

Adsorptive Removal of Chemical Oxygen Demand from Tannery Wastewater using Industrial By-Products “Blast Furnace Slag”

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Abstract

The characterization of tannery wastewater by analysis of physicochemical parameters showed a high pollution load expressed as a chemical oxygen demand, biological oxygen demand, turbidity, chromium and others. The treatment of these waters is required. The objective of this study is the removal of chemical oxygen demand from this effluent using the adsorption process on the blast furnace slag. The adsorption tests gave a removal rate around 69% with 0.2 g of blast furnaces slag for 25 minutes of contact time. The study of the influence of temperature and pH showed that at room temperature ($T = 20$ °C) and basic medium, optimal adsorption of pollutant is reached and it follows the Langmuir model. The adsorption kinetics is fast and it is pseudo-second-order type.

Keywords: Adsorption, Blast furnace slag, chemical oxygen demand, Tannery wastewater

Résumé:

La caractérisation des eaux usées de la tannerie par analyse de certains paramètres physico-chimiques a montré une charge de pollution élevée exprimée en demande chimique en oxygène, demande biologique en oxygène, turbidité, chrome et autres. Donc le traitement de ces eaux s'impose. L'objectif de cette étude est de l'élimination de la demande chimique en oxygène de cet effluent liquide par le procédé d'adsorption sur le laitier de haut fourneau. Les essais d'adsorption ont donné un taux d'élimination d'environ 69% en utilisant 0,2 g d'adsorbant pendant 25 minutes de temps de contact. L'étude de l'influence de la température et du pH du milieu a montré qu'à température ambiante ($T = 20$ °C) et un milieu basique ($pH = 12$), une adsorption optimale du polluant est atteinte et elle suit le modèle de Langmuir. La cinétique d'adsorption est rapide et de type pseudo-second ordre.

Mots clés: Adsorption, laitier de haut fourneau, demande chimique en oxygène, eaux usées de tannerie

INTRODUCTION

The tanning industry is considered to be a major source of pollution producing noxious gases, such as hydrogen sulfide, as well as wastewater and solid wastes, which negatively affect ecosystems [1].

Leather manufacturing transforms raw skins into stable and finished leather products by means of four distinct processing units: (1) Hide and skin storage and beam house operations, (2) tanyard operations, (3) post-tanning operations and (4) finishing operations.

In each of these operations, large amounts of water and chemical additives are used giving rise to characteristic pollutant loads. Water consumption is generally highest in

the pretanning stages (15 - 22 L of water per kg of hide processed), but significant amounts of water are also consumed in the tanning and post-tanning processes, e.g. 1-2 and 2 - 4 L per kg of hide processed, respectively [2].

The wastewater generated is characterized by a high chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS), total suspended solids (TSS), chromium (III) and phenolics with high pH, strong odor and dark brown color [3-5]. Organic and other ingredients are responsible for high BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) values and represent an immense pollution load, causing technical problems.

Thus, treatment of tannery wastewater is always required. It is an obligatory process that sanitizes leather effluents in order to avoid degradation of the receiving terrestrial and aquatic systems in the vicinity of the discharge points [6].

To remove part of the organic load, biological processes are usually used, because they are more economic than chemical processes. However, due to the high organic load, toxicity or presence of biorecalcitrant compounds, biological processes cannot be used, since no chemical oxygen demand (COD) removal is achieved biologically. For these wastewaters, the biochemical oxygen demand (BOD) is orders of magnitude lower than the COD. Thus a biological treatment is not feasible. In these cases, physico-chemical pretreatment can adequately reduce the COD prior to biological treatment [7]. Among these are coagulation, flocculation, ozonation, reverse osmosis, ion exchange, and adsorption.

Adsorption on activated carbon has been a useful and effective process for the purification of industrial and hazardous wastewaters, as well as for the removal of organic pollutants from water [8].

However, due to high cost of activated carbon, generally used as an adsorbent, the possibility of using inexpensive materials as alternatives was explored by many researchers in the past years [9].

The development of low-cost adsorbents has led to the rapid growth of research interests in this field.

