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Application of solid hide waste as an adsorbent for the treatment of industrial wastewater

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ABSTRACT

The adsorption process is an effective method for wastewater treatment for the removal of various types of pollutants. Numerous agro-industrial and domestic waste products have been used to create affordable adsorbents. Waste materials can be used as inexpensive adsorbents, which is appealing because it lowers the cost of waste disposal and helps to protect the environment. Therefore, this research aims to valorize the solid wastes produced during the tanning process. The accumulation of solid waste in tanneries is an environmental problem in many countries. This problem can be alleviated by optimizing the use of these pollutants. Chrome and white shavings were used (as adsorbent) for the treatment of industrial wastewater. The wastewater was collected from the chemicals and resin production factory. White shavings were pretreated before use. The functional groups located on the surface of the pretreated white shavings were investigated using the Fourier-transform infrared spectroscopy technique. The treated white shavings were ground to suitable grain size (0.5–1 mm). The treatment scheme consisted of settling (1 h), sand filtration (0.5–1.0 mm), and adsorption with the pretreated ground chrome and white shaving used for the treatment of wastewater. The influent chemical oxygen demand and biochemical oxygen demand were reduced from 8,025 to 890 and from 2,808.75 to 489.5 mg/L. The effluent met all national regulatory standards for sewer system discharge. Consequently, chrome and white shaving could be used as adsorbents for the treatment of industrial wastewater. These materials could be used as preferable adsorbents for the treatment of wastewater several times.

Keywords: Solid waste; Tanneries; White shavings; Reuse; Treatment

1. Introduction

Although millions of people worldwide struggle due to a lack of fresh, clean drinking water, water is a source of both life and energy. Recently, rapid industrialization, population expansion, and unplanned urbanization have led to the spread of water pollution all over the world with various types of hazardous pollutants such as organic compounds, dyes, heavy metals, viruses, and bacteria. Runoff from agricultural fields, industrial effluent disposal, and the discharge of untreated sanitary and toxic industrial wastes are the main causes of freshwater pollution. It is commonly known that water poisoning causes between 70% and 80% of all illnesses in impoverished nations, with women and children being especially vulnerable [1,2].

These pollutants are extremely hazardous to both humans and aquatic creatures. Most of the organic compounds that pollute the water streams are not naturally degradable because of their chemical characteristics. These compounds may bioaccumulate in the living organisms' bodies and cause catastrophic disorders such as inflammation,

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liver damage, ulcers, skin cancer, and kidney failure [3–5]. The organic pollutants are also found in abundance in industrial wastewater for some industries such as gas and oil extraction [6] and are considered toxic even if their concentrations are low [7]. The discharge of untreated wastewater into water bodies leads to the spread of diseases. Therefore, these pollutants, especially, must be removed to protect the environment and humans from their threats.

The permitted minimal concentration of these compounds is steadily dropping due to the development of more sophisticated analytical techniques and improved health monitoring systems. As a result, several nations have enacted strict rules regarding the presence of toxic chemicals in water, obliging enterprises to adequately cleanse industrial effluents before discharging them into natural water bodies that contain pure water [8].

Various treatment approaches, such as heterogeneous Fenton oxidation, have been used to remove dangerous organic materials from wastewater [9], electrocoagulation [10], photodegradation [11], etc. These technologies, however, have limitations such as high energy consumption, massive price, complex designs, and harmful by-product production. Thus, the application of these methods has become complex and impractical. Elimination of organic matter from wastewater requires ecologically safe, simple, better-performing, low-cost, and efficient treatment technologies [12].

Adsorption is an effective method for eliminating most contaminants from industrial wastewater in previous research. Although activated carbon is one of the most well-known adsorbents and is frequently utilized, it is still a costly substance [13]. Many functional groups are present on the surface of adsorbents, that facilitate both chemical and physical interaction with the pollutants in the wastewater [14]. Consequently, the sorbent retains pollutants from wastewater, and once saturated, they are activated for reuse [15].

