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Treatment of Tannery Effluent by Tunisian Clay

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Abstract: The tannery effluent from the wet finishing stage is a complex, highly charged rejected of organic and mineral matter. It has variable characteristics over time and is not readily biodegradable. Its physicochemical treatment by adsorption on the smectitic clay of Khlédia proves to be effective. The reduction of dye, BOD, COD, heavy metals are remarkable. The decrease of the conductivity is due to the phenomenon of the cations adsorption on the negatively charged support colloids.

Keywords: Smectite, Tannery, Treatment, Adsorption

1. Introduction

The tannery sector has occupied an important position in Tunisia. It has 23 industrial processing units for hides (sheep, cattle and goats) to manufacture leathert The Tunisian "star tannery" has been one of sectors which manufacturing and dyeing leather since 1980. It produces about 10000 m^3 of wastewater per year containing both organic and inorganic compounds. The characteristics of tannery wastewater vary widely depending on: the nature of the adopted tanning process, the amount of water used, the process of leather preservation, the leather processing capacity and the in-plant measures followed to reduce pollution. The organic compounds present in tannery wastewater are tannins which are highly toxic contaminants that are difficult to degrade [1, 2, 3]. Therefore, they must be removed from the wastewater before discharging into the environment. The treatment methods which are commonly employed for tannery wastewater are physical, chemical and biological processes. Distinct treatment methods like physicochemical methods such as sedimentation, electro floatation, filtration, membrane filtration, precipitation, coagulation, adsorption, ion exchange and biological

methods may exposes the chemicals into the environment after processes being carried out [4]. Adsorption technique is popularly used among all the available methods for effluents treatment because of its simplicity of operation, low initial costs of implementation and good performance for effluents treatment.

The main objective of this work was to assess the potential of natural clay to treat the tannery effluent by adsorption technical.

2. Materials and Methods

2.1. Material

The tannery wastewater from the wet finishing stage was supplied by the Industrial Tannery (Tannery Star Company), located in Megrine (Tunisia). It is a complex mixture of Acid Brown 75 dye (AR357, CAS: 8011-86-7, trade name: Brown EDR), metals and additives whose exact composition is unknown. The effluent was separated and used in the adsorption tests, by maintaining it under cooling (4°C) until use (for less than one week). Table 1 present the physico-chemical characterization of the effluent generated in the dyeing process.

Table 1. Physico-chemical characterization of tannery effluents before treatment.

Characteristic	Values	NT 106.3
pH	5,25 ± 0,7	6.5 - 9
Conductivity (µS/cm)	17580	7
MES (mg/l)	100	400

Characteristic		Values	NT 106.3
Turbidity (mg/l)		630	
COD (mg/l)		6400	1000
BOD (mg/l)		1150	400
BOD/COD (mg/l)		0.179	
	chromium	0.78	2
	zinc	0.5	
Heavy metals (mg/l)	lead	0.78	1
	copper	0.1	1
	iron	2	5
	cadimum	0,16	0.1
Dye concentration (mg/l)	C. I. Acid Brown 75	182	0

2.2. Methods

The adsorption tests were performed in a thermostatic shaker with controlled agitation. The pH of the effluent was adjusted to the study conditions with HCl or NaOH (0.1N) and the effluent was filtered with a mesh of approximately 0.5 mm to eliminate material (solids) in suspension. After equalizing the temperature of the adsorbent and the effluent, 20 mL of the effluent was added to the adsorbent, with samples of the supernatant being taken at intervals established for the calculation of the removal rate (1), and after every 2 hours, until equilibrium was observed, for the calculation of the adsorption capacity, in accordance with (2). The residual dye concentration in the supernatant was analyzed using a spectrophotometer (Perkin Elmer IV spectrometer Lambda 20) at a wavelength of 416 nm. While, the concentration of heavy metals remaining in the supernatant was determined by atomic absorption spectrometry (Hitachi Z-6100 model).

$$\text{Re}\,moval(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

Where C_0 (mg/L) is the initial dye concentration, C_e the final (equilibrium) dye concentration, m(g) the adsorbent mass used and V(L) the volume of dye solution. Biochemical Oxygen Demand (BOD) Tests were conducted in accordance with the standard dilution method (APHA "Standard Methods" No. 219 [5]) at 20 ±°C for a period of 5 days. Chemical Oxygen Demand (COD) Tests were conducted in accordance with the standard potassium dichromate method described in ASTM D 1252-67 [6].