The current study evaluated adsorption efficiency by removal of chemical oxygen demand from tannery wastewater on the blast furnace slag.

The ferrous metallurgy generates annually huge quantities of waste materials. Among these, the blast furnace slag has the greatest relative share, about 25-30% of the amount of the produced pig iron [10].

The blast furnace slag is non metallic product, accompanying the production of pig iron in blast furnaces. It is used as adsorbent for purification of water, containing heavy metal ions [11-17], phosphates and organic contaminants [18-22]. The polymineral composition of the slag has a key importance for the adsorption processes [23].

MATERIALS AND METHODS

Sampling Method of Wastewater

The main collector tannery output is selected as the sampling point. It is the meeting place of all rejects including river workshops, tanning and retanning. Sampling was performed manually using a bucket with a depth of meshing of about 1.5m. The sample is stored in containers in a dark and cool place at 4°C to avoid chemical modification.

Analysis Methods

All parameters of tannery wastewater were analyzed in the laboratory as soon as

possible in accordance with conservation rules and standardized analysis procedures [24, 25]. The pH of the solution was measured using a pH meter (HANNA HI 9812-5). The turbidity was evaluated by a turbidimeter (HANNA HI 88713-ISO Turbidimeter). The conductivity was determined by a conductivity-meter (ISO Method HACH 7027). The analysis of chromium content was realized by atomic absorption spectroscopy (AA spectrometer SOLAAR Thermo Elemental). Chlorides were analyzed by Mohr method (Rodier 1996). The analysis of biological oxygen demand for five days (BOD₅) was performed according to the experimental protocols of the French standard [24]. The chemical oxygen demand (COD) analysis was achieved via the experimental protocols of ISO 6060-1989 standard.

Slag characterization

Slag used in this study comes from the blast furnaces of the metallurgical complex of El-Hadjar (eastern Algeria).

The sample was placed in the oven immediately after collection to dry for 24 hours at 105°C, then crushed to about 0,5mm.

The characterization of the blast furnace slag sample required the use of several analytical methods: X-ray diffraction (XRD) analysis, X-ray fluorescence (XF) and scanning electron microscopy (SEM). The surface area is determined by the BET method, using the Micromeritics ASAP 2010 type apparatus.

Adsorption test of chemical oxygen demand from tannery wastewater

The determination of removal efficiency of chemical oxygen demand on used slag necessitates previous optimization of two key parameters: the mass of the adsorbent and the contact time.

To do this, various masses of slag (0.2, 0.4, 0.6, 0.8 and 1g) are mixed with 50 mL of tannery wastewater solution in a series of erlenmeyer flasks with a capacity of 250 mL. After stirring at 1 hour of contact time, maintained at a constant temperature in a water bath (Memmert), the samples are filtered and then the residual concentration of chemical oxygen demand is measured via the experimental protocols of ISO 6060-1989 standard. The calculation of COD removal rate, expressed as a percentage, is based on the following formula:

$$T = \frac{(CI - CF)}{CI} 100 \quad (1)$$

T(%): Removal rate of COD

C_I: initial concentration of COD (mg/L)

C_F: final concentration of COD (mg/L)

The effect of the contact time (5, 10, 15, 20, 25, 30, 60 minutes and 0.2 g of slag), temperature (20, 30, 50, 60°C; 0.2g of slag and 1 hour of contact time), the medium pH (2, 4, 7, 10, 12) and the initial concentration of COD (1 hour of contact time, and 0.2g of slag) has been studied.

The adsorption capacity of slag is calculated using the expression:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Q_e: the adsorption capacity, at equilibrium, of COD per unit mass of the adsorbent (mg/g),

C₀: the initial COD concentration (mg/L),

C_e: the concentration at equilibrium (mg/L),

m: the mass of adsorbent (g),

V: the solution volume (L).

In order to investigate the adsorption mechanism, the Langmuir [26] and Freundlich [27] models were used to fit COD adsorption isotherm data onto slag. The linearized Langmuir adsorption isotherm equation, which is valid for monolayer sorption onto a surface with finite number of identical sites, and Freundlich adsorption isotherm equation, which adopts multilayer adsorption on heterogeneous surfaces are, as follow:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \quad (3)$$

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

Q_e: adsorption capacity, at equilibrium, of solute per gramme of adsorbent (mg/g);

C_e: concentration of solute at equilibrium (mg/L);

Q_m: maximum adsorption capacity of Langmuir (mg/g);

b: Langmuir constant (L/mg);

K_f and n: empirique constants of Freundlich (the capacity and the intensity of adsorption).

