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Integration of Fenton Oxidation with Nano-Graphene Oxide to Eliminate The Hazardous Effect of Chromated/Dyed Tannery Effluents

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Abstract

Effective management of tannery effluent is needed for this time. Tanning industry is one of the worst industries from an environmental point of view, where is the prominent sources of pollution to the aquatic environment. Wet-finishing effluent is the most dangerous step, which generate the obnoxious effluent in the tanning industry. The conventional treatments of such waste showed deficiency to coop with the required limits of national regulatory standards. In the present study, an advanced oxidation technique based on modification of Fenton reaction combined with high porous nanomaterials was applied as an alternative treatment. Variable doses of H_2O_2, Fe^{+2}, CaO and pH were investigated to determine the optimum operating conditions. The obtained results indicated a good quality of the treated effluent. Residual concentrations of COD, BOD and TSS were 98.51%, 98.11% and 98.82% removal, respectively. The most obnoxious material (Cr) was highly removed (98.92%). Also, decolourization value (Y_{COL} values) was obtained using Nano GO (99%) and/or active charcoal (88.08 %) with CaO. The residual effect of H_2O_2 was reduced by MnO_2, SnO and Fe powder than sod. thiosulphate. The treated effluent could meet to the National regulatory standard for discharging into the sewerage systems with respect to the studied parameters.

Keywords: Hazardous wastes, wet-finishing effluent, Fenton's oxidation process, conventional treatment, COD, BOD.

1. Introduction

Quality of water bodies decreased with noticeable scale due to discharging of tannery waste in large scale. Discharging Chromium (Cr) species into the environment cause dangerous outcomes by changing the optimum physicochemical parameters of water and soil. In Egypt at 1950s, the leather industry can be considered as the second largest source of national income. However, in the present days, the tanning and finished leather works constitutes the fifth largest industrial sector in local market in Egypt, employing more than 250,000 persons. Therefore, tanning industry can be significant contributor to the economy industrial revenue and provides large scale employment opportunity for people of economically weaker part of the society, all over the world. But Leather industry is one of the most industries responsible for generation of large amount of wastes throughout the converting raw skins/hides into leather. In all tanning technology operations, it is commonly associated with emanate huge composite tanning effluent and solid wastes as well as atmospheric emissions and odors, which discharged in the raw state, without any pretreatment from the medieval methods of processing [1-2].

In general, one of the world greatest environmental problems is the water pollution. The tanning processes was classified a highly polluted industry, especially effluents which contain high

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content of organic and inorganic suspended solids accompanied by high chemical oxygen demand and toxic metal salt residues. Unfortunately, it is one of the major industries consuming a large amount of water, which is largely discharged as wastewater during the leather processing [3-6]. In addition, the leather sector is well known for its high pollution problems. Therefore, the environmental regulations enforced by various pollution control bodies make a very challenging task on the tanning industry to maintain the discharged norms of the chemicals in the treated water.

In Egypt about 45 to 50 m^3 of water were consumed to produce only one ton of raw hide compared with 16 to 25 m^3 in Germany [7-9]. As a result of the tanning process, only one ton of raw hides produce about 0.26-ton leather and around 0.64-ton solid waste [6]. The leather industry classified into five main steps which are hide preservation, beam-house operations, tanning, wet-finishing and the final dry finishing step. The impact of the tanning processes and the characteristics of different waste effluents on the environment have been examine by many researchers [7,10-13].

Wet-finishing process mainly include re-tanning, neutralization, dyeing and fat-liquoring operations and sometimes performed in a one single float. Therefore, it generates large amounts of highly loaded organic hazardous wastewater. The major pollutants of the wet-finishing operations are re-tannage agents as fat liquoring agents, chrome tan, syntans, vegetable tans, dyestuff residues, and other organic matter [14] as well as biological oxygen demand (BOD), chemical oxygen demand (COD) and suspended solids (SS). Dying is considered as a key factor as it gives desired color in leather industry. It is worth to mention here that, large amount of total dissolved solid (TDS) as well as total suspended solids (TSS) and organic compounds are released to the wastewater through dyeing and re-tanning process [15-17]. Sever environmental anxiety could be appear due to the discharge of wet finishing effluents to water bodies which increase the environmental pollution and health risks. The characteristics of effluents vary according to several factors such as the amount of water, chemicals used and the nature of the wet-finishing adopted process [18].

In fact, many methods have been developed for treatment of such tanning effluent, but many of the organic compounds used in leather tanning resist conventional wastewater treatment processes [19-21]. Additionally, the conventional wastewater treatment process does not comply with the required limits and alternative treatment technique for removing the pollutants and also was not sufficient to comply with limits for several parameters (e.g. dyestuff, fat-liquor, and COD) [22-23].

Additionally, biological treatment of such wastewaters will not be feasible due to the presence of toxic and refractory compounds which require long period of time to degrade [21,23]. Consequently, other techniques are needed instead of classical physico-chemical and biological treatment technologies. These technologies include phase separation such as microfiltration and adsorption processes, or pretreatment followed by biological oxidation techniques [24] or methods which degrade the pollutants (chemical oxidation/reduction) [25]. Advanced oxidation processes (AOPs) as alternative technique are widely used for removal of resistive organic moieties from industrial effluents. Most methods of them use a mix of strong oxidizing agents (e.g. H_2O_2, O_3) with catalysts (e.g. transition metal ions) and irradiation (e.g. ultraviolet, visible) [26-29].

In recent study a modification of an advanced oxidation technique based on Fenton generation was applied for treatment of wet-finishing effluent as an alternative for conventional chemical and biological processes. Fenton oxidation process is the most active systems for the oxidation of organic matters in water [6, 26-29]. The reactivity of AOPs is due to in situ generation of highly oxidative species (hydroxyl radicals) as a result of the dissociation of H_2O_2 molecule. Fenton's oxidation process takes place by addition of hydrogen peroxide to the aqueous medium having an organic substrate and ferrous sulfate in a in the presence of strong acid.

