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Bicarbonate Alternatives in the Neutralization Phase of Leather Tanning to Ensure Sustainability

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Article

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ABSTRACT

The post-tanning procedure involves neutralizing the iso-electric point, which ensures that there is no imbalance between carboxylic groups and amino groups. This balance allows for the penetration of dyes, fatliquoring agents, and other chemical materials. Bicarbonate is used during the neutralization phase, and to eliminate it, 4 metric tons of water are needed for each metric ton of leather. Additionally, this leads to an elevation in both Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). The objective of the research was to substitute bicarbonate with sodium borate, sodium acetate, and sodium formate, and neutralise syntan to decrease the quantities of pollutants generated from this process, minimize the consumption of water, and improve the quality of the produced leather. Each experimental group's BOD, COD, microscopic micrographs, physical, chemical, and organoleptic parameters were determined. The use of sodium borate, neutralizing syntan, sodium acetate, and sodium formate resulted in a significant decrease in the discharge of BOD, COD, and water consumption. Furthermore, the use of 2.5% sodium borate has proven to be the most effective neutralizing agent in reducing water consumption by 80%, total oxygen demand by 39% and costs of neutralization chemicals by 0.62%. Also, the physical and chemical properties of the leather product were similar to those of the control. Therefore, the leather that has been neutralized with sodium borate is considered to have the best organoleptic characteristics compared to the control.

KEYWORDS

bicarbonate, chrome tanning, borax, leather properties, sodium acetate, tannery waste, sustainability

INTRODUCTION

Tannery wastewater is distinguished by elevated levels of organic and inorganic contaminants, resulting in significant chemical oxygen demand (COD) and biochemical oxygen demand (BOD) [1].

The leather tanning process primarily consists of four stages: pre-tanning, tanning, post-tanning, and finishing [2]. Soaking, lime, deliming, degreasing, bating and pickling are all processes of pre-tanning [3]. There are several kinds of tanning materials used; approximately 90% of all tanning products are composed of chromium-based tanning, while the other 10% are vegetable sources, syntans, aldehydes, oils and other minerals [4]. The post-tanning process involves neutralization, dyeing, fatliquoring, and fixation [5].

An essential step in the leather tanning process, neutralization eliminates acidity in the leather, allowing dye and fatliquoring to penetrate evenly and thoroughly and neutralizing the leather to a pH of around 5.5 - 6 [6]. Substances such as bicarbonate, borax, neutralizing syntan, sodium acetate, and sodium formate, etc are used [7]. Depending on the required pH level, neutralizing materials can be applied at a rate of up to 4% of the tanned weight. The amount often used in tanneries is a mixture of neutral chemicals, most notably formate and bicarbonate, and varies from 2 to 3 per cent. All post-tanning wastewater effluents as well as washing wastewater are gathered together. Emission statistics are therefore not accessible for every process unit. Usually, 10 - 20% of the total COD in tannery effluent comes from post-tanning processes [8].

It is important to mention that the production of each ton of rawhide or skin necessitates the use of 30 to 40 tons of water [9]. The post-tanning phase accounts for roughly 38% of the wastewater formed in the leather tanning sector and is responsible for consuming around 30% of the chemicals used [5]. In addition, the neutralizing process demands five tons of water per ton of raw skin or hide [10,11].

The research aims to substitute bicarbonate with sodium borate, sodium acetate, and sodium formate, and neutralise syntan during the neutralization phase to decrease the quantities of pollutants generated from this process, minimize the consumption of water, and improve the quality of the produced leather.

EXPERIMENTAL

Materials

All the chemicals used in the leather processing were of commercial grade and are commonly utilized in leather tanning. Sodium formate (HCOONa), bicarbonate ($NaHCO_3$), sodium borate (Na_2BO_7), and sodium acetate (CH_3COONa) were purchased from the El-Gomhouria Company, while neutralizing syntan "syntel (CX/N)" was from the Biokimica Company.

Male wet-salted sheep skins were the raw materials used in the tanning process.

Methods

The tanning processes were conducted in Sayed Hamdan tannery in Robbiki Leather City, Egypt. Fifteen sheep skins were common in the pre-tanning and tanning stages as shown in Table (1) presents the tanning techniques according to [12].