RESULTS AND DISCUSSION

Characterization of the studied tannery wastewater

In order to evaluate the pollution degree of any kind of wastewater (domestic, agriculture or industrial) on the aquatic organism and the environment, it is important to determine the physicochemical parameters of each wastewater depending on water nature and its uses. Among these parameters, and for tannery wastewater case, the chromium, turbidity, BOD₅ and COD are essential to assess the degree of pollution. Table 1 shows the physicochemical analysis of the studied tannery wastewater. It demonstrates a comparison between the obtained values of this wastewater with the Algerian national standards defining the values limits of industrial effluent liquids discharges [28]. From this table, it is clear that some values such as turbidity (2179 NTU), chromium concentration (20 mg/L), BOD₅ (1214 mg/L) and COD (2247 mg/L) are exceeded the Algerian standards.

In view of these results, it is worth to note that this tannery wastewater has mineral and organic nature. Thereby, the biodegradation of these matters causes oxygen consumption so a possible eutrophication of the receiving environment with a deterioration of the fauna and flora and the creation of harmful resistant species can take place.

In addition, due to continuous rinsing techniques and the direct recycling of baths of pelannage and tanning, it results a wastewater contains mainly a high load of soluble proteins extracted from skins and excess chemicals. All these observations make sure that this wastewater must be treated before being discharged into the environment.

So as we said earlier, the objective of this study is the removal of COD of tannery wastewater by adsorption on blast furnaces slag.

Tableau 1: Physicochemical characteristics of the tannery wastewater

Parameters	Values	Algerian standards of industrial tannery wastewaters
Temperature (°C)	25	30
Color	Dark gray	Colorless
pH	6.98	6.5-8.5
Conductivity (ms/cm)	8.30	-
Turbidity (NTU)	1356	-
Chlorides (mg/L)	1750	1200
CDO (mg/L)	4900	130
BDO ₅ (mg/L)	593	40
Chromium (mg/L)	12.57	3

Characterization of blast furnace slag

The knowledge of the physicochemical characteristics of the adsorbents is necessary for the understanding of many phenomena such as adsorption, desorption, ion exchange and others. Table 2 represents the chemical composition of the major elements determined by the X-ray fluorescence. The results obtained show that the blast furnace slag consists mainly of Fe₂O₃ (95.84%).

Table 2: Elemental chemical composition of blast furnace slag

Element	Fe ₂ O ₃	CaO	CeO ₂	V ₂ O ₅	Na ₂ O	Al ₂ O ₃	MnO	Cr ₂ O ₃	CuO	BaO	TiO ₂	MgO
Percentage	95.84	0.39	0.13	0.05	0.87	0.67	0.2	0.14	0.12	0.09	0.08	0.02

X-ray diffractometry analysis (Fig. 1) revealed that the sample consists of the following phases:

- Hematite Fe₂O₃
- Magnetite Fe₃O₄
- Gypsum Ca S O₄
- Plustite Fe O

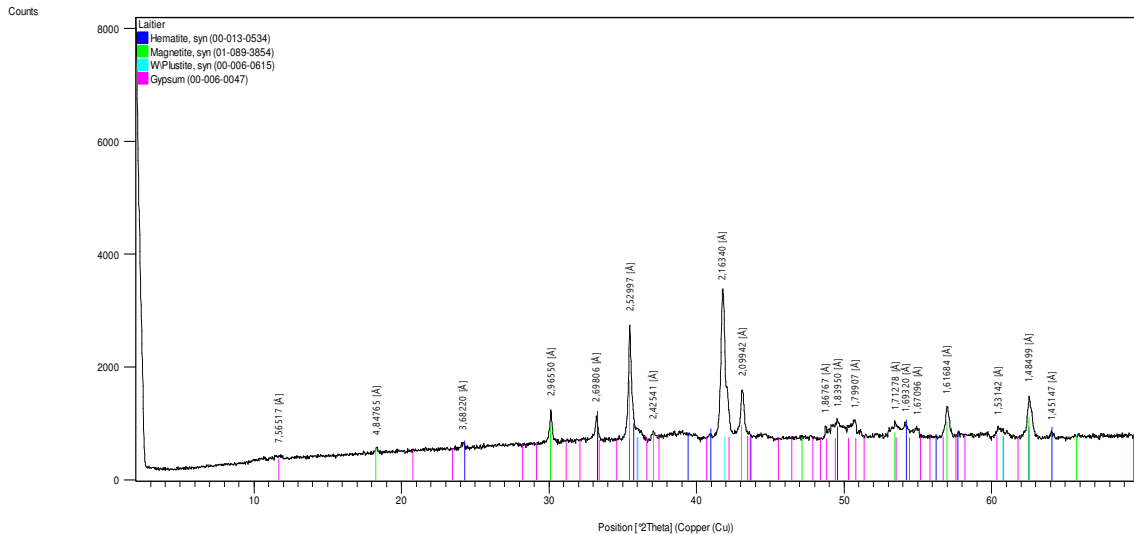


Fig. 1. Diffractogram X-ray of slag

The scanning electron microscope observations were made to visualize the texture of the adsorbent. Fig. 2 shows particles of irregular shapes at different sizes, which shows the low crystallinity of the slag.

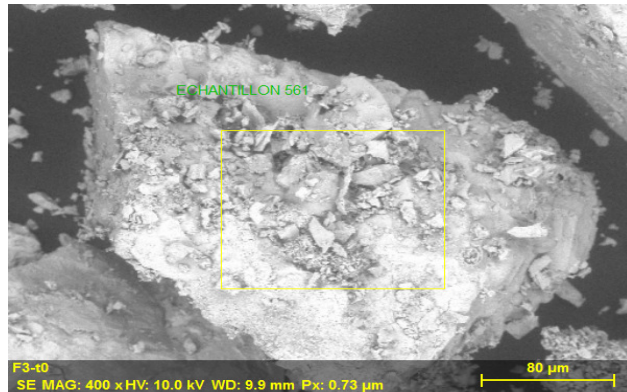


Fig. 2. Slag observation by scanning microscopy coupled with EDX microanalysis

Figure 3 shows the EDAX spectra of the slag; the presence of atomic iron in large percentage (85%), plus the presence of carbon (4.61%), oxygen (2.49%), aluminum (1.67%), calcium (0.54%) and silicon (0.51%).

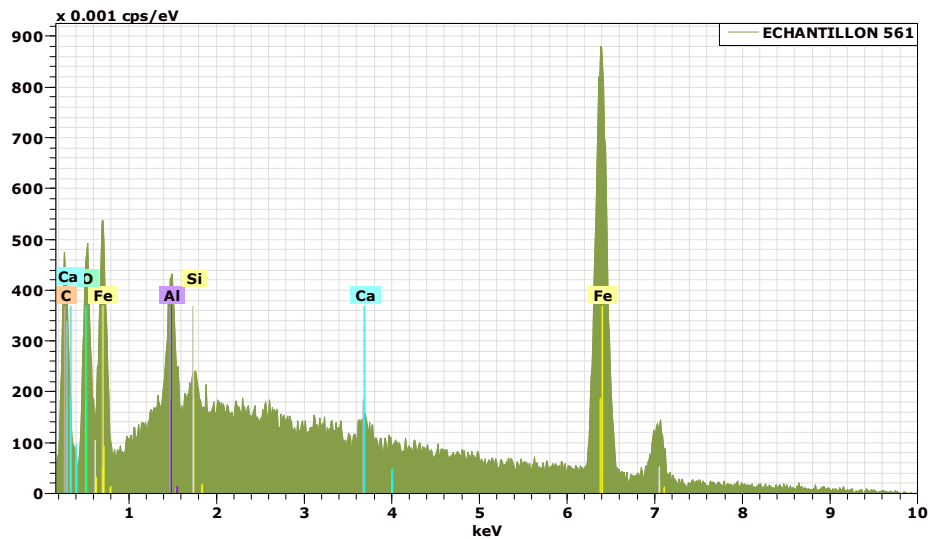


Fig. 3. Analysis of the mineral composition of slag by MEB-EDX

The surface area of slag is 21.54 m²/g, this value is comparable to those found by some authors. Mihailova et al. [23] showed that the specific surface area of slag is 19.3m²/g.