The possible complex redox reactions are represented as follow:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$
$$RH + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O \quad (2)$$
$$R^{\bullet} + H_2O_2 \longrightarrow ROH + {}^{\bullet}OH \quad (3)$$
$${}^{\bullet}OH + H_2O_2 \longrightarrow HO_2{}^{\bullet} + H_2O \quad (4)$$
$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \quad (5)$$

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$$R^{\bullet} + Fe^{3+} \longrightarrow R^+ + Fe^{2+} \qquad (6)$$

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^- \qquad (7)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \qquad (8)$$

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2H^+ \qquad (9)$$

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad (10)$$

Thus, the present work was devoted to find an acceptable and applicable solution to eliminate the environmental impact resulted from the discharge of wet-finishing wastewater as an alternative method to the traditional or classical methods. This wastewater was selected because it has high polluted effluent in the tanning industry; it contains chrome/dyed as well as other different pollutants. An evidence of the applicability of using the advanced oxidation (AOPs) for the treatment of such waste could be provided. In general, this study is an attempt aiming towards zero pollution treatment for the worst effluent in tanning industry.

2. Materials and methods

2.1. Materials

Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), Hydrogen peroxide (H_2O_2 30%), sulphuric acid (H_2SO_4 98%), acetone, ($NaNO_3$) sodium nitrate, ($KMnO_4$) potassium permanganate, sodium Hydroxid (NaOH), All the chemicals are analytical grade, commercially available, were purchased from Merck company and used without further purification.

Graphite (99%) was purchased from Fluka Switzerland. Manganese dioxide, Tin (IV) oxide, Fe powder, stannous oxide (SnO) and sod. thiosulphate were purchased from Merck company.

2.2. Tanneries location, Description and Sampling

Egyptian tanneries wastewater located in south of Cairo city is currently discharged directly into the domestic sewer network without pre-treatment. For this reason, the infrastructure sewer utilities under this area are seriously polluted and became strongly damaged. Consequently, the municipal wastewater treatment plant failed to achieve reasonable success due to the toxicity in the treated stream.

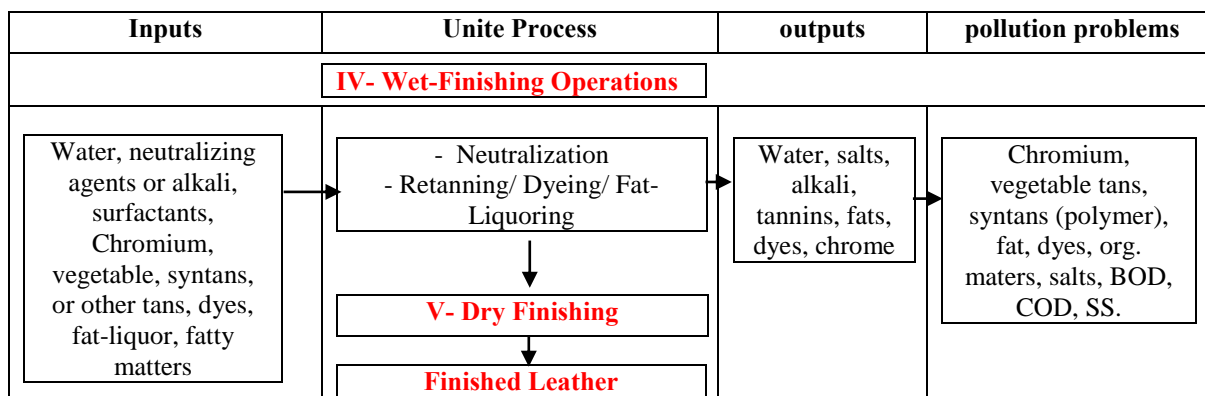Scheme (1) illustrates the general processes of leather tanning operations and the environmental impact of the wet-finishing steps, which can be considered as multi operation but usually performed in one drum. The chemicals that are used in each process and the by-products are shown in Scheme (1).

Extensive program for sampling was designed to collect bi-weekly samples from a manhole of some local tanneries to conduct the present study. Each composite sample represents the discharge of wet-finishing effluents. The physico-chemical parameters of the wastewater were determined according to [27].
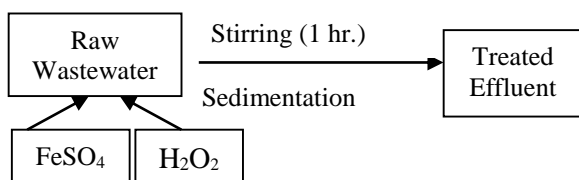
2.3. Synthesis of Graphene Oxide (GO)

According to Hummers–Offeman method modification; pure graphite powder is oxidized to graphene oxide (GO) [30]. In typical procedure, (115 mL, 98 wt %) cold concentrated sulphuric acid was transferred to a dry ice bath. graphite powder (5 g) and sodium nitrate (2.5 g) was dispersed in sulphuric acid and potassium permanganate ($KMnO_4$, 15 g) was added gradually under vigorous stirring and cooling to prevent the temperature from exceeding 20°C. The ice bath was replaced by a water one and the mixture temperature was raised to 35°C for (30 min.) with gas release under vigorous stirring, followed by slow addition of deionized water (230 mL), which produced a rapid increase in the mixture temperature up to a maximum of 98°C. The reaction was maintained for (40 min.) to increase the oxidation degree of the graphite oxide product and then the resultant bright-yellow suspension was terminated by the addition of more distilled water (140 mL) followed by hydrogen peroxide solution (H_2O_2, 30 mL). The product was separated by centrifugation at (3000 rpm) and washed initially with (5% HCl) until sulphate ions were no longer detectable with barium chloride. The product was rewashed three times with acetone and air-dried overnight at 65 °C. After sonication for 30 min, the graphite was transformed into graphene oxide.

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Scheme (1): Schematic diagram shows the environmental impact of Wet-Finishing Operations.

Inputs	Unite Process	outputs	pollution problems
	IV- Wet-Finishing Operations		
Water, neutralizing agents or alkali, surfactants, Chromium, vegetable, syntans, or other tans, dyes, fat-liquor, fatty matters	- Neutralization - Retanning/ Dyeing/ Fat-Liquoring **V- Dry Finishing** **Finished Leather**	Water, salts, alkali, tannins, fats, dyes, chrome	Chromium, vegetable tans, syntans (polymer), fat, dyes, org. maters, salts, BOD, COD, SS.

2.4. Treatment scenario

An integrated for the treatment of tannery wastewater consisting of wet H_2O_2 catalytic oxidation (WHPCO) using Fenton' reagent has been investigated (Scheme 2).