3. Results and Discussion

3.1. Localization of Studied Clay Deposit and Characterization

The smectite-rich clay (AS) used in the present study was collected from Ain el Morra (Khledia region) (Figure 1). The adsorbent employed was characterized [7] by X-ray diffraction, chemical analysis, infrared spectroscopy, specific surface area, cation exchange capacity and point of zero charge.
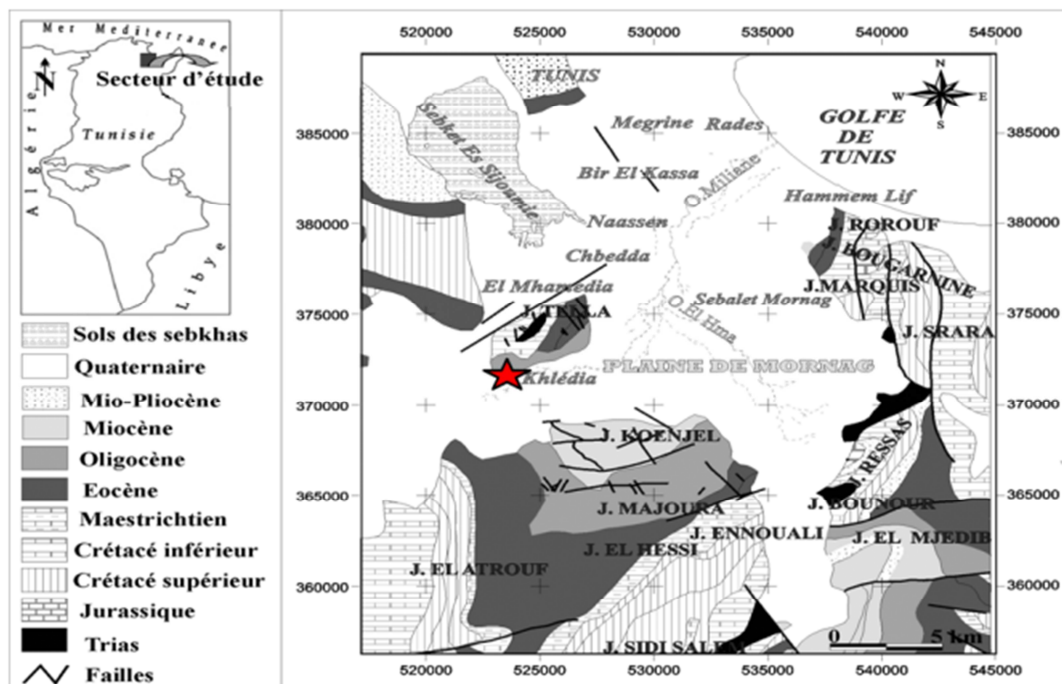