Researchers were interested in using agricultural waste for wastewater treatment, particularly for heavy metals and organic contaminants. Sawdust [16,17], rice peel [18,19], sugar cane [20], coconut shell [20], neem bark [21], and other agricultural wastes are the most well-known. The cost of the adsorbent material depends on its local availability and the degree of treatment required. It is a low-cost resource if it is available in the environment, or if it is a by-product or waste material from another sector. The good adsorption capacity may offset the additional processing cost [22]. As a result, it is required to investigate a variety of low-cost adsorbents, particularly those derived from agricultural residues that may be used to eliminate a variety of contaminants from wastewater, which is the purpose of the current research.

2. Materials and methods

2.1. Materials

Commercial white shavings (bovine hide) were collected from Robiky Tanneries Industrial District, Egypt. The shavings were first washed many times with water by shaking in a 300% float for about 30 min. The water was drained off, and then sodium chloride (10%) was added to the floating ratio. After 15 min of contact with sodium chloride, the shavings were washed with 1% sodium formate for a further 10 min. After that, the leather pieces were washed with water for another 10 min. Some white shavings were modified or tanned by 2% BCS. Chrome shavings were ground and sieved to adjust the particle size to 2–4 mm. The ground shavings were washed five times using hot distilled water (60°C–80°C) and then dried at 50°C for 24 h. White shavings are a by-product produced from the shaving of de-haired hide during leather processing. It is removed from the flesh side of a hide until the thickness of the entire hide is precisely adjusted. The chrome shavings were obtained from the.

Commercial grade sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$), sodium formate (HCOONa), and sodium chloride (NaCl) were used. Nitric acid (HNO_3) and hydrochloric acid (HCl) were analytical-grade brought by Merck Co.

Raw industrial wastewater was collected from one of the resins, polymers, and chemicals factory, on the 6th of October City, Egypt. It produces solvent-based alkyds, acrylics, unsaturated and saturated polyesters, water-based emulsions, adhesives, and specialty chemicals.

2.2. Methods

The pH, total suspended solids (TSS), total phosphorus (TP), total Kjeldahl nitrogen (TKN), settleable solids chemical, and biological oxygen demand (COD and BOD) were all assessed using APHA guidelines [23]. The pH values of raw and treated effluents were determined using a pH/conductivity meter (WTW). LoviBond (Model RD 125), and LoviBond photometer were used for the determination of the chemical oxygen demand (COD). The Koettermann incubator was used to determine the biochemical oxygen demand (BOD). Gerhardt distillator (Model Vapodest) and digester (Model Kieldatherm) were utilized to determine total Kjeldahl nitrogen (TKN).

2.3. White shaving treatment

White shavings were cleaned many times with water before soaking in 300% liquor for 30 min. After that, sodium chloride (10% of the liquor ratio) was added and the mixture was stirred for 15 min. The pickled hide pieces were then rinsed with 1% sodium formate for another 10 min. After that, the shavings were rinsed in water for another 10 min. The debris from white shavings was ready to be used as a filter [24].

2.4. Reactions of white shavings with chrome

White shavings waste was treated with sodium carbonate to elevate pH to around 5.5, followed by 2% chrome (basic chromium sulfate). Modified white shaving created through this procedure can be applied repeatedly to the treatment of wastewater.

2.5. Fourier-transform infrared spectroscopy characterization

Tannery waste samples of white and chromated white shavings were chopped into little parts and ground in a hardened steel vial with two hardened steel balls. The vial was placed in a Spex-mixer and spun for 2 min each. To obtain fine powder without subjecting the material to high temperatures, grinding is performed numerous times in a fractionated method. Fourier-transform infrared spectroscopy (FT-IR; Type Jasco FT-IR 6100) with a resolution of 4 cm^{-1} and a wave-number range of 537 to 4,000 cm^{-1} was used to determine the functional groups of the material.

2.6. Scanning electron microscope examination

Specimens for this study were cut from the samples. To develop a conducting medium, a circular specimen with a diameter of 10 mm was coated with gold ions using a sputter coater (Edwards' model S 140A). The JEOL Model JSM-T20 scanning electron microscopy (SEM) was used to scan the sputter-coated samples.