Table 1. Pre-tanning and tanning steps applied in the experiment

Step	%	Addition	Time (min)	Notes
Soaking	300 0.5 0.3	Water Soap Bactericide	30	Percentages were calculated based on soaking weight. Drum speed 1 cyc./min. Overnight then out.
Painting	80-100 g/L 100 g/L 500 g/L	Sodium sulphide Soap Lime	120	Lime may be increased to adjust the paste. The paste was applied on the flesh side and skins were piled in pairs flesh to flesh. Time may be increased till unhairing is done easily and completely.
Reliming	30 1 2 0.25	Water Sodium sulphide Lime Soap	15	Drum speed 1 cyc./min. Overnight.
Washing	300	Water	10	
Degreasing	80 1 1	Water Degreasing Agent Soap	30	Percentages were calculated based on fleshed weight. Drum speed 3 cyc./min
Washing	200	Water	10	Drum speed 3 cyc./min
Deliming	20 1 0.5 1.5	Water Ammonium chloride Soap Ammonium sulphate	30	Drum speed 3 cyc./min. Drain and Wash.
Bating	0.05	Orpone bate	60	Orpone concentration 7000 IU. Bating pH (8.5-9) Drain and wash four times
Pickling	100 10 0.25 0.6	Water Salt Soap Formic acid	15 40	Skins were drummed with water and salt for about 15 min then acids added gradually. Bé = 9 – pH 4.5.
Tanning	50 8 8 0.3 4% from Cr weight	Water Salt Chrome 33 Fungicide Magnesium oxide	10 60 10 480	Bé = 7 Check Cr penetration before adding magnesium oxide. MgO calculated from Cr weight. Overnight with 5 cyc./hour. pH = 4.2 Check the boiling test before the next step.
Wet blues horsed up for three weeks then shaving and weight leathers				

After the chrome tanning step, wet-blues were divided randomly into five groups (three wet-blues in each group). The difference among studied groups was at the naturalization step as explained in Table (2) according to [11], the percentage of neutralizing materials used in the neutralization stage was calculated, whereas Table (3) shows the post-tanning steps done on wet blues. During the neutralization step, water consumption of used water in washing tanned leathers was recorded. Additionally, the total cost of chemicals used in the tanning process was calculated for each experimental tanned leather group.

Table 2. Experimental groups due to the neutralization step

Group	Neutralizing material	Addition	Water used in washing after neutralization
Control	Sodium formate	2%	400%
	Sodium bicarbonate	0.5%	
Sodium formate	Sodium formate	2.5%	0%
Sodium borate	Sodium borate	2.5%	0%
Sodium acetate	Sodium acetate	2.5%	0%
Neutralizing syntan	Syntel (CX/N)	2.5%	0%

Table 3. Post-tanning steps applied in the experiment

Step	%	Addition	Time (min)	Notes
Neutralization	100	Water	60	The neutralizing agent changed according to the experimental group.
	0.25	Soap		pH = 5-5.5
	2.5	Neutralizing agent		Drain and wash differed according to the experimental group.
Re-tanning and dying	2	Acrylic	30	Check dye penetration by the end of the step.
	3	Phenolic syntan	60	
	3	Melamin syntan		
	3	Dye Green		
Fatliquoring	8	Synthetic oil	60	Water temperature 40 °C.
	3	Sulphonated oil		Check fat liquor in float before the next step.
Fixation	1	Formic acid	30	Drain and wash. pH = 3.5
	1	Formic acid	30	Horse up and overnight. Next day samming and drying.

Environmental Parameters

The BOD and COD contents were measured in the spent liquid obtained from the neutralization step, according to methods utilized by [13].

Tanned leather properties

The evaluation of all completed leathers included conducting several mechanical and chemical tests in accordance with ASTM standards. The specimens were conditioned to a controlled environment with a temperature of 20 ± 2 °C and a relative humidity of 65% ± 4% for 48 hours. The mechanical parameters, including density, thickness, tensile strength, elongation% at the break, split tear strength, water absorption, and permeability to water vapour, were tested using the ASTM standard protocols. The stated results were calculated as the mean of six samples, consisting of three measurements taken along the backbone and three measurements taken across the backbone. The chemical characteristics assessed were moisture content, total ash content, and pH according to [14].

In addition, a group of five experienced tanners evaluated the leathers using a scale of 1 - 10 points for each functional attribute, with greater scores indicating better quality. The mean value of the five tanners was documented for each sample [15].