Scheme (2): Experimental set-up of treatment steps using Fenton process (WHPCO)

2.5. Fenton reaction process

Fenton reaction was carried out at pH value 3.0 ± 0.1 by the addition of (0.1) N H_2SO_4 before startup operation using the jar-test apparatus at room temperature for the treatment of the wet-fishing wastewater effluents. Various doses of Fe^{2+} ranging from (0.2-1.6 g/L) were added at the beginning, followed by the addition of H_2O_2 ranging from 20 to 50 g/L dose. The latter was added to each jar under high speed followed by slow mixing at 100 rpm. The reaction was maintained for (60 min.) in order to determine H_2O_2 optimum dose. Fenton reactions cannot continue at pH > 10; therefore (1 M) sodium Hydroxide, under high speed, was added for (5 min) to increase pH more than 10 and also to remove excess of H_2O_2 before any analysis [24]. Flocculation process was carried out and the mixing speed was slowed down to (30 rpm) for (20 min). The system was stopped at zero speed for (60 min.) to allow

sedimentation occurred. The same above experimental procedure was carried out again for the determination of the optimum dose of Fe^{2+} catalysts using a fixed amount of the predetermined optimum dose of H_2O_2. The examined Fe^{2+} doses ranged from (0.20) to (1.6) g/L.

2.6. Analytical Methods

Evaluation of the efficiency of treatment method was tested by monitoring the water quality of the wet-finishing wastewater and effluents of each treatment step. The physico-chemical parameters covered: pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total Kejldahl nitrogen (TKN). All the analysis carried out according to Standard Methods for Examination of Water and Wastewater [27].

2.7. Atomic Absorption Spectrophotometer

Atomic absorption Spectrophotometer used in measurements is model Specter AA 220. Chrome (Cr) was measured at 357.9 nm and deuterium background correction was applied to correct for background fluctuation. The detection limit achieved with this line at the used operating conditions was (9.07) µg ml^{-1} with a linear dynamic range between (0.1) and (10)µg ml^{-1}. Acetylene/nitrous oxide flame was used with fuel and the flow rate of (4.51) min^{-1} and oxidant flow rate of (3.51) min^{-1}.

2.8. UV- Spectrometer

Ultraviolet–visible spectroscopy of the samples was carried out using UV-vis JASCO-V630 spectrophotometer at room temperature, in the range

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of 200 −1100 nm with band width 1.5 nm, Scan speed 400 nm/min and Light source D2/WI with source change at 340 nm.

2.9. Surface Texture of GO

2.9.1. X-ray diffraction

X-ray diffraction (XRD) was measured at room temperature by using a Philips diffractometer using Model PW-3710. The patterns were progressed with Ni-filtered copper radiation ($\lambda = 1.5418$ A˚) at 30 kV and 10 mA with a scanning speed of $2\theta = 5\circ$/min. The mean crystallites size was calculated using the Debye–Scherrer Eq. (11), in which K is a constant equal 0.9, λ is the wave length of the Cu K radiation, β is the half peak width of the diffraction peak in radiant [31-33].

$$D = (K\lambda)/(\beta\,Cos\,\theta) \qquad (11)$$

2.9.2. FTIR spectroscopy

The Fourier transform infrared (FT-IR) spectra were monitored via a single beam Thermo scientific Nicolet iS10 instrument. The samples were grounded with KBr (1:100) to form tablets, and thus confined into the sample holder in the spectrometer cavity to record the measurements in the 4000–400 cm^{-1} region.

2.9.3. N_2 adsorption

The surface texturing properties namely BET surface area, total pore volume (Vp) and mean pore radius (r) were determined from N_2 adsorption isotherms measured at 77 K using a conventional volumetric apparatus. The samples were out-gassed at 473 K for 3 h under a reduced pressure of 10^{-5} Torr before starting the measurement. The total pore volume was taken from the desorption branch of the isotherm at p/p^0= 0.95, assuming complete pore saturation.

3. Results and Discussions

3.1. The Texture of graphene oxide (GO)

3.1.1. X-ray diffraction

GO pattern of XRD shows a strong peak centred at ($2\theta = 11.7°$), corresponding to the (0 0 1) interlayer spacing of 7.43 Å [34], together with a small one at 42° due to the (200) plane, figure (1). The obtained data indicates the formation of GO matrix in angstrom size (smallest Nano-form).
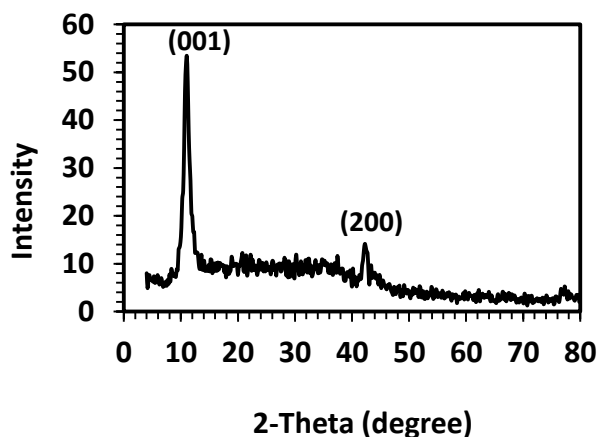

Fig. 1. XRD Pattern of GO

3.1.2. IR and Raman studies

The existence of oxygen-containing functionalities and structural changes for GO investigated using FT-IR spectroscopy figure (2). The FT-IR spectrum of GO exhibits the characteristic peaks of carboxy C-O (1417 cm^{-1}), C=O (1721 cm^{-1}), alkoxy C-O (1049 cm^{-1}), aromatic C=C (1615 cm^{-1}), epoxy C-O (1217 cm^{-1}), stretching C-O-C (850 cm^{-1}) and surface OH groups and absorbed water molecules at 3346 cm^{-1} beside another one at 1407 cm^{-1}
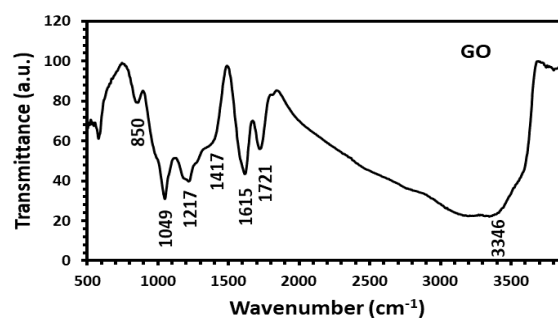