Figure 1. *Localization of the investigated clay deposits.*

3.2. Characterization of AS

X-ray diffraction patterns of AS are presented in Figure 2. A characteristic reflection peak of smectite (S) at 2θ=5.8° (d=12.32 Å) can be observed with greater intensity. The appearance of the diffraction peaks at 2θ=12° (d=7Å) and 2θ=9° (d=10Å) revealed the presence of kaolinite (K) and illite (I), respectively. The basal reflection of quartz (Q) appearing at 27° (3.33 Å). The chemical analysis showed that the main constituents of AS are silica (60.16%), alumina (16.95%) and iron oxides (7.42%) (Table 2). The loss of ignition (LOI) is 7.64%. It is mainly attributed to the loss of H_2O from clay minerals, especially smectite. The FT-IR spectrum of AS sample (Figure 3) shows that absorption bands at 3624 and 917 cm^{-1} are attributable to Al-Al-OH$^-$ stretching and bending modes of vibrations [8]. The bands appeared at 1030 cm^{-1} correspond to Si-O of clay minerals. The specific surface area of AS was about 250m^2/g. This value is relatively low compared to other smectitic clays studied by other authors [9, 10]. This could be explained by the high content of quartz which has an influence on the specific surface area [11]. The Cation exchange capacity (CEC) of this clay sample is about 34meq/100g. Results show that pH_{zpc} of AS was 8.0.
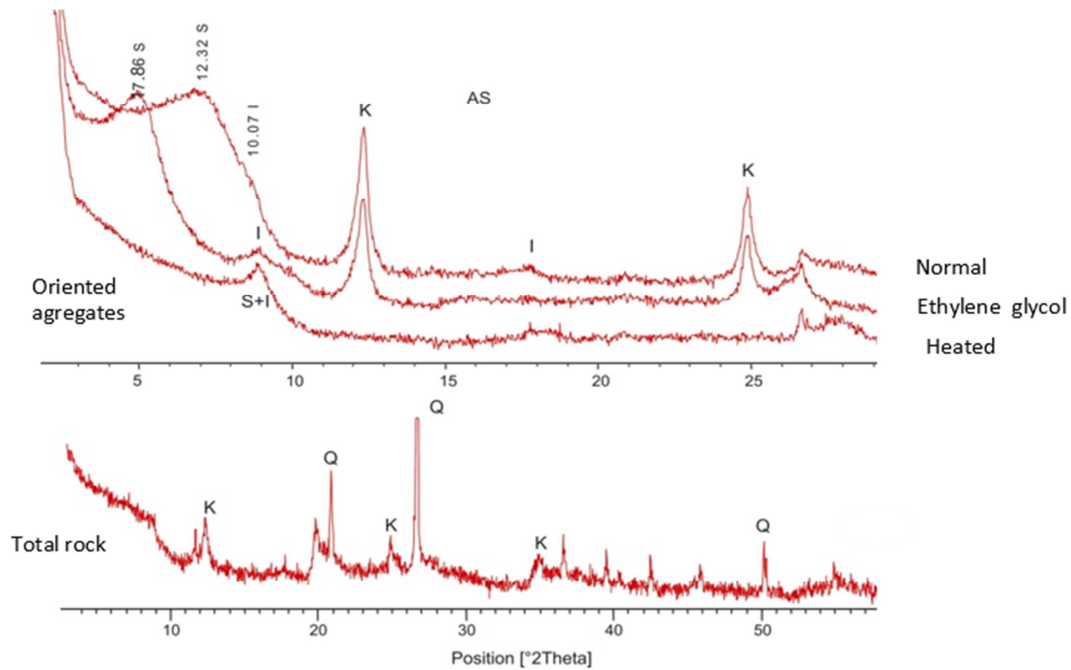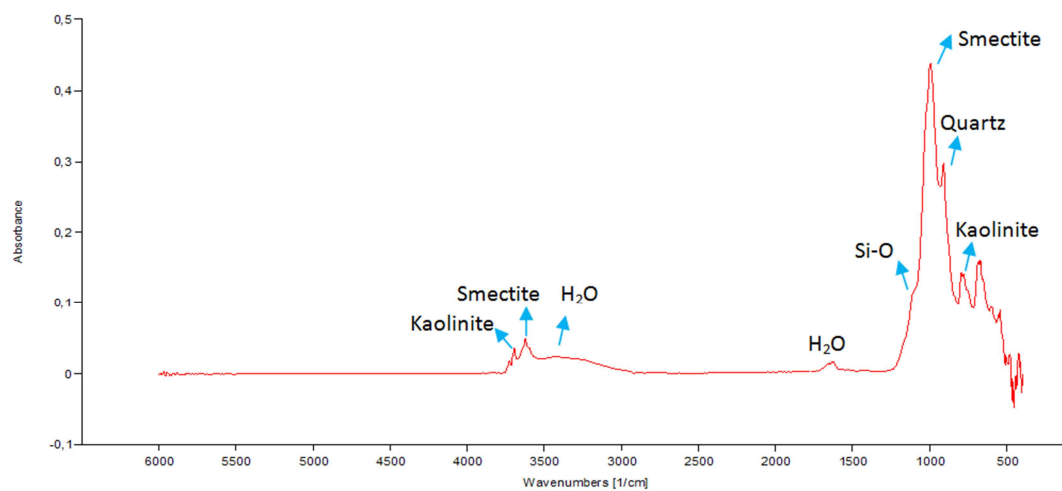

