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Study of the Impacts of the Malam Yaro Tannery on Environmental Components in the City of Zinder (Niger) and Application of Activated Carbon Produced for the Elimination of Chrome in Wastewater

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ABSTRACT:

This work presents a study of the impacts of the Malam Yaro (MY) tannery on the environmental components in the city of Zinder (Niger) and the application of Elaborated Activated Carbon (EACs) for the elimination of chromium in its wastewater. The EACs used come from the recovery of local agro-food waste. A survey containing 44 questionnaires was conducted at the level of the said company. Sampling of wastewater was carried out under the conditions described by Jean Rodier et al., in Water Analysis (9th edition). The activated carbons developed were used for the removal of chromium and the retention of the material biodegradable or not in wastewater. The results show that the tannery has a workforce of 29 employees and the treatment of the skins involves the following main steps : re-greening or tempering, peeling, fleshing, candying, pickling and tanning. The MY Tannery did not have a service responsible for environmental hygiene. The chromium removal rate results on EACs and CAC vary from 72.85 to 84.28% when the pH = 2 for AC-BA-H_2SO_4-25% and AC-HT-H_3PO_4-25% respectively and from 48.57 to 48.57% when the pH = 8 for CA-ZM-H_3PO_4-25% and AC-BA-H_2SO_4-25% respectively. It should be noted that six (6) samples of EACs have chromium removal rates that exceed the CAC (pH = 2) and three (3) samples of EACs have exceeded the CAC (pH = 8). The reduction rates of the material (biodegradable or not) are greater in the weakly acidic environment (10%) regardless of the biomass considered.

Keywords: Impacts; Activated carbon; Chromium; Wastewater, Tannery.

INTRODUCTION

Discharges of toxic mineral or organic substances are the source of pollution. The latter deteriorate the quality of water and the environment. In addition, water is becoming increasingly polluted [1,2]. The discharge of these effluents constitutes a major danger for humans and ecosystems [2]. These discharges cause serious environmental problems, particularly on water quality, with significant consequences for human health and the ecological balance of the environment [3,4]. The industrial world is increasingly confronted with the problem of controlling the emissions of toxic substances into the environment, particularly in the form of liquid effluents [5]. In this regard, the leather and skin treatment techniques implemented in the industrial or semi-industrial tannery in Niger using formulations based on chromium salts, as in several industrial tanneries around the world, have contributed considerably to water pollution [6,7]. The discharge of tannery wastewater most often generates effluents that do not comply with the chromium discharge standards, set at 1 mg L^{-1} for discharge into sewers [2,8]. Currently, on a global scale, between 70 and 80 % of leather is produced by chromium tanning processes [9]. However, given the complexity of transforming animal skin into leather, tanning industries use a large number of chemical agents and consequently produce enormous volumes of wastewater [10]. This practice was carried out despite the various national laws and regulations on the protection of water and the environment that strictly govern the process of evacuation and disposal of effluents and other industrial waste, including Law No. 98-56 of December 29, 1998, establishing the framework law on environment al management, Ordinance No. 93-014 of March 2, 1993, on the water regime in Niger, Order No. 141/MSP/LCE/DGSP/DS of September 27, 2004, setting the standards for the potability of drinking water, Ordinance No. 93-13 of March 2, 1993, establishing a public hygiene code for Niger, among others [2,10]. It is therefore essential to limit this pollution as much as possible by implementing a chromium removal technique adapted to our locality (Niger). There are various methods to remove chemicals (heavy metals, dyes, phenols, etc.) from effluents. Among the methods, adsorption is the most widely used technique due to its efficiency, ease of implementation and affordable investment cost [3,6,11]. This method requires the choice of an adsorbent with good characteristics (high adsorption capacity, availability, low cost, etc.) [12,13,14,15]. For this purpose, the use of activated carbon (AC) as an adsorbent is of interest in the treatment of industrial wastewater [16,17,18,19,20,21,22]. This is why this work consists of an application of Elaborated Activated Carbons (EACs) and a Commercial Activated Carbon in the decontamination of Tannery Wastewater loaded with Chrome [23, 24,25]. These activated carbons were produced from local lignocellulosic biomasses, in particular the shells of the kernels of Balanites aegyptiaca (L.) Del. (Adoua), Hyphaene thebaica (L.) Mart. (Gorouba), Zizyphus mauritiana (L.) Lam. (Magaria) and the Balanites aegyptiaca (L.) Del. meal by chemical activation with orthophosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) [2,26, 27].