Fig. 2. FT-IR spectra of GO

GO raman spectra shows peaks at 1347 cm⁻¹ (due to the D band, diagnosed for dis-orderings) and 1589 cm⁻¹ (attributed to the G band for graphite) as shown in Figure (3)
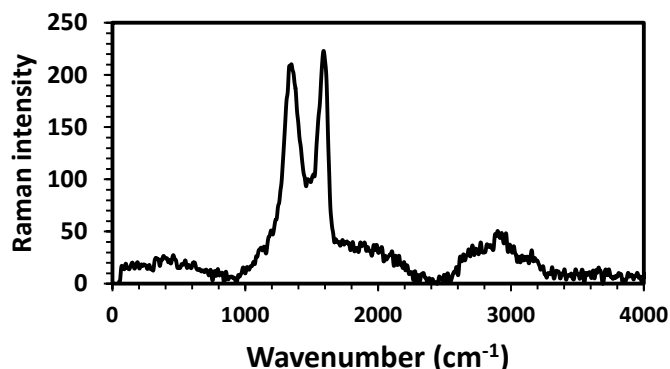

Fig. 3. Raman spectra of GO

3.1.3. N₂ adsorption

The pore size distribution and adsorption-desorption isotherms curves were described in Figure (4). The BET surface area, pore volume and pore radius of GO indicate higher SBET and lower pore volume and radius values (176 m² g⁻¹, 0.38 cm³ g⁻¹, and 19.1 Å). The desorption isotherms of GO show major capillary condensation steps at the relative pressure range from 0.4 to 0.7.

3.2. Treatment of Raw Tannery Effluent

In this research we choice the wet-fishing process because it's the worst step from environment stand point as well as Hexavalent chromium was determined in a mixture of Cr (III) and Cr (VI) in some Egyptian tanneries. Trivalent chromium is low toxic whilst hexavalent chromium is very toxic for both plant and animal life [13].

Samples were collected from three different tanneries. The main average characteristics of the wastewater were listed in Table (1). The data showed a high value of all determined parameter where, COD concentrations were ranged from 17130 to 13120 mg/L with an average of 15125 mg/L, while, BOD

average concentrations and TSS were 6300 mg/L and 2556 mg/L respectively. Also, BOD/COD ratio was about 0.41. Where, chromium species was found about 300 mg/L which affects the biodegradability of effluent. Consequently, chemical treatment is recommended to be carried out by this recent study.
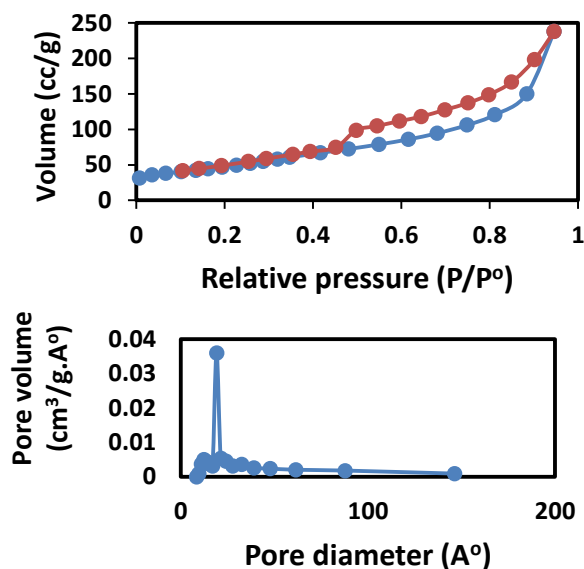

Fig. 4. Adsorption-desorption isotherms and its corresponding pore size distribution curve of GO.

Table 1
Characteristics of Raw Tannery Effluent

Parameters		Tannery Effluent
pH		4.3±0.2
COD	mg/L	15125±2005
BOD	mg/L	6300±60
TKN	mg/L	252±200
TSS	mg/L	2556±850
Chrome	mg/L	280±20

3.2.1. Fenton treatment

Treatment process was carried out at doses of ferrous sulfate (0.4g/L), H₂O₂ (30 g/L) and CaO (0.625 g/L) at a constant time (1 hr.), to shows the efficiency of Fenton oxidation process for wet-finishing wastewater treatment.

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3.2.1.1. Effect of pH values

The key parameter in the coagulation process of wastewater treatment is the pH value [28-29]. Using of a coagulant at its optimum pH indicates maximum pollutant removal. The pH values were adjusted using 4N H_2SO_4 solution in order to determine the optimum pH of the process. It's obvious from the obtained result that the optimum pH was 3.0 at which the most decreased in COD of effluent occurred, Figure (5).
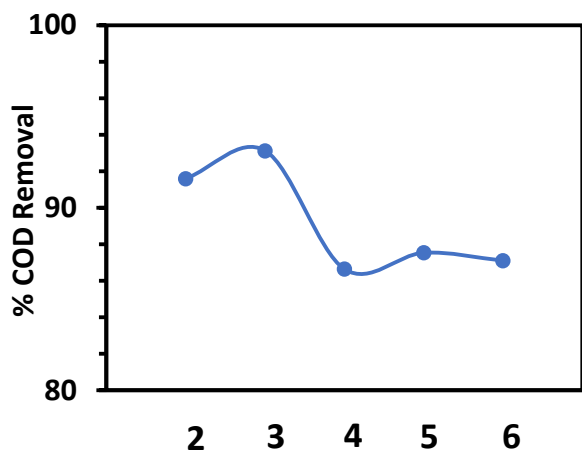

Fig. 5. Concentration of COD at different pH values

3.2.1.2. Hydrogen peroxide dose

The treatment process was applied at the optimum pH value 0f 3±0.1. Figure (6) shows the effect of different doses of hydrogen peroxide on COD concentration. At all doses of hydrogen peroxide, the concentration of COD was complying with the National regulatory standard for treated effluent discharge to the sewerage system [35]. This could be
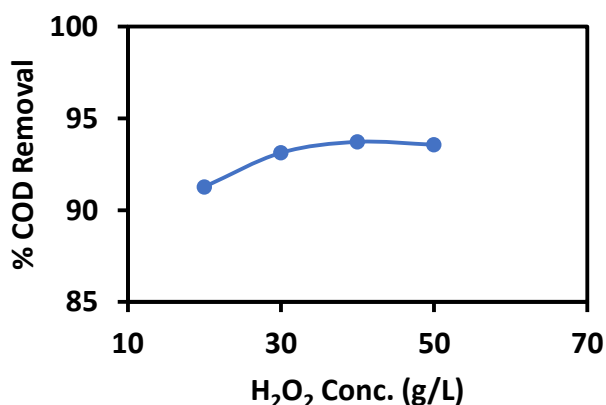

Fig. 6. Concentration of COD at different hydrogen
peroxide doses.

attributed to the highly oxidative species of hydroxyl radicals resulting from H_2O_2 dissociation. Hydroxyl radicals are highly reactive non-selective oxidants for oxidation of organic matter in aqueous solution. From the above Figure (6), it was observed that the most effective concentration of H_2O_2 was 30 g/L (93.13 removal percent), but after that dose the change in COD percent almost steady state. This meaning that, increasing of hydrogen peroxide doses from 40 to 60 g/L no extra change (93.71 and 93.57 removal efficiency was not affected). Thus, 30 g/L dose of hydrogen peroxide was chosen to be the optimum one due to economic reasons and carrying out the rest of the experimental study.

