a 30 de abril de 2014.

FERREIRA, E. L. Pele, Couro, Moda: a matança de animais e o cromo. In: Etnobotanica, 2011. Disponível em: <http://www.etno-botanica.com/2011/02/pelescouro-moda-matanca-de-animais-e-o.html>. Acesso em: 03/10/2018.

GUERRA, D. L.; SANTOS, M. R. M. C. and AIROLDI, C. Mercury adsorption on natural and organofunctionalized smectites - thermodynamics of cation removal. Journal of Brazilian Chemical Society, v.20, n.4, p.594-603, 2009.

HARVEY, C. C., LAGALY, G. Conventional applications. In: Bergaya, F., Theng, B. K. G., Lagaly, G. (editors). Handbook of clay science. Developments in clay science. Amsterdam: Elsevier; 2006.

HEIDEMANN, E. Depósito e Reciclagem de Materiais Curtidos ao Cromo. Revista do Couro, Estância Velha, v. 18, n. 86, p. 48-50, jun./julh. 1992.

JAIN, A. K.; GUPTA, V. K.; BHATNAGAR, A.; SUHAS. Utilization of industrial waste products as adsorbents for the removal of dyes, J. Hazard. Mater. B101, p. 31-42. 2003.

JONES, B. H. Chromium Recovery Through Incineration of Liquid and Solid Tannery Wastes –"The Ultimate Solution". *Journal of American Leather Chemists Association (JALCA)*, Easton, Pa, v. 74, n. 11, p. 395 – 403, Nov.1979.

JORDÃO, C. P.; DA SILVA, A. C.; PEREIRA, J. L.; BRUNE, W.; Nova Química. 22, 47. 1999.

LUNA, F. J; SCHUCHARDT, U. Argilas Pilarizadas – Uma introdução. Instituto de Química da Universidade de Campinas, 1997.

MARTINES, A.M. et al. Ammonia volatilization in soil treated with tannery sludge. Bioresource Technology. Universidade de São Paulo, 2010.

MELLO, F. de A. *et. al.* Fertilidade do solo. São Paulo: Nobel, 1983. 400 p.

MILACIC, R.; STUPAR, J.; KOZUH, N.; KOROSIN, J.; GLAZER, I. Fractionation of Crand Determination of Cr (VI) in Blue Shavings. *Journal of American Leather Chemists Association (JALCA)*, Easton, Pa, v. 87 p. 221 – 232, 1992.

Norma Brasileira Associação Brasileira de Normas Técnicas 10004/2004. Disponível em: <http://www.ccs.ufrj.br/images/biosseguranca/CLASSIFICACAO_DE_RESIDUOS_SOLIDOS_NBR_10004_ABNT.pdf>. Acesso em: 01/10/2018.

PAIVA, L. B.; MORALES, A. R; DIAZ, F. V. Argilas organofílicas: características, metodologias de preparação, compostos de intercalação e técnicas de caracterização. Cerâmica vol. 54 no.330 São Paulo Apr./June 2008.

SANTOS, P. S. Ciência e Tecnologia das Argilas. Vol1, 2ed. São Paulo:Editora Edgard Bücher Ltda. 408p. 1984.

SANTOS, P. S. Ciência e Tecnologia de Argilas, 2ª edição, Vol. 1, Editora Edgard Blücher Ltda, São Paulo, Brasil (1989) 215.

SANTOS, P. S. Tecnologia de argilas: aplicada as argilas brasileiras - fundamentos. Sao Paulo: Edgard Blucher/Ed. USP. 1975.

SANTOS, P. S.; Santos, H. S. 1989-1992. Ciência e tecnologia de argilas. 2. ed., rev. e ampl. São Paulo: E. Blucher, 3v. 1089p.

SANTOS, P. S.; SANTOS, H. S. Ciência e tecnologia de argilas. 2. ed. rev. e ampl. São Paulo: Edgar. Blucher, 3v. 1989-1992, 1089p.

SILVA, A. A. Estudo de argilas organofílicas destinadas à separação óleo/água. Dissertação apresentada ao Programa de Pós-Graduação em Engenharia Química do Centro de Ciências e Tecnologia da Universidade Federal de Campina Grande. Campina Grande – PB, Novembro de 2005.

SILVA, A. A.; PEREIRA, K. R.; RODRIGUES, M. G. F; WIEBECK, H. VALENZUELA, D. F. R. Uso de Argilas Organofílicas na Purificação de Efluentes

VALENZUELA, D. F. R. Preparação, a nível de laboratório, de algumas argilas esmectíticas organofílicas - 256p. Tese de Doutorado, Engenharia Química, Universidade de São Paulo, São Paulo - SP. 1994.

****