Microscopic micrographs

The leather samples (1 cm^2) were obtained from the designated sampling location based on ASTM-D2813. To capture two micrographs of each sample, the novel JSZ6S Stereo Microscope was utilized at a magnification of x100, focusing on the cross-section and grain surface.

Statistical Analysis

Data were analyzed using the GLM procedure of [16] to evaluate the differences among produced leathers. Significant differences were detected using the Duncan Multiple Range Test. The following model was used in the analysis:

$$Y_{ij} = \mu + T_i + e_{ij}$$

Where Y_{ij} is the observation taken on finished leather, μ is the overall mean, T_i is a fixed effect of neutralizing group and e_{ij} is the random error assumed to be normally distributed with mean = 0 and variance = $\sigma^2 e$.

RESULTS AND DISCUSSION

Environmental Parameters

Figure (1) shows the total (COD), (BOD), and (OD) of the spent liquor for each group of experiments, obtained after the neutralization stage. Based on the results, the values exhibited variation among various neutralizing materials. Upon comparing the treated groups with the control groups, it was seen that all treatments resulted in a pollution reduction. Therefore, the control group had the greatest levels of COD and BOD. The reason for this is that the control group necessitates two washes as a result of the presence of bicarbonate, which leads to an elevation in the levels of COD, BOD, and OD. Notably, sodium borate is the least contaminated among all the treatments. Zhou et al. employed sodium acetate and sodium bicarbonate in the neutralizing stage and measured COD and BOD, which were consistent with the results found in this study [17].

Humayra et al. measured the level of pollutants in the neutralizing step's effluent and found COD (7867) and BOD (2212), which are higher than the numbers found in this study [10].

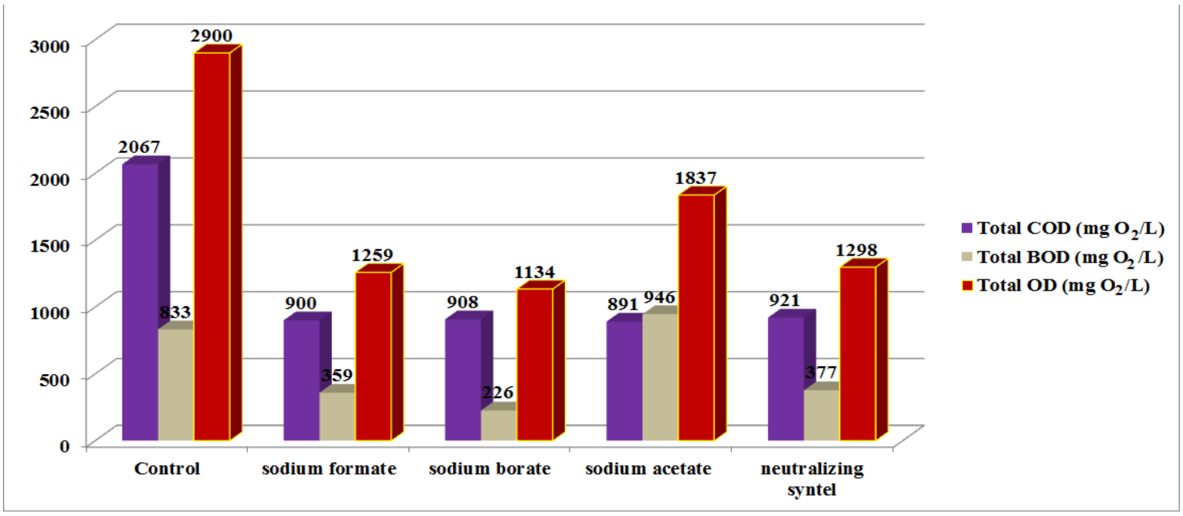

Figure 1. Total COD, BOD and OD of spent liquor after the neutralization stage

Tanned leather properties

The physical properties of the tanned leathers are presented in Tables 4 and 5, while their chemical properties are shown in Figure 2. All of the tanned leathers successfully passed the flexibility test without any damage, even after being flexed up to fifty thousand times. The differences among studied groups in all physical and chemical properties were insignificant, which indicates the similar effect of the neutralization step on tanned leather and no negative effects were found by changing the neutralization material.