3.2.1.3. Effect of Ferrous sulfate dose

The effect of variable doses of $FeSO_4$ on the performance of treatment process was carried at optimum pH value (3) and H_2O_2 dose (30 g/L). Figure (7) shows the removal efficiency of COD was affected by the addition of ferrous salt at different doses (varied from 0.2 to 1.6 mg/L). It was noticed from Figure (7) that, the highest removal efficiency of COD was 98.55 % at dose of 0.8 g/L of ferrous sulfate.
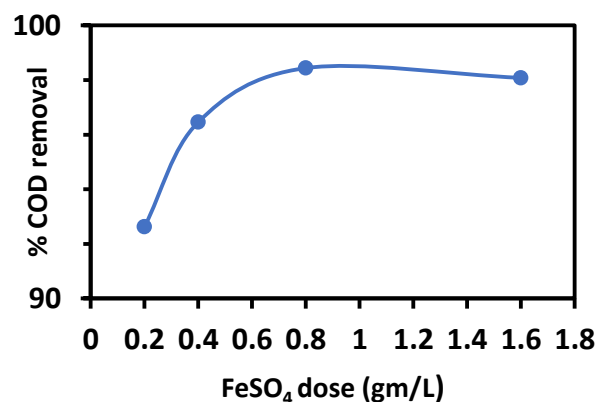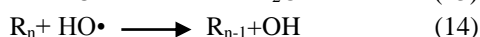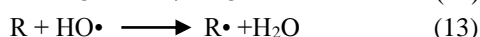

Fig. 7. Concentration of COD at different doses of ferrous sulphate

COD concentrations reduced from 15125 mg/L to 1040 mg/L at dose of 0.2 mg/L of the ferrous sulfate dose. But the concentration of COD was still over the permissible level for discharging to the sewerage system (1100 mg/L) [35]. By increasing the dose of ferrous sulfate, the reduction of COD increased up to 220 (98.55 % removal).

In this study Fenton's reactions was considered as a good solution for the treatment of wastewater. The

AOPs mechanism function is due to the generation of highly reactive hydroxyl radicals (HO•) in suite which are effective and non-selective oxidants. The resulting free radicals attack the organic matter and facilitate its degradation in the reaction medium. The destroying of organic materials due to reactive radicals (HO•, electron preferring) that react non-selectively and rapidly with all electron-rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions comparing to conventional oxidants [25]. Once the hydroxyl radicals were generated can attack the organic materials by radical addition (Eq. 12), hydrogen abstraction (Eq. 13) and electron transfer (Eq. 14).

$$R + HO• \longrightarrow ROH \qquad (12)$$
$$R + HO• \longrightarrow R• + H_2O \qquad (13)$$
$$R_n + HO• \longrightarrow R_{n-1} + OH \qquad (14)$$

R= reacting organic compound

3.2.1.4. Effect of Calcium oxide dose

Calcium oxide was used as a coagulant with ferrous salt at the end of Fenton oxidation treatment. The effect of calcium oxide doses were carried out at the obtained optimum results (0.8 g/L ferrous sulfate, 30 g/L hydrogen peroxide and pH value of (3). Figure (8) reveals that, increasing of calcium oxide doses from 0.625 to 7.50 g/L increases the pH and decreases the COD concentration. According to Figure (8) the optimum doses of calcium oxide were 0.625 and 5.0 g/L, but the colored dye still present at 0.625 and 2.5 doses. Therefore, the optimum dose of CaO was 5 g/L was selected at which colored dye was colorless as shown in Figure (8).

It was noticed that at higher pH the residual H_2O_2 was volatized. Consequently, the COD demand due to excess H_2O_2 was reduced [36]. Also, it was observed that, at higher doses of calcium oxide above 5.0 g/L, the COD concentration was slightly decreased (97.79 %). The removal efficiency of the innovative integrated treatment system ranges from 73.4 to 98.9%. The treated effluent concentrations for BOD, COD, TKN, TSS, and Chrome were 119±20, 225±20, 67±5, 30±5 mg/L and 3 ppm, respectively.
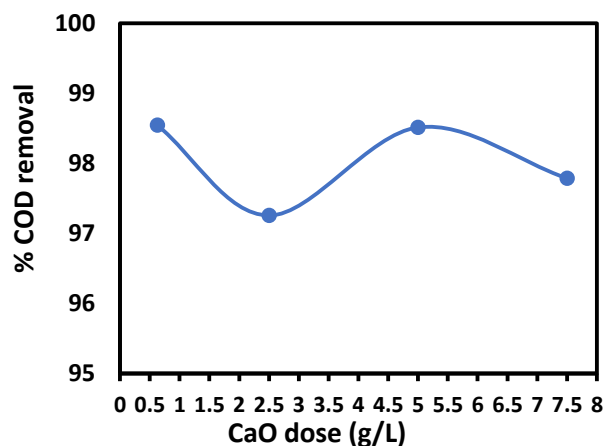