Figure 2. *X-ray diffraction of AS.*

Figure 3. *Infra-red spectrum of AS clay sample.*

Table 2. *Chemical analysis of AS.*

Sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	LOI	Total
AS	60.16	16.95	7.42	1.89	2.02	0.39	2.15	7.64	99.60

3.3. Treatment of Tannery Effluent by Clay

3.3.1. Removal of Dye

a. Influence of pH

The solution pH range was adjusted between 3 and 9. According to reported studies on the adsorption of dyes with different chemical structures, the effect of pH on the solute uptake by clays can be highly, moderately or slightly significant [12]. The adsorption is affected by the changes in the pH of the effluent because this parameter affects the degree of ionization of the dye and the surface properties of the sorbents. As a general rule, pH values lower than pH_{pzc} result in lowering the number of negatively charged sites of the clay sample, thereby increasing the number of positively charged sites which enhances the adsorption of anionic dyes. At pH values greater than pH_{pzc}, the hydroxyl ion concentration increases and the number of negatively charged sites on the surface of the clay sample increases so that the extent of adsorption of colour is decreased because of ionic repulsion between the negatively charged surface and the anionic dye molecules. In our case, the results show that the extent of adsorption decrease even at acidic pH (Figures 4). This suggests that other compounds present in the effluent compete for the adsorption sites, reducing the adsorption capacity.
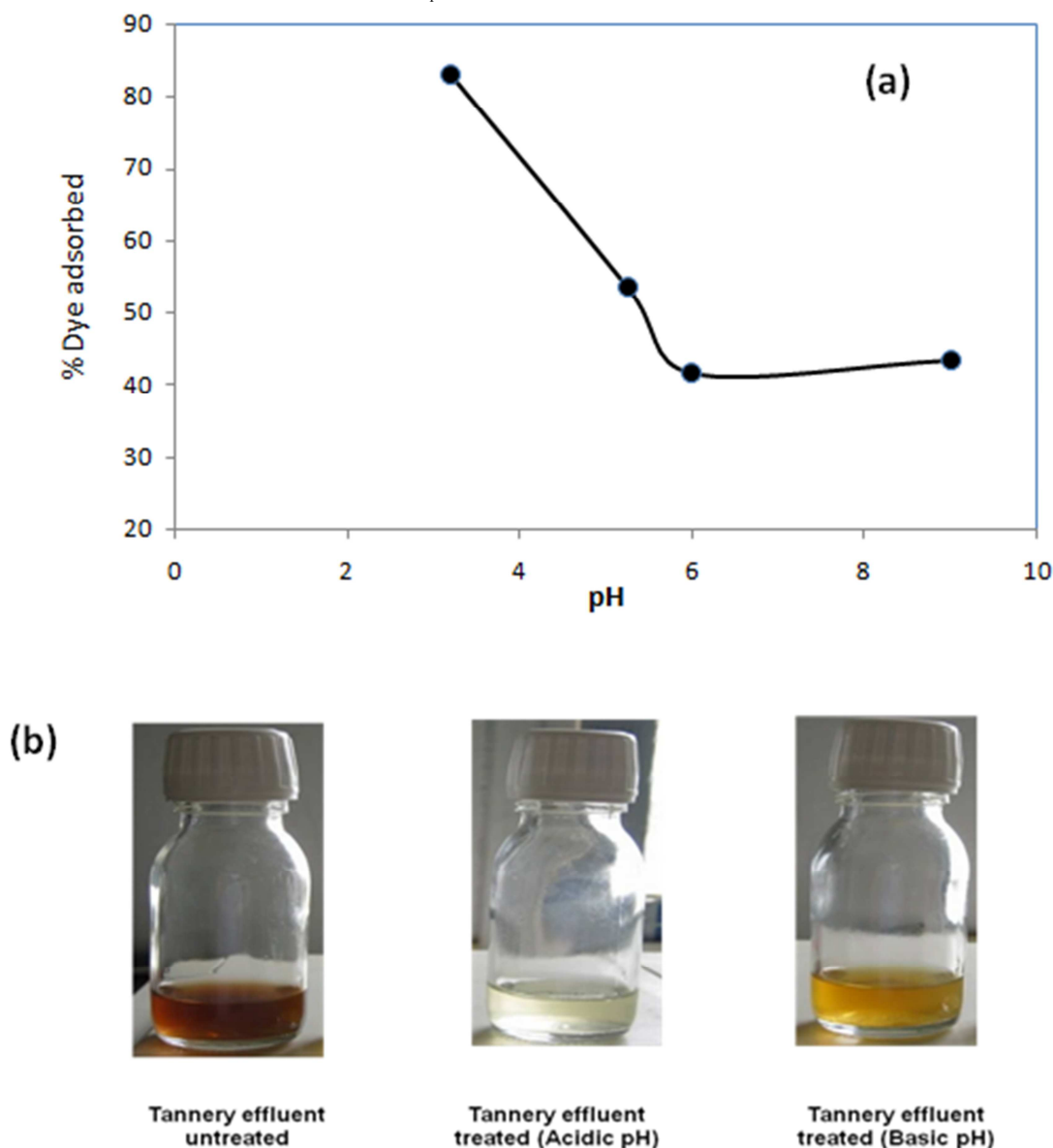