Result of the influence of the adsorbent mass on the adsorption of chromium

Fig. 4, representing the influence of the mass of blast furnace slag on the removal of COD from tannery wastewater, indicates that the optimum performance is achieved with a mass of adsorbent equals to 0.2g (the removal rate is 69%), beyond that mass, percentage of COD removal remains constant.

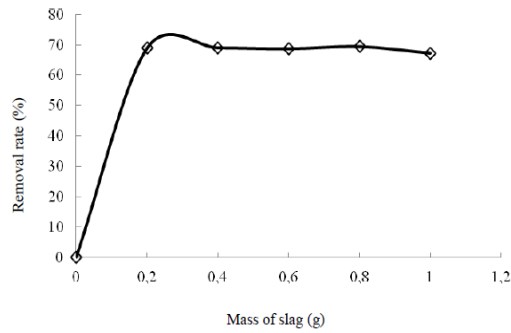


Fig. 4. Influence of the adsorbent mass on the removal of COD on slag

Influence of the adsorption kinetics

Fig. 5 shows that the pseudo equilibrium is reached after 25 minutes of contact. The shape of the kinetic curve possesses two parts. The first shows the exponential adsorption after 25 minutes, while the second part is stationary platen with slower adsorption to saturation of slag.

Nur-E-Alam et al. [29] found an adsorption equilibrium time for COD on Spent Tea Leaves of 60 minutes

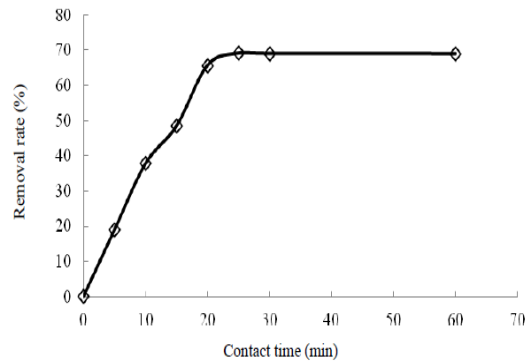


Fig. 5. Adsorption kinetic of COD on slag

Determination of kinetic model

In the order to investigate the mechanism of adsorption kinetics of COD onto anthracite, the kinetics models pseudo-first order [30] and pseudo-second order [31] were applied to the experimental data.

The linearized form of these models are respectively :

$$\ln(q_e - q) = -K_{Lag}t + \ln q_e \quad (4)$$

$$\frac{t}{q} = \frac{1}{K_b q_e^2} + \frac{t}{q_e} \quad (5)$$

q_e and q : quantities of COD adsorbed by the slag in equilibrium time and at time t (mg/g).

K_{lag} and K_b : adsorption constants (g/mg/min).

According to Fig. 6 and 7, the plot of t/q versus t for pseudo-second order model yields very good straight lines (correlation coefficient $R^2 > 0.999$) as compared to the plot of pseudo-first-order ($R^2 = 0.964$). Hence, the pseudo-second order kinetic model seems to be best fitted for the experiment with rate constant K_b equals 1.006 g/mg/min. Consequently, the adsorption reaction may be seen as diffusion controlled. In this context, it is extra-particle transfer material (transfer of material from the liquid phase towards the outer surface of the particles, step may be neglected due to the stirring of the sample), the intraparticle transfer under the influence of a concentration gradient of the material from the outer surface of the particles to the active sites and pores, and finally the adsorption reaction itself [32].