Material And Methods

Presentation of the sampling site

The sampling site is the Tannerie Malam Yaro in Zinder (Niger). It is located in the premises of the former Nigerien Leather and Skin Collection Society (NLSCS) located in the industrial zone of the city of Zinder. It was created to fill the gap left in the sector of processing leather and skins into tanned products. It is located between 13°46'46''North latitude and 9°0'13.6''East longitude with an area of 7,000 m^2 acquired from the company's own funds. It is located in the Birni (Franco) district of Zinder and limited to the East and North by various constructions of the inhabitants of the Franco district, to the West by the former millet processing company, and to the South by the Maikilago Gendarmerie and the regional livestock management of Zinder [2].

The Tannerie Malam Yaro was a limited liability company. On February 13, 1996, it was registered in the Niger commercial register under Nº. 7022 / B with a capital of twenty million CFA francs (20,000,000 FCFA) and a production capacity of 200,000 skins per year. It started its activities on February 16, 1996. After four years, an investment of about seventy-five million CFA francs (75,000,000 FCFA) allowed the modernization of the factory in 2000. From 2001, the year the tannery began to use chemicals (chromium salts, lime, etc.), production increased from 200,000 skins in 1996 to 700,000 skins per year in 2001. In 2010, it became a Public Limited Company with a capital of 50, 000,000 CFA francs (Report, 2013). Currently, the tannery processes 2,000 to 3,500 skins (goats and sheep) per day. With a huge use of chemicals, it is the only operational modern business unit for processing skins into leather in Niger [22].

Survey and interview

A survey containing 44 questionnaires was conducted at the company level, the main objective of which is to collect the data necessary for the description of the receiving component, in particular the method of supplying the hides, the conditions of processing the hides, the use of chemicals (chromium derivative), the discharge of wastewater, etc. It focused on the technicians and at their head the production manager. In addition, an interview was conducted with resource persons, in particular the manager of the tannery, to understand the tanning process.

Sampling

The sampling was carried out under the conditions described by Jean Rodier *et al.*, in Water Analysis (9th edition). Figure 1 presents the entire wastewater discharge environment of the company.

Figure 1: Wastewater from the Malam Yaro tannery in Zinder

The wastewater sample was taken in one (1) liter polyethylene bottles until it overflowed at the point of discharge into nature (Figure 2) in order to determine the physicochemical parameters of the wastewater.

Figure 2: Wastewater sampling equipment (TMY)

Determined parameters

The following parameters were determined :

- ✓ temperature (T°C) ;
- ✓ hydrogen potential (pH) ;
- ✓ dissolved oxygen ;
- ✓ oxidation-reduction potential (E_H) ;
- ✓ conductivity ;
- ✓ Kjeldahl nitrogen ;
- ✓ COD.

Chromium removal from wastewater by activated carbons

Chromium removal on CAEs and CAC was carried out as follows: in a 100 mL beaker, a mass m of 25 mg of each of the CA sample weighed using a precision balance (to 1/10000 of Precisa brand) was introduced into 25 mL of wastewater containing Chromium at 44.1 ppm. The mixture is stirred for 2 hours (h). The residual concentration of chromium in wastewater is measured using a Micro-Plasma Atomic Emission Spectroscopy (MP-AES) flame spectrophotometer. The chromium removal rate is given by equation (1) [9] :

$$R = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

Elimination of Chemical Oxygen Demand by Activated Carbons

The chemical oxygen demand is the concentration expressed in mg L^{-1} O_2 equivalent to the amount of dichromate consumed by dissolved and suspended matter. It was carried out according to the French standard (NFT 90-101). The objective of this experiment is to see the performance of activated carbons developed for the retention of matter (biodegradable or not).