Figure 4. *(a) Effect of pH, (b) Photos of decolorization.*

The smectitic clay can adsorb dye at acidic pH via different mechanisms (Figure 5): (1) formation of inner-sphere complexes through SiO− and AlO− groups at the clay particle edges [13] (2) interaction between the polyvalent metal cations (Al^{3+}), constituents of the terminal sites which may form bridges between clay particles and organic anions (3) the interlayer cations Ca^{2+} have a polarizing power of water molecules which can then serve as adsorption sites for
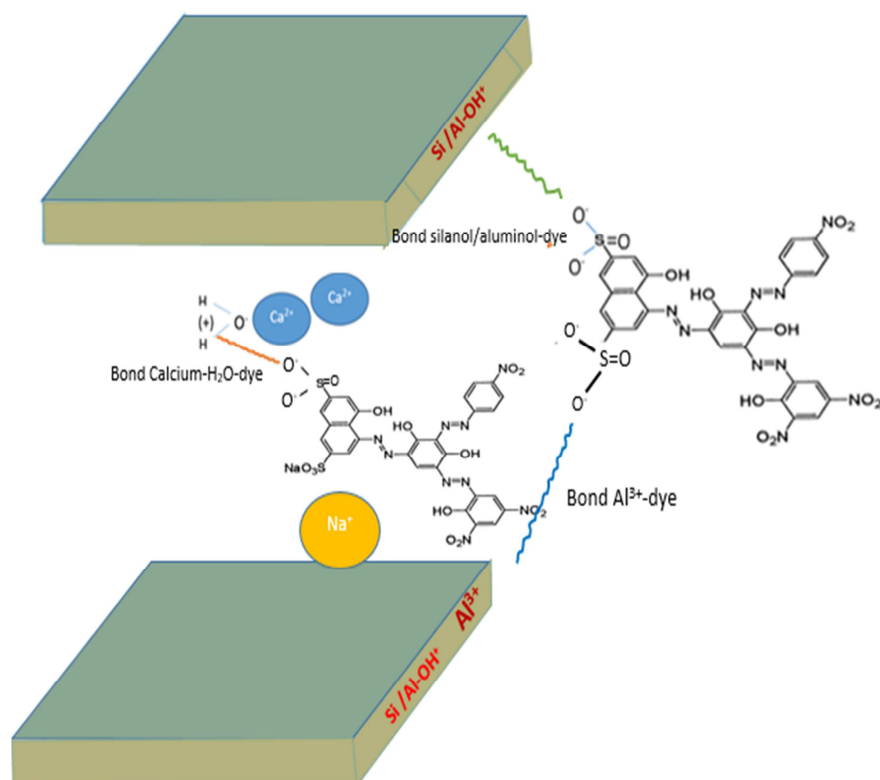
organic compounds [14].