Fig. 8. Concentration of COD at different doses of calcium oxide

3.3. Dye and Chromium Removal

One of the most criteria in this treatment was the removal of dye and chromium species of the effluent. Colored dye solutions of the treated samples become colorless at 400-700 nm as illustrated in figure (9), where curve A represent the treated sample and curve B represent the raw wastewater sample. The color was disappeared after treated with CaO at 5 g/L dose, and before that dose it was still persist. The Color removal yield (Y_{COL}) could therefore be defined as follows:

$$Y_{COL} = [Ai − At/Ai] ×100 \quad (15)$$

Which A_i is the initial absorbance of dye wastewater and A_t is the final absorbance of dye wastewater after treatment.
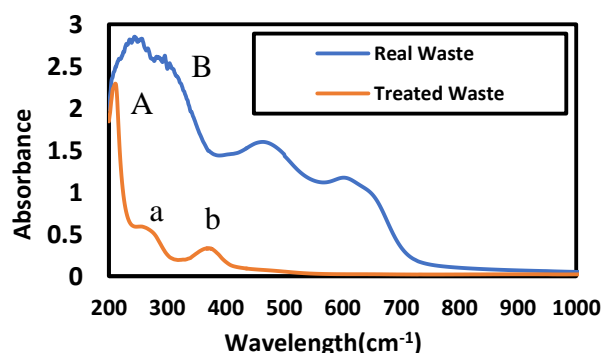

Fig. 9. Absorbance curve of treated samples by CaO (5 g/L) at Optimum conditions of AOPs and real waste

The Colour removal yield (Y_{COL}) can be taken as a function of absorbance. Experimental data show that Fenton oxidation reaction (FOR) gave satisfactory results, i.e. Y_{COL} values higher than 95 %, for coloured dye removal (curve A- b region) and higher than 78% for organic matters in UV margin (curve A- a region). In Figure 9, the Y_{COL} curve show a maximum absorption beak at 468 & 280 nm which indicated a high load of dyed matters (visible region) and for coloured matters in UV margin. This meaning that, the decolourization was obtained at the optimum condition of Fenton oxidation reaction with CaO at 5 g/L dose.

On the otherwise, the use of a high percentage of CaO is not preferred in hydrotherapy. Therefore, the waste was treated first with active charcoal and/or GO to minimize the using percentage of CaO. The observed result, Figures (10 & 11), indicated that a good the colour eliminated at using low CaO percent (0.625 g/L). Where Y_{COL} values (elimination percent of dye) were more than 99% by GO with CaO and higher than 87.6% by AC with CaO at 612 nm and at 467 nm the coloured dye removal was 98.11 % and 88.08% respectively. While, in UV margin at 248 nm the Y_{COL} values were 59.57% and 45.61 %.

Therefore, the collective results for the all materials used and their effect on the dye disposal were shown in Figure (12). It obvious from figure that, graphene oxide with CaO (0.625 g/L) is the best one especially in visible region 400-700 Cm^{-1}.

With respect to the chromium effluent cause serious environmental impacts. Therefore, tannery effluent containing chrome must be treated separately before discharging into environment when treated with the classical treatment. But in recent study advanced
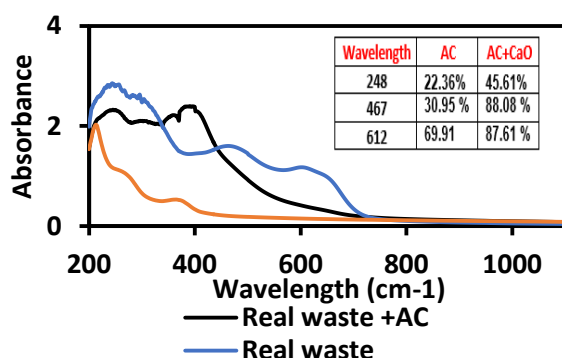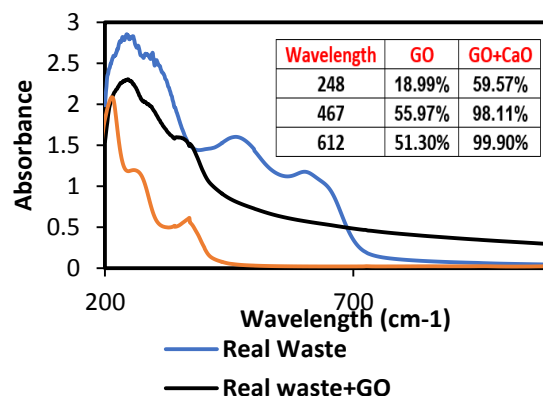

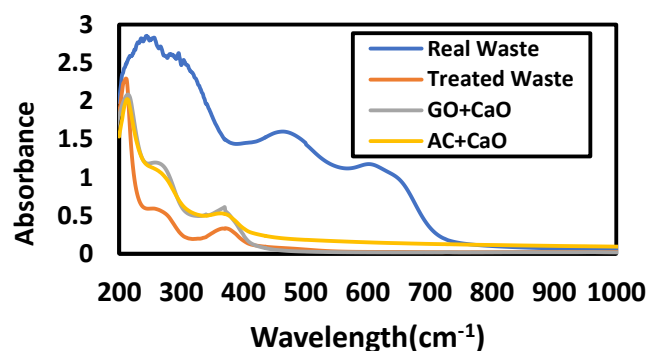Fig. 11. Absorbance curve of treated samples by graphene

Fig. 12. Collective absorbance curve of treated samples by graphene oxide, active charcoal with CaO (0.625 g/L) comparing with optimum condition of AOPs and real waste

oxidation process is an effective method for the chrome effluent elimination than the classical one.

Fig. 10. Absorbance curve of treated samples by active charcoal with CaO (0.625 g/L) and real waste, Where the most efficient removal classical method was precipitation by NaOH (80%R) and adsorption by charcoal and Al_2O_3 (76.6 & 74.9 % R). While, the FOR was achieved over 98 % R for chromium species as illustrated in table (2).

3.4. Elimination of H_2O_2 residual

It was used a different category of reducing agents (MnO_2, SnO, Fe powder and sod. thiosulphite) to stop the residual effect of H_2O_2. Where, the presence of remaining H_2O_2 increase the COD percent and consequently the measuring of

Fig. 10. Absorbance curve of treated samples by active charcoal with CaO (0.625 g/L) and real waste

COD will be wrong. The obtained results in figure (13) reveals that, MnO_2 is the best one, followed by SnO and Fe powder. Although, sod. thiosulphite has a high reducing characteristic, but, the obtained results were not what was expected, as COD increased more than the original material. This can be explained on the basis of redox system, where, the presence remaining traces of Fe^{2+} with sod. thiosulphate together form a redox reaction produces a free radical as following equation:

$$Fe^{2+} + Na_2S_2O_8 \longrightarrow Fe^{3+} + SO_4^{--} + SO_4^{-\cdot} \quad (16)$$