This part was carried out as follows: in matras, 10 mL of the sample was introduced. Then, 5 mL of potassium dichromate solution was added. Then, 15 mL of sulfuric acid-mercury sulfate is added slowly while carefully stirring the matras. The matras are connected to the condensers and the whole is brought to boiling at reflux at 150 °C for two (2) hours. After cooling, the internal wall of the condenser was washed with distilled water, collecting the washing water in the flask. After disconnecting the condensers, the solution was transferred to a 250 mL Erlenmeyer flask. Then, the flask was rinsed to approximately 75 mL. The solution was titrated with the iron (II) sulfate and ammonium solution in the presence of 3 drops of ferroin. Blank test (distilled water) and control test (ref) were carried out in the same way. The chemical oxygen demand (COD) expressed in milligrams of oxygen per liter is given by equation (2) [2] :

$$DCO = \frac{8\,000\ C\ (V_0 - V_1)}{V} \quad (2)$$

V_0 being the volume of iron and ammonium (II) sulfate required for the blank test expressed in mL, V1 the volume of iron and ammonium (II) sulfate required for testing the sample in mL, C the titer of the iron (II) and ammonium sulfate solution in mol L^{-1} and V the volume of the test portion in mL.

Result

Survey and interview results

The processing of hides at the Malam Yaro Tannery in Zinder involves the following major stages : re-greening or quenching, liming, fleshing, batting, pickling and tanning.

Figure 3: MY Tannery dump site

Figure 4: Drainage channels of the MY Tannery

Figure 5: Dumping site for all tannery waste

Figure 6: Wastewater from the Malam Yaro Tannery in Zinder

Figure 7 shows the wastewater from the MY Tannery in Zinder after treatment.

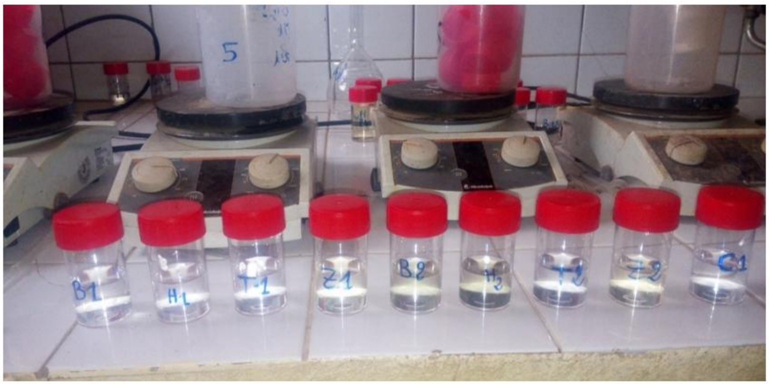

Figure 7: Wastewater from the MY Tannery after treatment

Physicochemical characteristics of the tannery wastewater

Table no 1 : Shows metabolic parameters of patients of the three groups before treatment.

Parameters	Values	WHO Standards
Temperature (T °C)	32.1	≤ 20
Potential of hydrogen (pH)	7.21	6.0 – 9.5
Dissolved oxygen (%)	101.4	-
Oxidation-reduction potential (mv)	-0.43	-
Conductivity (µs/cm)	5370	-
Kjeldahl nitrogen (mg L-1)	110.5	-
COD (mgo2 L-1)	410.0971	≤ 100

Chromium removal rates in tannery wastewater

Table I shows the Chromium removal rates in the water of the MY tannery in Zinder.

Table I: Chromium elimination rates

CAEs	pH=2	pH=8
CA-BA-H_3PO_4-25%	80.71	65.00
CA-BA-H_2SO_4-25%	72.85	66.07
CA-HT-H_3PO_4-25%	84.28	65.35
CA-HT-H_2SO_4-25%	73.57	64.28
CA-TB-H_3PO_4-25%	83.21	64.28
CA-TB-H_2SO_4-25%	82.50	63.57
CA-ZM-H_3PO_4-25%	77.85	48.57
CA-ZM-H_2SO_4-25%	75.00	64.28
CAC	73.57	64.28

(m_{CA} = 25 mg ; V = 25 mL ; $[Cr]_0$ = 44,1 ppm ; t = 2h)

Rate of retention of the material (biodegradable or not)

Figure 8 shows the COD removal rates on H_3PO_4 EACs (10 and 40 %) in the wastewater from the MY tannery in Zinder.