Figure 5. *Adsorption of acid brown 75 onto smectite sheet.*

b. Influence of Contact Time

Figure 6 shows the residual dye concentration versus contact time. The results indicate that the contact time needed to reach the adsorption equilibrium of AB75 on clay sample is approximately 40 min. Therefore, the chosen contact time of 2 h, used in our experiments, is more than sufficient to reach equilibrium. As shown in Figure 5 the rate of adsorption of the dye was initially rapid, and then gradually slowed until it reached an equilibrium; once equilibrium was reached, there was no significant increase in the dye removal. This observation can be explained by the fact that the adsorption rate is fast at the beginning, because the dye is adsorbed by the exterior surface of the clay sample. When the exterior adsorption surface reaches saturation, the dye enters into the pores of the adsorbent and is adsorbed by the interior surface of the particles.
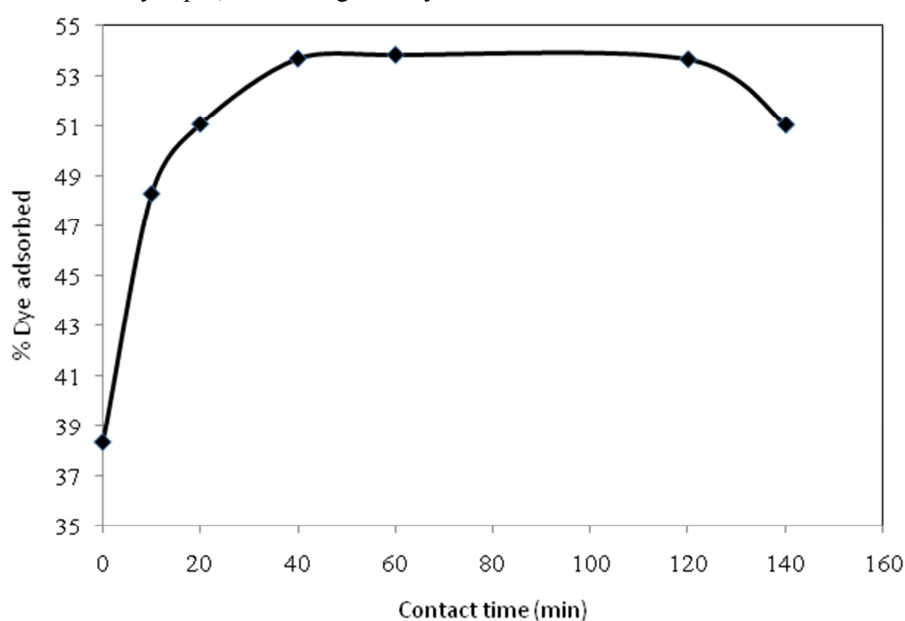

Figure 6. *Effect of contact time.*

3.3.2. Removal of Organic Matter by Clay

The results (Figure 7) show the removal efficiency of the organic matter by the Khledia clay. The COD and BOD$_5$ values decrease after adsorption with reduction rates equal to 48 and 26%, respectively. The decrease in organic matter is explained by the fact that the latter acts as a complexing agent (ligands) by adsorbing on the clay surface via the metal ion according to the following reaction [15, 16].

$$S\text{-}OH + Me^{z+} + Lig \rightarrow S\text{-}OMe - Lig^{(z-2)} + H^+ \qquad (3)$$
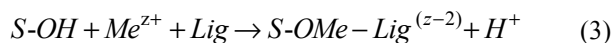
Where S: silanol or aluminol groups at the edge of clay layer, Lig: ligand and Me: metal.