2.7. Treatment system

The treatment system was plane sedimentation (PS), sand filter (SF), and white shavings filter (WSF). The filtration system used in this study was a sand filter (SF) and hide filter (HF). The wastewater samples were allowed to settle for 1 h. The supernatant was fed to the SF, and then the HF. The diameter of the filter (SF or WSF) was 0.1 m and a height of 0.5 m. The grain size of the sand ranged from 0.5–1.0 mm. The flow rate was 30 mL/min. Table 1 shows the operating conditions of the SF and WSF during the study.

3. Results and discussions

3.1. ATR-FT-IR

The popularity of FT-IR spectroscopy has skyrocketed, making it one of the most versatile analytical techniques available [25,26]. The solid tannery wastes examination was done using horizontal attenuated total reflection (HATR) FT-IR spectroscopy [27]. Fig. 2 shows the FT-IR spectra of de-pickled white shavings. The attenuated FT-IR/absorbance spectra of the samples in the spectral region 4,000–530 cm^{-1} are shown in Fig. 2. The –NH stretching vibration of NH_2 and the asymmetric stretching vibration of CH_2 groups were attributed to the absorption stretching bands associated with 3,195 and 2,926 cm^{-1} in the FT-IR spectra of white shavings (Fig. 1). Two bands at 1,452 and 1,337 cm^{-1} represent CH_2 bending and wagging vibrations, respectively. The C O stretching band, which is linked with COO and assigned as the amide I, can be seen at 1,650 cm^{-1} (-helix). A band at 1552 cm1 results from NH_2 bending combined with CN stretching vibration in the amide group designated as amide II. At 1,240 cm^{-1}, the amide III –NH bending appears. The two bands showing at 1,626 and 1,650 cm^{-1} were attributed to the B-form and -helices, respectively, according to Fig. 2. Finally, the skeleton stretching vibration bands occurred at 1,081 and 668 cm^{-1} [27], whereas the hydroxyl groups were assigned to the strong broad bands at 827, 3,527, and 3,475 cm^{-1}.

The chromated sample's FT-IR spectra (Fig. 3) revealed a distinct absorption band at 1,636 cm^{-1} that reflected chromium birching with carboxylate groups (–Cr–OOC–). The C–O stretching vibration of COOH, amide I, was moved from 1,650 to 1,637 cm^{-1}. The peak at 1,558 cm^{-1} (amide II),

Table 1
Operating conditions for the SF and HF

Parameter	SF	WSF
Diameter (m)	0.1	0.1
Height (m)	0.5	0.5
SLR ($m^3/m^2{\cdot}h$)	0.23	0.23
OLR ($g{\cdot}COD/m^2{\cdot}h$)	957.3	908.8

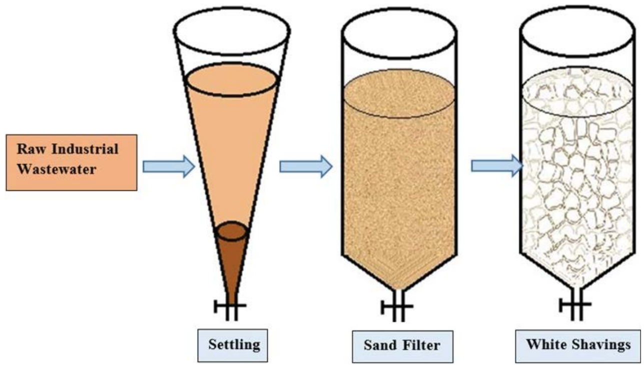

Fig. 1. Sequence of the treatment process.

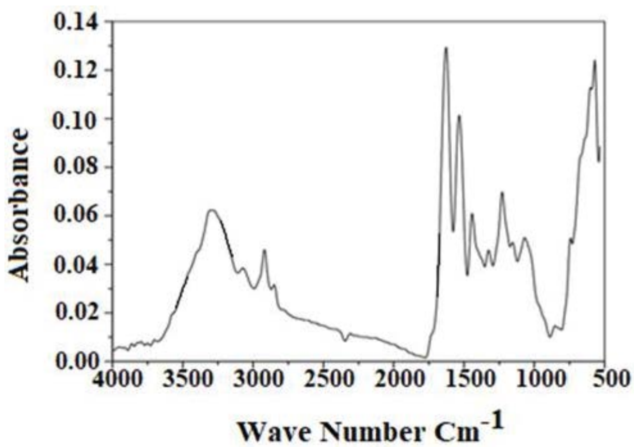

Fig. 2. FT-IR of the white shavings hide.