According to the above equation of redox system, it produces a free radical which increase COD percent.
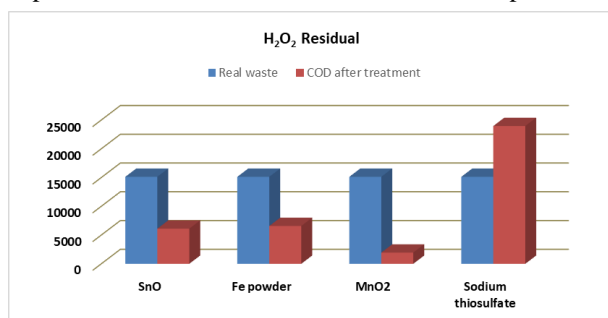

Fig.13. Elimination of H_2O_2 residual by different categories of reducing agents

3.6. Performance of the treatment process

It was observed from table (3) that, the performance of Fenton oxidation reaction (FOR) for the treatment of wastewater at optimum operating conditions. The obtained results show that the wet-finishing biodegradability of wastewater was enhanced by employing the Fenton reaction treatment process. After Fenton reaction, the BOD/COD ratio of the studied wastewater was changed from 0.41 to 0.52 as an indication of effluent improvement. Meanwhile,

3.5. Classical physico- chemical Methods

The most common traditional process as adsorption methods (Amberlite IRC-50(H), Al_2O_3, charcoal and dowex 50Wx8) and perception method using NaOH were applied for treatment of the effluent comparing with AOPs reaction. In general, adsorption method was used because of simple operation conditions, low cost and it can be used for wide range of treating effluents. It was thinks that, adsorption methods can be considered a combination of both separation and purification process which removes the pollution causing substance that are not biodegradable [37-40] but in our effluent is not efficient as obvious of the obtained result because, this effluent contains different types of effluent. Table (2) reveals that, both absorption methods by different materials and precipitation by NaOH are less efficiency than Fenton oxidation process.

the average COD removal rate reached 98.51% [41] Confirmed that the biodegradability was improved with Fenton's reaction and the toxicity of the wastewaters is reduced. The overall treatment process of the obtained optimum operating conditions is shown in Table (3).

Table 3

Collective Parameters and Efficiency of the treatment process at the optimum operating conditions*

Parameters	Raw Effluent	After treatment	Removal, %	National Regulatory Standards (Decree 44/2000)
pH	4.3±0.2	9.1±0.2		
COD (mg/l)	15125±2005	225±20	98.51	1100
BOD (mg/l)	6300±60	119±20	98.11	600
BOD/COD ratio	0.41	0.52		0.6
TKN (mg/l)	252±200	67±5	73.41	100
TSS (mg/l)	2556±850	30±5	98.82	800
Chrome (mg/l)	280±20	3±2	98.92	0.5 (Cr VI)

* Optimum operating conditions are 0.8 gm/L ferrous sulfate, 30 gm/L hydrogen peroxide and 5 gm/L for calcium oxide

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4. Conclusion

The present work was interested on the wet-finishing wastewater treatment, due to its high levels of organic pollutants, inorganic waste and hazardous polluted effluent (fat, Chrome and dye). Such wastes threatening the environment so, it must be treated before discharging from tanneries into the environment.

The recent research showed that modified AOPs treatment is an effective method for the removal of non-biodegradable portions of the wastewater.

The obtained results revealed that COD, chromium species reduction reached to 98.51% and 98.92%, respectively.

The dye removal percentage (Y_{COL} values) was reached to 99% using GO with CaO.

The final effluent could be discharged safely to the sewerage network without potential of environmental risk, and then many pollution problems can be overcome based on the using of modified AOPs.

5. Conflicts of interest

There are no conflicts to declare.

6. References

[1] C. Huber, S. De, Toxicity of tannery effluent: the next concern?, The Journal of the American Leather Chemists Association (USA) (1990).

[2] J.M. Morera, A. Bacardit, L. Ollé, E. Bartolí, M.D. Borràs, Minimization of the environmental impact of chrome tanning: A new process with high chrome exhaustion, Chemosphere 69(11) (2007) 1728-1733.

[3] S.V. Kanth, R. Venba, B. Madhan, N. Chandrababu, S. Sadulla, Cleaner tanning practices for tannery pollution abatement: role of enzymes in eco-friendly vegetable tanning, Journal of Cleaner Production 17(5) (2009) 507-515.

[4] R.S. Makdisi, Tannery wastes definition, risk assessment and cleanup options, Berkeley, California, Journal of hazardous materials 29(1) (1991) 79-96.

[5] C. Sastry, Characteristics and treatment of wastewater from tanneries, Indian Journal of Environmental Protection 6(3) (1986) 159-168.

[6] K. Alexander, V. Donahue, Cleaner technologies in the tanning industry. EPA environmental challenge of the 1990s, International conference on pollution prevention: clean technologies and clean products, 1990, pp. 19-31.

[7] D. Tsotsos, Tanneries: a short survey of the methods applied for wastewater treatment, Water science and technology 18(9) (1986) 69-76.

[8] Z.-R. Guo, G. Zhang, J. Fang, X. Dou, Enhanced chromium recovery from tanning wastewater, Journal of Cleaner Production 14(1) (2006) 75-79.

[9] C. Zhao, W. Chen, A review for tannery wastewater treatment: some thoughts under stricter discharge requirements, Environmental Science and Pollution Research 26(25) (2019) 26102-26111.

[10] M. Chuan, J. Liu, Release behavior of chromium from tannery sludge, Water Research 30(4) (1996) 932-938.

[11] F. Balkau, Tanning and environment in the 1990 s, Journal of the Society of Leather Technologists and Chemists 74 (1990) 104-6.

[12] S. Skrypski-Mäntele, T. Bridle, Environmentally sound disposal of tannery sludge, Water Research 29(4) (1995) 1033-1039.

[13] K. Eid, E. Nashy, A. Mahdy, E. El Askar, M. Eid, Sample preparation procedures for determination of Cr_2O_3 in leather samples using ICP-AES and AAS, Journal of the American Leather Chemists Association (2004).

[14] T. UNEP, the environment. A technical guide to reducing the environmental impact of tannery operations, Technical Report Series.

[15] M. Chowdhury, M. Mostafa, T.K. Biswas, A.K. Saha, Treatment of leather industrial effluents by filtration and coagulation processes, Water Resources and Industry 3 (2013) 11-22.

[16] J. Akan, E. Moses, V. Ogugbuaja, J. Abah, Assessment of tannery industrial effluents from Kano metropolis, Kano State, Nigeria, Journal of Applied Sciences 7(19) (2007) 2788-2793.