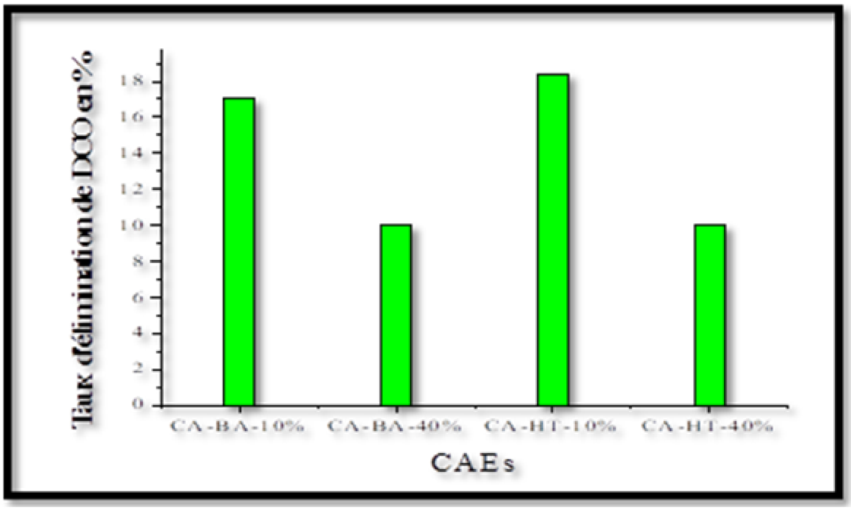

Figure 8: COD reduction rate

(m_{CA} = 100 mg ; V = 50 mL ; 50 mg de O_2)

Discussion

With a workforce of 29 agents, the Tannerie Malam Yaro of Zinder has the capacity to process about 5 tons of skins (goats and sheep) per day. It collects fresh skins from different regions of Niger through trucks. Their supply method undergoes a preservation treatment using salt to prevent bacterial development. The skins are sorted and the non-manufacturable and non-marketable parts (long legs, testicles, udders and poorly opened necks) are eliminated using a knife before re-greening or soaking. They use enzymes (acid hydralase or acid phosphatase) as additives. The degradation of non-collagenic proteins is carried out by the formation of a semi-solid colloidal gel. The keratinous materials (hair, hair roots, epidermis) and fats of the skins are eliminated by a combination of chemical and mechanical treatment. They use sodium sulfite for 30 min to destroy the hair and polymel ECO for 60 min to break the hair roots inside the hides in order to facilitate the hair pulling. For this treatment, they also use lime, Alysol, salt-Sodha ASH. Excess organic matter (connective tissue and fat) is removed using Alysol-NOF limelux. For batting, the hides are put in the fulling mill using meta bisulfite, Alysol-NOF detergent, P.L.V. or ammonium sulfate at a temperature of 35 °C. To lower the pH, ammonium sulfate, metabusulphite and formic acid are used. An aqueous medium with an organic solvent (Alysol), non-ionic surfactants and degreasing agents are used for degreasing. The pre-tanning process used is Wet-blue. Aluminum salts and syntans (tannins) are used as pre-tanning agents. Tannins are synthesized using H_2SO_4. For tanning hides, the tannery uses a modern method. It is interested in this method because it improves the quality of hides and profitability. A combination of chemicals is used for

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tanning namely chrome, sodium formate, sodium bicarbonate and aducid. After tanning, the hides are rinsed and wrung out. Then, they are bagged and exported to Bangladesh for bri-entage. Finally, they are exported to Italy for finishing (shoes, clothes, car seat shirts, etc.). It should be noted that the tannery activities consume about 55 m3 of water per day. MY Tannery produces waste and wastewater but it does not have a treatment plant for the treatment of this wastewater.

The MY Tannery did not have any service responsible for environmental hygiene. This industrial unit, which produced a lot of waste and a large volume of wastewater, used to dump them just around the site. But with the advancement of the city, the Zinder town hall has authorized them to dump all their waste at the old lateritic quarry about five (5) km on the road to Mirriah, since 2009 (Figure 3). The site has undergone redevelopment by building dikes and compartments to prevent the flow of chrome water into nature, especially since the site is surrounded by millet and peanut fields. An employee is responsible for the evacuation of wastewater and solid waste to the receiving environment. Every day, a drainer with a capacity of 11,000 liters makes up to eight (8) rounds. This wastewater is evacuated to the quarry without any prior treatment. In addition, the drainer discharged wastewater throughout the journey. Every week, the flesh from the fleshing and the manually cleaned sludge are evacuated. The packaging is thrown away. The cans, barrels and other containers are collected and used by the employees. Similarly, the quarry is not fenced and has not undergone waterproofing treatment. However, to slightly reduce the bad odors, a perfumed detergent Alysol NOF is used at each stage of production (from re-greening to tanning), then at the level of the settling basins, the used oils, the sleet and the perfumed mineral essences are spread on the surface of the wastewater. As for the pieces of raw hides, after three (3) to four (4) days of drying, they are put in bags to be sold in Nigeria.