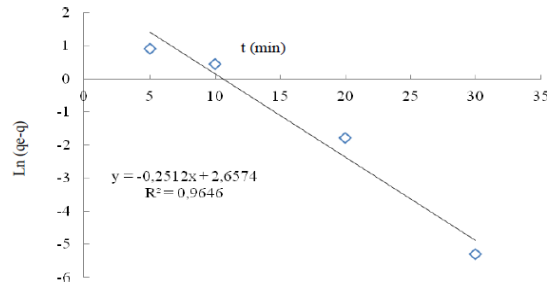


Fig. 6. Representation of the kinetic model of the pseudo first order adsorption of COD on slag

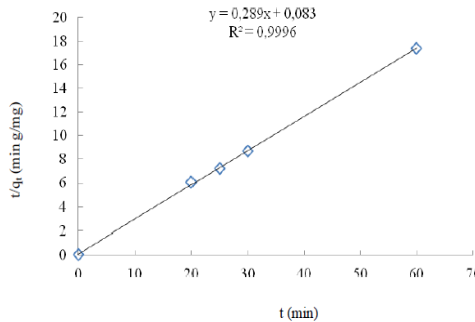


Fig. 7. Representation of the kinetic model of the pseudo second order adsorption of COD on slag

Effect of temperature

Measurements of the performance of removing of COD at different temperatures (20, 30, 50 and 60°C) yields the results illustrated in Fig. 8. At 20°C, the reduction rate of the concentration of the COD on the slag is 69%. The increase in sample temperature at 30, 50 and 60°C reduces the effectiveness of treatment. At 60 °C, the removal rate was reduced by about 60% compared with the test at 20°C. Thus, the increase in temperature reduces considerably the stability of bonds between the active sites of slag and adsorbate.

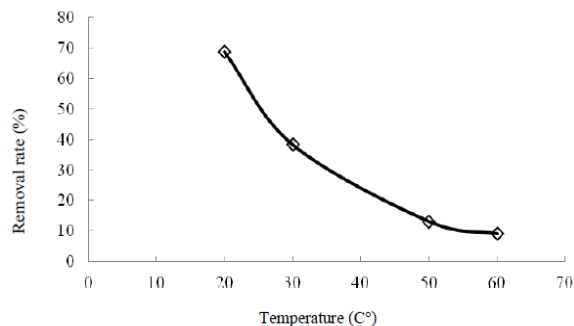


Fig. 8. Influence of temperature on removal of COD

Effect of the pH

pH is an important parameter to consider as it affects the solubility and charge of the surface of the adsorbent. The results shown in Fig. 9, concerning the adsorption efficiency of COD as a function of pH, shows that the COD abatement rate is high when the pH of the medium increases. The yield reaches its maximum (83%) at a basic pH equal to 12. The reason for the better adsorption observed at higher pH attributed to the co-precipitation of the organic matters and the other chemicals responsible for COD with the colloidal $\text{Cr}(\text{OH})_3$. At comparatively lower pH, formation of $\text{Cr}(\text{OH})_3$ was not sufficient and hence not suitable for coagulation [33].

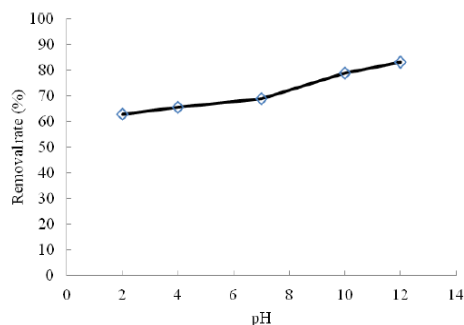


Fig. 9. Influence of pH on the removal rate of COD

Modeling of the adsorption equilibrium

The sorbed concentration depending on the initial concentration of the pollutant is shown in Fig. 10 which indicates that the adsorption capacity of the COD is not significant at low concentrations. As the concentration increases, the adsorbed amount increases greatly.

Referring to the classification of Giles *et al.* [34], this corresponds to the isotherm type L.

In this type of adsorption isotherm, the initial part informs about the availability of active sites for the adsorbate and the bearing means forming a monolayer. The curve indicates that a large amount of organic matter adsorbed at low concentrations when active sites are available. When the concentration increases, it becomes increasingly difficult to pollutant to find vacant sites to set which promotes forming a monolayer.