In terms of leather efficiency for manufacturing purposes, the mechanical and chemical property values demonstrated the feasibility of using all tanned leathers in various manufacturing uses such as shoes, upholstery, bags, and clothing [18-21].

Table 4. Least square means ± SE of density, thickness, tensile strength, tear strength and elongation as affected by neutralizing materials

Group/Property	Density (g/cm^3)	Thickness (mm)	Tensile strength (kg/cm^2)	Tear strength (kg/cm)	Elongation (%)
ASTM	D2346	D1813	D2209	D4704	D2211
Control*	0.86 ± 0.06	0.90 ± 0.10	208.21 ± 36.81	44.72 ± 1.39	84.89 ± 6.41
2.5% Sodium formate	0.71 ± 0.04	0.95 ± 0.05	213.09 ± 46.44	43.58 ± 3.16	79.81 ± 7.68
2.5% Sodium borate	0.80 ± 0.03	0.95 ± 0.15	241.95 ± 58.80	33.11 ± 0.36	76.69 ± 1.94
2.5% Sodium acetate	0.86 ± 0.01	0.78 ± 0.03	237.43 ± 19.95	46.39 ± 4.33	68.56 ± 1.27
2.5% Neutralizing syntan	0.80 ± 0.07	0.75 ± 0.01	279.87 ± 12.17	46.53 ± 4.40	72.14 ± 6.25
Overall the means	0.80 ± 0.03	0.87 ± 0.04	236.11 ± 16.48	42.86 ± 1.97	76.42 ± 5.58
Significance	ns	ns	ns	ns	ns

*Control group neutralized by conventional method using 2% Sodium formate and 0.5% Sodium bicarbonate;
ns = not significant

Table 5. The least-square means ± SE of water absorption and permeability to water vapour (PWV) as affected by neutralizing materials

Group/Property	Water Absorption (%)		PWV
	2 hrs	24 hrs	($mg/cm^2/h$)
ASTM	D1815		D5052
Control*	248.95 ± 2.86	257.11 ± 4.77	1.86 ± 0.01
2.5% Sodium formate	215.38 ± 1.01	227.89 ± 1.97	1.80 ± 0.02
2.5% Sodium borate	212.34 ± 8.74	221.97 ± 8.13	1.81 ± 0.01
2.5% Sodium acetate	201.58 ± 7.75	219.47 ± 9.97	1.84 ± 0.02
2.5% Neutralizing syntan	211.94 ± 6.47	224.49 ± 4.12	1.80 ± 0.07
Overall all of the means	218.04 ± 7.44	230.18 ± 7.61	1.82 ± 0.01
Significance	ns	ns	ns

*Control group neutralized by conventional method using 2% Sodium formate and 0.5% Sodium bicarbonate;
ns = not significant