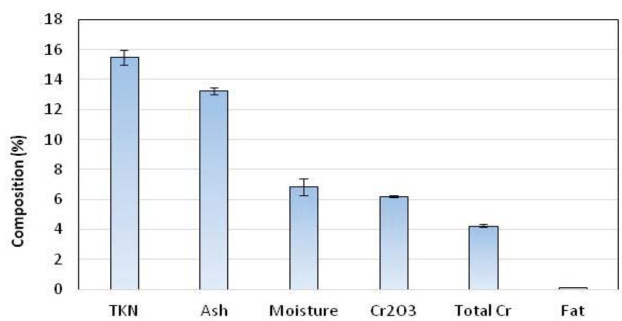

Fig. 3. Composition of the chrome shavings.

which represents chromium interaction with amino groups (–Cr–NH–), was also displaced from 1,552 to 1,537 cm^{-1}. The noted shift in these peaks was accompanied by a decrease in the intensity of the corresponding peaks. This was attributed to the chromium effect, which formed a chromium complex by coordinating with the active centers of the collagen (amides I and II). However, the remaining distinctive bands at 1,454; 1,337; 1,236; 1,077, and 1,027 cm^{-1} did not see a decline in strength, nor did change.

To achieve a particle size of around 4 mm, chromated white shavings were ground and sieved. Five times the ground chrome shavings were rinsed. Fig. 4 depicts the chemical properties of dried chromated white shaving, which has a high percentage of total Kjeldahl nitrogen, and very little fat.

3.2. Scanning electron microscope

The grain surface smooth and cross-section fiber bundles were demonstrated in morphological analysis of white shavings hide. The grain surface and cross-section SEMs were performed at the (X200).

The SEM is ideal for studying the surface of fibers and grains. This microscope provides high-resolution imaging of the internal fiber and grain surface. SEM was used to evaluate the surface and cross-section morphological features of white and chromated shavings (Figs. 4, 5a and b). The fiber bundles were separated in the SEM images of cross-sections for two samples, and the porosity of the chromated grain surface was enhanced, resulting in excellent fiber resolution and higher absorption uptake.

Table 1 shows applied operating conditions during the treatability study.

Table 2 shows the physico-chemical characteristics of raw industrial wastewater as well as treated effluents. Fig. 6 shows the appearance of the treated wastewater.

The wastewater used was almost neutral. The pH value was still unchanged during the treatment steps. The primary sedimentation process lowered the TSS, COD, and BOD from 450, 8025, and 8025 to 125, 4175, and 1878.8, with corresponding removal rates of 72.2, 48, and 33.1, respectively. The low removal rate of BOD is due to the presence of some toxic compounds that affect the activity of bacteria for the degradation of the organic loads [28,29]. What confirms this, the ratio of BOD/COD increased from 0.35 to 0.45 after settling. The level of COD, BOD, and TSS was minimized from 4,175; 1,878.8, and 125 to 2,963; 1,222, and 40 mg/L with removal rates of 29%, 35%, and 68%, respectively.