The experimental adsorption data were evaluated by means of the Langmuir and Freundlich adsorption isotherm presented in Fig. 11 and 12. The different characteristic

constants of these two isotherms and that of the correlation coefficients are grouped in table 3.

The correlation coefficient is higher in Langmuir than in the Freundlich model, so the adsorption equilibrium is described better by the first one. This may be explained by the continuous distribution of adsorption sites and also by the presence of unsaturated sites.

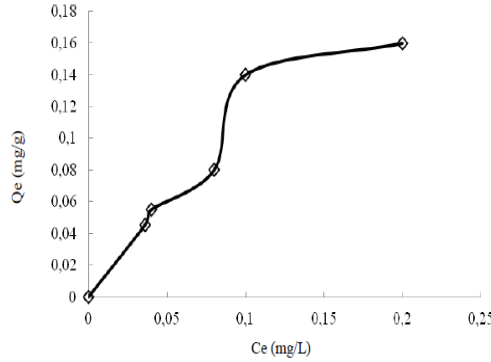


Fig. 10. Adsorption isotherm of COD on slag

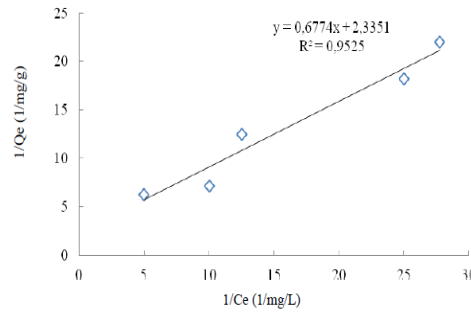


Fig. 11. Isotherm adsorption modeling of COD on slag according to Langmuir equation

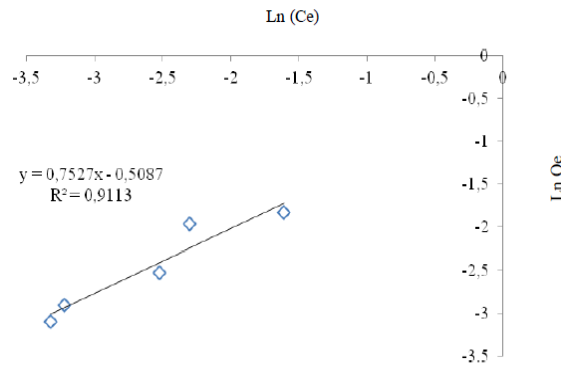


Fig. 12. Isotherm adsorption modeling of COD on slag according to Freundlich equation

Table 3 : Values of characteristics constant of the two adsorption models

<i>Langmuir isotherm</i>			<i>Freundlich isotherm</i>		
<i>Q_m (mg/g)</i>	<i>b (L/mg)</i>	<i>R²</i>	<i>k_f</i>	<i>n</i>	<i>R²</i>
0.43	3.44	0.9525	0.60	1.32	0.9113

CONCLUSION

The physicochemical analysis of the studied tannery wastewater indicates that Algerian standards defining the limits of discharges of industrial liquid effluents are often exceeded for many parameters (chromium, turbidity, organic matter, etc.), so treatment of these waters is imposed.

In a second time, we proceeded to the characterization of a blast furnace slag by implementing different methods of specific analyzes.

The study proved that our adsorbent consists mainly of Fe₂O₃ (95.84%). The X-ray diffractometry analysis revealed the presence of the following phases: Hematite, Magnetite, Gypsum and Plustite with the surface area of 21.54 m²/g, which gives it good adsorption properties.

The objective of our work is to removal of chemical oxygen demand from tannery wastewater by the adsorption process on blast furnace slag.

The study of adsorption tests allows us to achieve the following results:

- The equilibrium time is fast, it is reached after 25 minutes, with 0.2g of adsorbent and the kinetic is pseudo-second-order type.
- The increase of the medium temperature and acidic pH causes a decrease in the efficiency of the removal of COD.
- The adsorption isotherms could be well fitted by the Langmuir isotherm

Finally, we can say that the treatment process selected in this work, gives a very acceptable removal efficiency of organic matter. The improved results obtained by the use of other conditions, is possible to get the most of this industrial by-products.

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