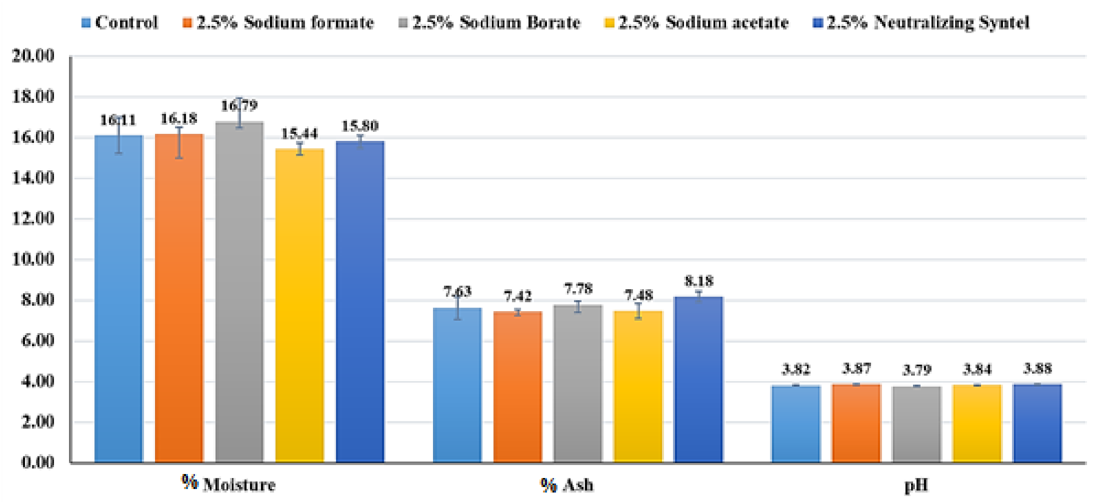

Figure 2. Chemical properties of tanned leather groups

Organoleptic properties for tanned leathers

Table (6) shows the findings of the organoleptic evaluation conducted on tanned leathers. The data indicates that the leather groups exhibit similarities in terms of fullness and grain tightness. However, it was observed that the leather neutralized with sodium acetate had the lowest level of grain smoothness, and this difference was statistically significant compared to the other leathers. On the contrary, the leather groups neutralized with sodium formate and sodium borate demonstrated superior softness and general appearance, with a statistically significant difference. Consequently, the leather neutralized with sodium borate is regarded as having the highest quality in terms of organoleptic properties, followed by the sodium formate leathers. In contrast, the sodium acetate and syntan groups exhibited lower quality, similar to the leathers in the control group.

Table 6. Organoleptic properties of tanned leather groups

Group/Property	Fullness	Grain tightness	Grain Smoothness	Softness	General Appearance
Control*	10.00 ± 0.00	8.00 ± 0.32	8.00 ± 0.32^{a}	8.00 ± 0.32 ^{b}	8.00 ± 0.32^{ab}
2.5% Sodium formate	10.00 ± 0.00	9.00 ± 0.45	9.00 ± 0.32^{a}	9.00 ± 0.32 ^{a}	9.00 ± 0.32^{a}
2.5% Sodium borate	10.00 ± 0.00	9.00 ± 0.32	9.00 ± 0.32^{a}	9.00 ± 0.32 ^{a}	9.00 ± 0.45^{a}
2.5% Sodium acetate	10.00 ± 0.00	8.00 ± 0.32	7.00 ± 0.32^{b}	6.00 ± 0.32 ^{d}	7.00 ± 0.45^{c}
2.5% Neutralizing syntan	10.00 ± 0.00	8.00 ± 0.32	8.00 ± 0.32^{a}	7.00 ± 0.00 ^{c}	7.00 ± 0.32^{c}
Overall all of the means	10.00 ± 0.00	8.40 ± 0.17	8.20 ± 0.20	7.80 ± 0.26	8.00 ± 0.24
Significance	ns	ns	**	**	**

*Control group neutralized by conventional method using 2% Sodium formate and 0.5% Sodium bicarbonate

This means that the same column with different superscript letters are significantly different (P<0.05)

Microscopic micrographs

Figure (3) presents microscopic micrographs of the cross-sections and grain surfaces of tanned leather samples from all experimental groups, magnified 100 times. The micrographs reveal a high degree of similarity between the groups, with no discernible changes in the fibre structures of the collagen bundles. This observation aligns with the measured properties of the tanned leather, suggesting that varying the neutralization material during processing did not significantly impact the microscopic structure of the leather.