[17] T. Kalburcu, N. Öztürk, N. Tüzmen, S. Akgöl, A. Denizli, Cholesterol removal onto the different hydrophobic nanospheres: a comparison study, Journal of Industrial and Engineering Chemistry 20(1) (2014) 153-159.

[18] O. Tünay, I. Kabdasli, D. Orhon, E. Ates, Characterization and pollution profile of leather tanning industry in Turkey, Water Science and Technology 32(12) (1995) 1-9.

[19] A. Cassano, E. Drioli, R. Molinari, D. Grimaldi, F. La Cara, M. Rossi, Enzymatic membrane reactor for eco-friendly goat skin unhairing, Journal of the Society of Leather Technologists and Chemists 84(5) (2000) 205-11.

[20] H. Springer, The 1994 John Arthur Wilson Memorial Lecture: treatment of industrial wastes of the leather-industry: is it still a major problem?, The Journal of the American Leather Chemists Association (USA) (1994).

[21] P. Thanikaivelan, J.R. Rao, B.U. Nair, T. Ramasami, Approach towards zero discharge tanning: role of concentration on the development

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of eco-friendly liming–reliming processes, Journal of cleaner production 11(1) (2003) 79-90.

[22] S. Schrank, H. Jose, R. Moreira, H.F. Schröder, Elucidation of the behavior of tannery wastewater under advanced oxidation conditions, Chemosphere 56(5) (2004) 411-423.

[23] T. Ramasami, P. Rao, International consultation meeting on technology and environmental upgradation in leather sector, New Delhi, T1-1 T1-30 (1991).

[24] T.P. Sauer, L. Casaril, A.L.B. Oberziner, H.J. José, R.d.F.P.M. Moreira, Advanced oxidation processes applied to tannery wastewater containing Direct Black 38—Elimination and degradation kinetics, Journal of hazardous materials 135(1-3) (2006) 274-279.

[25] M. El-Khateeb, E. Nashy, A.-A.A. Nayl, Combining Chemical Coagulation Process and Innovative Aerobic Reactor for the Treatment of De-Hairing Wastewater, Waste and Biomass Valorization (2020) 1-8.

[26] A. Stasinakis, Use of selected advanced oxidation processes (AOPs) for wastewater treatment–a mini review, Global NEST journal 10(3) (2008) 376-385.

[27] A.P.H. Association, A.W.W. Association, W.P.C. Federation, W.E. Federation, Standard methods for the examination of water and wastewater, American Public Health Association.1915.

[28] M. El-Khateeb, E.-S.H. Nashy, N.A. Ghany, A.M. Awad, Environmental impact elimination of chrome tanning effluent using electrocoagulation process assisted by chemical oxidation, Desalin. Water Treat 65 (2017) 147-152.

[29] P. Canizares, C. Jiménez, F. Martínez, M.A. Rodrigo, C. Sáez, The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters, Journal of Hazardous Materials 163(1) (2009) 158-164.

[30] A. Eslami, A. Yazdabakhsh, H. Daraee, F.S. Karimi, Removal of 4-Chlorophenol from aqueous solutions using graphene oxide nanoporous adsorbent, Journal of Water and Wastewater 26(1) (2015) 19-26.

[31] A.M. El Nahrawy, B.A. Hemdan, A.B. Abou Hammad, A.L.K. Abia, A.M. Bakr, Microstructure and antimicrobial properties of bioactive cobalt co-doped copper aluminosilicate nanocrystallines, Silicon 12(10) (2020) 2317-2327.

[32] A.B. Abou Hammad, B.A. Hemdan, A.M. El Nahrawy, Facile synthesis and potential application of Ni0. 6Zn0. 4Fe$_2$O$_4$ and Ni0. 6Zn0.

2Ce0. 2Fe$_2$O$_4$ magnetic nanocubes as a new strategy in sewage treatment, Journal of Environmental Management 270 (2020) 110816.

[33] B.A. Hemdan, A.M. El Nahrawy, A.-F.M. Mansour, A.B. Abou Hammad, Green sol–gel synthesis of novel nanoporous copper aluminosilicate for the eradication of pathogenic microbes in drinking water and wastewater treatment, Environmental Science and Pollution Research 26(10) (2019) 9508-9523.

[34] J. Fan, S. Liu, J. Yu, enhanced photovoltaic performance of dye-sensitized solar cells based on TiO$_2$ nanosheets/graphene composite films, Journal of Materials Chemistry 22(33) (2012) 17027-17036.

[35] H.I. Abdel-Shafy, A.M. Al-Sulaiman, M.S. Mansour, Anaerobic/aerobic treatment of greywater via UASB and MBR for unrestricted reuse, Water Science and Technology 71(4) (2015) 630-637.

[36] F. El-Gohary, M. Badawy, M. El-Khateeb, A. El-Kalliny, Integrated treatment of olive mill wastewater (OMW) by the combination of Fenton's reaction and anaerobic treatment, Journal of hazardous materials 162(2-3) (2009) 1536-1541.

[37] P. Senthil Kumar, R. Sivaranjanee, U. Vinothini, M. Raghavi, K. Rajasekar, K. Ramakrishnan, Adsorption of dye onto raw and surface modified tamarind seeds: isotherms, process design, kinetics and mechanism, Desalination and Water Treatment 52(13-15) (2014) 2620-2633.

[38] S. Suganya, P.S. Kumar, Kinetic and thermodynamic analysis for the redemption of effluents containing Solochrome Black T onto powdered activated carbon: a validation of new solid-liquid phase equilibrium model, Journal of Molecular Liquids 259 (2018) 88-101.

[39] P. SenthilKumar, R. Gayathri, S. DineshKirupha, P. RajKumar, J. Nandagopal, S. Sivanesan, Adsorption of dye from aqueous solution using silver wood sawdust carbon, Environmental Engineering & Management Journal (EEMJ) 10(3) (2011).

[40] K.G. Pavithra, V. Jaikumar, Removal of colorants from wastewater: A review on sources and treatment strategies, Journal of Industrial and Engineering Chemistry 75 (2019) 1-19.

[41] H. Tekin, O. Bilkay, S.S. Ataberk, T.H. Balta, I.H. Ceribasi, F.D. Sanin, F.B. Dilek, U. Yetis, Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater, Journal of hazardous materials 136(2) (2006) 258-265.

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