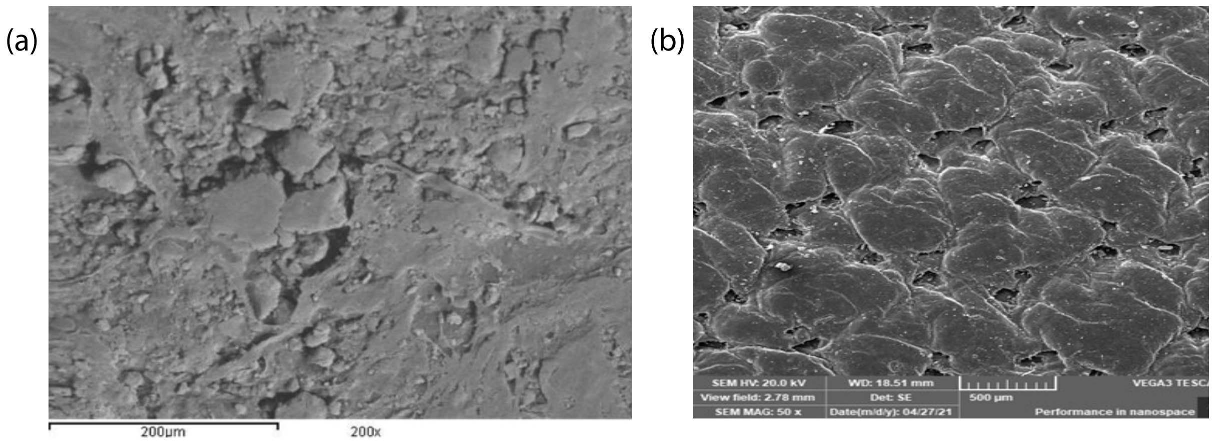

Fig. 4. SEM of grain surface of (a) white shavings (X200) and (b) chromated white shavings (X500).

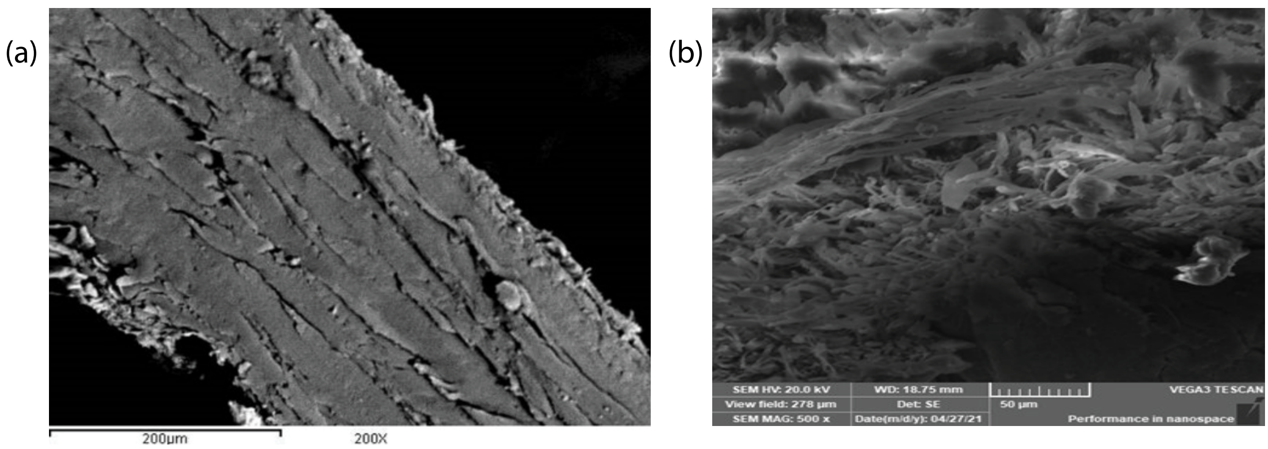

Fig. 5. SEM of cross-section of (a) white shavings (X200) and (b) chromated white shavings (X500).

Table 2
Average physico-chemical characteristics of raw wastewater and treated effluents

Parameter		Raw	Primary sedimentation	%*R* by settling	Sand filtration	%*R* by sand filter	Hide filtration	%*R* by hide filter
pH		6.7 (±0.9)	6.7 (±0.9)		6.7 (±0.9)		6.8 (±0.8)	
COD (mg·O_2/L)		8,025 (±1,805)	4,175 (±658)	48.0 (±8)	2,963 (±365)	29 (±7)	890 (±120)	77.5 (±12)
BOD (mg·O_2/L)		2,808.8 (±540)	1,878.8 (±325)	33.1 (±8)	1,222 (±258)	35 (±8)	489.5 (±90)	72.6 (±11)
BOD/COD		0.35 (±0.09)	0.45 (±0.1)		0.45 (±0.9)	–	0.55 (±0.1)	–
Settleable solids	15 min	220 (±39)	0	–	0	–	0	–
Settleable solids	30 min	180 (±28)	0	–	0	–	0	–
TSS (mg/L)		450 (±95)	125 (±31)	72.2 (±15)	40 (±8)	68 (±11)	8 (±1)	80 (±15)
TKN (mg·N/L)		25 (±9)	17 (±5)	32.0 (±9)	15 (±5)	11.8 (±4)	8 (±1.5)	46.7 (±10)
TP (mg·P/L)		3 (±0.7)	2 (±0.3)	33.3 (±9)	2 (±0.3)	0	1 (±0.1)	50 (±11)