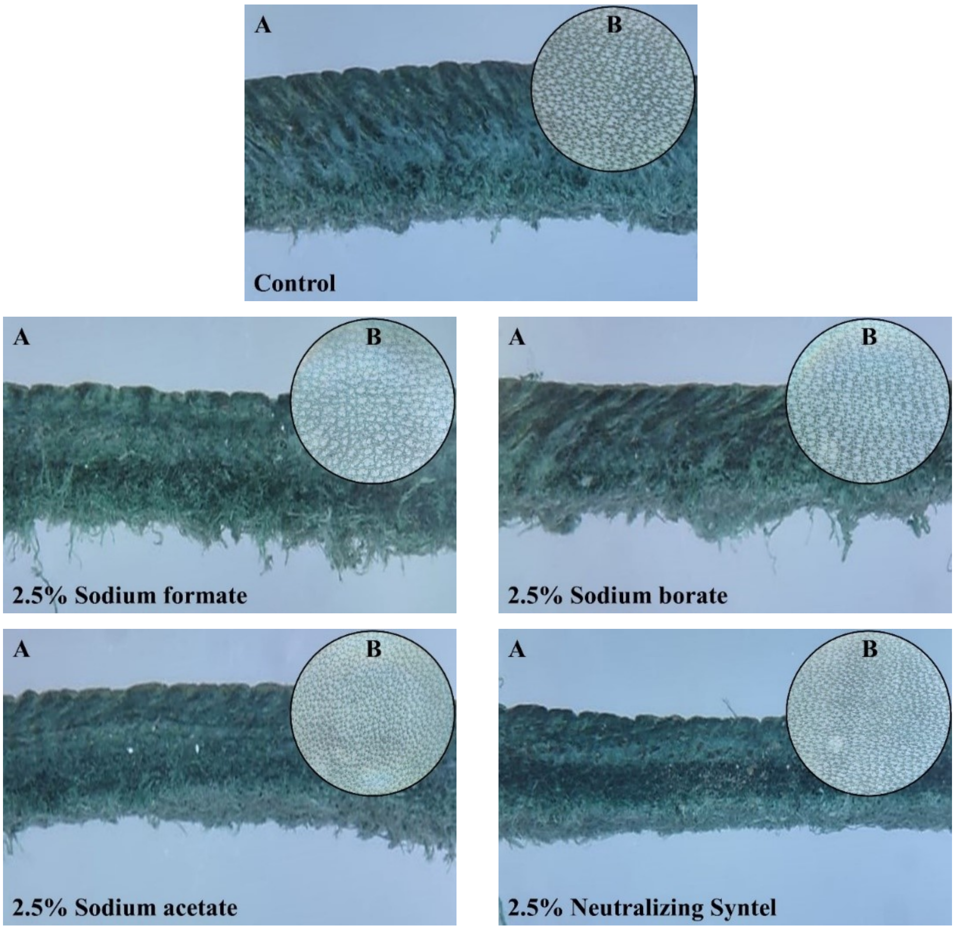

Figure 3. Micrograph depicted at x100 for all tanned leather groups; (A) cross section and (B) grain surface

Water consumption per metric ton of sheepskins

It was observed from the results of recording the water consumption during the neutralization step that the first group consumed about five times the amount of water used by the other groups. This is because sodium bicarbonate requires more water to remove [10,11]. Therefore, the use of other neutralizing agents was more effective in reducing water consumption.

Total chemical cost of leather tanning

The results of calculating the costs of the chemicals used in leather tanning in Table (5) showed that the use of sodium borate and sodium acetate were the least expensive, with production costs of $1102 and $1103 per ton of tanned sheepskins, respectively. The use of the traditional method and sodium formate had medium costs of $1109 and $1111, respectively. In comparison, the use of the commercial material, neutralizing syntan, was the most expensive by a clear margin, with a cost of $1131. Thus, using 2.5% sodium borate has proven to be the most effective neutralizing agent in reducing the costs of chemicals used in leather tanning by 0.62%.

Table 5. The costs of the chemicals used in leather tanning per ton of tanned sheepskins and the change in cost as a percentage of control group

Group	Control*	2.5% Sodium formate	2.5% Sodium borate	2.5% Sodium acetate	2.5% Neutralizing syntan
Cost ($)†	1109	1111	1102	1103	1131
%	0	0.18	-0.63	-0.54	1.98

** Control group neutralized by conventional method using 2% Sodium formate and 0.5% Sodium bicarbonate*

† The prices shown are calculated in US dollars according to the market prices in the study area

CONCLUSION

This study successfully identified effective alternatives to traditional bicarbonate neutralization in leather tanning. All substitutes resulted in a notable decrease in pollutant discharge (BOD, COD) and water consumption compared to the traditional method. Notably, 2.5% sodium borate emerged as the most promising option, achieving significant reductions in water usage (80%), total oxygen demand (39%), and neutralization chemical costs (0.62%). Importantly, the leather treated with these alternatives exhibited comparable physical and chemical properties to the conventionally produced leather, with sodium borate-treated leather demonstrating superior organoleptic characteristics. These findings offer a viable solution for the leather industry to lessen its environmental footprint while maintaining product quality.

Author Contributions

Conceptualization – Ali RM; Methodology – Ali RM, Nasr AI, El-Shemy KA, El-Khateeb MA; Formal analysis – Nasr AI; Investigation – Ali RM; Resources – Ali RM, Nasr AI, El-Shemy KA, El-Khateeb MA; writing-original draft preparation – Ali RM; writing-review and editing– Nasr AI; Visualization –Ali RM; Supervision – Ali RM, Nasr AI, El-Shemy KA, El-Khateeb MA. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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