The removal efficiency of smectitic clay remained slightly lower compared to maximum sorption capacities of bentonite and Fouchana Tunisian clay reported in previous studies [17, 18].
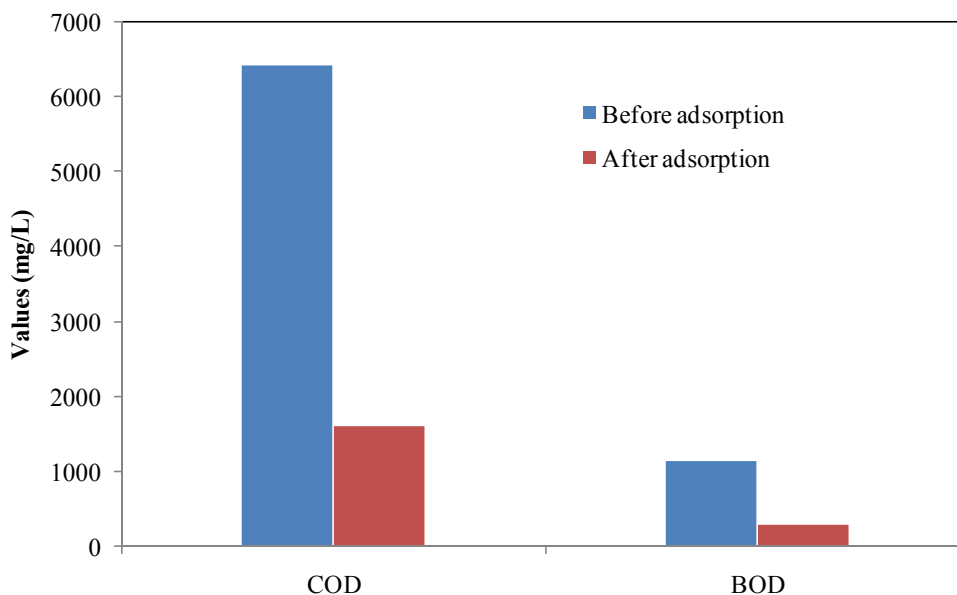

Figure 7. *Efficiency of Removal of organic matter by clay.*

3.3.3. Removal of Heavy Metals by Clay

The atomic dosage of the effluent indicates the presence of heavy metals (Cr, Cd, Fe, Pb, Zn, Cu) of variable grades which show a decrease after contact with clay (Figure 8). This could be explained by the reaction cited above.
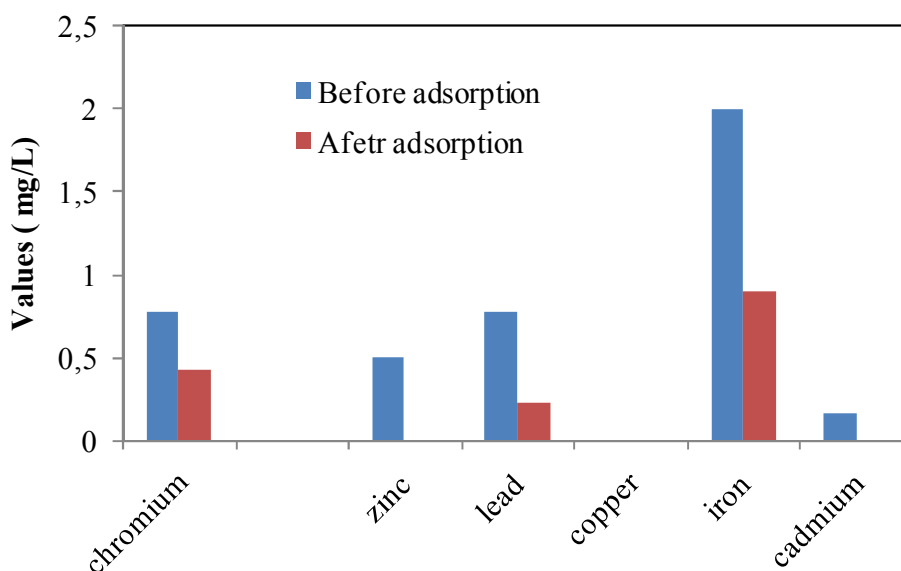

Figure 8. *Efficiency of Removal of heavy metals by clay.*

4. Conclusion

In this work, the adsorption of the dye Acid Brown 75 (AB75), present in wastewater tannery, by AS, was evaluated. The treatment of wastewater tannery with clay material was found to be effective for the reduction of dye and some physicochemical parameters.

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