Number of tests was 7 (standard deviation between brackets).

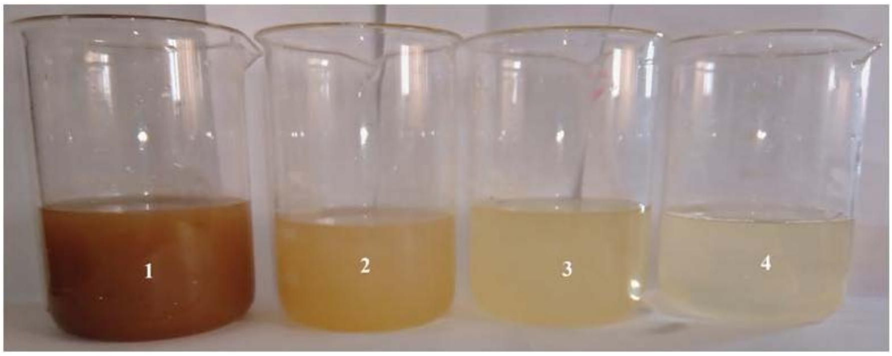

Fig. 6. Treated wastewater (1, raw wastewater, 2, after settling, 3, after sand filter, and 4, the white shavings effluent).

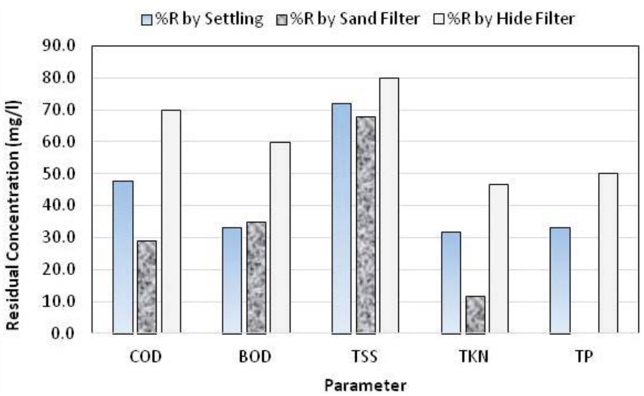

Fig. 7. Efficiency of the combined SF/WSF for the treatment of industrial wastewater.

Table 3
Correlation of the quality of the treated effluent and the regulatory standards

Parameter	Hide filtration	Ministerial Decree 44/2000 (28)
pH	6.8	6.5–9
COD (mg·O_2/L)	890	80
BOD (mg·O_2/L)	489.5	50
TSS (mg/L)	8	60

The removal of organic loads expressed by COD and BOD could be due to the interaction with the surface of the white shavings. The presence of hydroxyl, carbonyl, and amine groups could interact with the organic matter [30].

3.3. Valorization of the treated effluent

Table 3 depicts the relationship between the quality of the treated effluent and Ministerial Decree 44/2000, which governs wastewater discharge into the sewage system. Concerning the levels of pH, COD, BOD, and TSS, the treated industrial wastewater was complying with the National regulatory standards [31].

4. Conclusions

The present study was devoted to studying the protection of the environment and humans from hazardous pollutants by using a natural highly inexpensive adsorbent waste material. Valorization of chrome shavings as solid waste produced during leather tanning was achieved during this study. The treatment scheme consists of settling, sand filtration, and chrome shavings filter that can produce industrial treated effluent complying with the National regulatory standards for discharge on sewerage system (if COD is not more than 10,000 mg/L) [32].

The application of such a technique will reduce the accumulation of a considerable part of solid waste within the tanneries.

Declarations

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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