The storage and drying of raw hides and pieces from the scraps of these hides on the one hand and the mixing of waste water with hair and flesh on the other hand cause steam emissions and foul odors. In addition, the waste water drainage channels and basins are open (Figure 4). This could cause the release of toxic gases likely to pollute the air.

Soil pollution is believed to be due to the daily discharge of raw waste water containing chemicals and hair on the route and at the quarry level. It is also believed to be due to the storage of solid waste (sludge, packaging, flesh), the storage of hides and chemicals without a retention system. The decomposition of solid waste at the landfill and the discharge of sludge from the settling basins are parameters that contribute to soil pollution (Figure 5). These constitute a potential source of soil pollution that is likely to induce salinization, loss of plant cover and modification of the texture and structure of the soils concerned.

The production and accumulation of large quantities of solid waste in the dumping area has led to the alteration of the landscape and affects hygiene and sanitation in times of strong winds. In addition, the spreading and drainage of wastewater has caused the proliferation of invasive species such as Prosopis juliflora (Sw.) Dc. (Bayahonde) around the Tannery and the dumping site. The Tannery is known for the nauseating odors it releases, constituting olfactory nuisances. Employees are not at all aware of the environmental and health risks associated with their activities, they handled chemicals without PPE and in addition the products did not have a safety data sheet or handling procedures. The cleaning of the basins was done manually with buckets and the workers only wore giants and boots. Indeed, skin or eye contact with chemicals can cause irritation of sensitive organs and respiratory, pulmonary or skin diseases. Also, at the level of the chemical storage warehouse, the ventilation system is insufficient. This risks causing employees infections by inhalation of gases, dermatitis, digestive disorders or excess of certain products in the blood. The noises and nauseating odors cause headaches and sore eyes; these odors affect workers and local populations.

Tanning activities (collection and processing of skins) generate income at the tannery and contribute to the development of income-generating activities (IGAs), in particular the sale of donuts, cola, cigarettes for local populations. They create jobs for young people and increase the State's tax revenues through taxes and duties. The Tannery consumes significant quantities of drinking water, leading to the production and discharge of large volumes of wastewater into the natural environment without any treatment (Figure 6). At this level, pollution could be due to the discharge of chemical substances (chromium) contained in the wastewater, which can run off under the effect of heavy rains and reach waterways. This could lead to a decrease in oxygen levels, poisoning and disruption of aquatic ecosystems (death of living organisms). It could contaminate the human body through the food chain and groundwater through the phenomenon of infiltration.

The results of chromium removal rates on CAEs and CAC vary from 72.85 to 84.28% when pH = 2 for CA-BA-H_2SO_4-25% and CA-HT-H_3PO_4-25% respectively and from 48.57 to 48.57% when pH = 8 for CA-ZM-H_3PO_4-25% and CA-BA-H_2SO_4-25%. It should be noted that six (6) CAE samples have chromium removal rates that exceed the CAC (pH = 2) and three (3) CAE samples exceeded the CAC (pH = 8).

The COD reduction rates are higher in the weakly acidic environment (10%) regardless of the biomass considered.

Conclusion

A study of the impacts of the Malam Yaro tannery on environmental components in the city of Zinder (Niger) was carried out. At the end of this study, we can retain the following information :

- ✓ the tannery has a workforce of 29 agents ;
- ✓ the processing of hides involves the following major stages: regreening or quenching, liming, fleshing, batting, pickling and tanning ;
- ✓ the MY Tannery did not have any department responsible for environmental hygiene ;
- ✓ The chromium removal rates on CAEs and CAC vary from 72.85 to 84.28% when pH = 2 for CA-BA-H_2SO_4-25% and CA-HT-H_3PO_4-25% respectively and from 48.57 to 48.57% when pH = 8 for CA-ZM-H_3PO_4-25% and CA-BA-H_2SO_4-25% respectively ;
- ✓ Six (6) Elabored Activated Carbon samples have chromium removal rates that exceed the CAC (pH = 2) and three (3) CAE samples exceeded the CAC (pH = 8) ;
- ✓ The material removal rates (biodegradable or not) are higher in the weakly acidic environment (10%) regardless of the biomass considered.

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