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Utilizing Some Synthesized Nanostructured Materials to Improve The Functional Properties of Cotton Fabric for Possible Applications

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THE potential of the synthesized Copper Oxide (CuO) and Graphene Oxide (GO) nanostructures as an efficient modifier for cotton fabric surface, to enhance its functional properties when dyed with C.I. Reactive Yellow 160 (RY 160) was investigated. For this purpose, Copper Oxide nanoparticles (CuO NPs) and Graphene Oxide nanoparticles (GO NPs) were synthesized and characterized through SEM, and EDX analysis, TEM analysis, FTIR spectrum analysis and X-ray diffraction (XRD) analysis. The cotton fabric was first treated separately with CuO NPs and GO NPs, and then dyed with RY160. The dye exhaustion percentages (E%) of pretreated cotton fabric samples were compared with their corresponding values obtained through conventional dyeing of untreated cotton. Dye adsorption rate constants according to pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic models were calculated. Moreover, the diffusion coefficients and the activation energy of diffusion of RY160 into cotton fabrics were calculated before and after NPs treatment. The activation energy of diffusion of RY160 into pretreated GO NPs-cotton fabric was the lowest value, saving 44.06% of the energy required for conventional dyeing completion. The overall adsorption process follows pseudo-second order kinetics and intraparticle diffusion model. The corresponding thermodynamic parameters, namely enthalpy (^{0}), entropy (), and free energy changes (), were also calculated for untreated cotton fabric and compared with the data obtained for treated cotton fabrics after surface modification via synthesized nanomaterials, CuO NPs and GO NPs. The NPs treatment produces a cotton fabric with advanced color fastness and antibacterial properties enabling them to improve human health care and decrease the environmental impacts and fabric damage.

Keywords: Copper Oxide nanostructures, Graphene Oxide nanostructures, SEM, TEM, Kinetic models, Antibacterial properties.

Introduction

With the growth in world population and the spread of diseases, the number of antibiotic-resistant microorganisms is rising along with the resonance of infections from these microorganisms. Textiles can provide suitable substrates for the growth of micro- organisms [1]. The major problem in health care especially in hospitals is the transmission of bacteria and pathogens from the patients to the workers and vice versa through the textile's usage and handling. Antimicrobial properties of the textiles can be developed by introducing antimicrobial agents through surface modification process, [2]. The use of antimicrobial agents for the modification of textiles has been limited due to their toxicity, need of complex post-treatment processes, and environmental pollution [3,4]. To overcome these downfalls, several researches have been attempted in the recent decades for using nanostructure materials (1–100 nm) for textile surface modification with multifunctional properties due to their ability to sense and detect pathogens [5].

The nanostructure materials such as CuO, GO, Ag, ZnO, and TiO_2 have been effectively embedded to the textile fabrics by several surface modification processes such as dip coating, sono-chemical method, sol-gel method, chemical reduction method, pad-dry-cure method and sputtering of nanoparticles using plasma polymerization [6]. Not only are the significant advantages of using nanostructure materials for the preparation of antimicrobial textiles limited to the antibacterial property, but also, they improve the thermal stability of the textile fabric, developing photo catalytic property in the textiles, which can deprive the growth of organic contaminants in the textiles leading to the self- cleaning property [7].

In the conventional dyeing process of cellulose, a large amount of energy and a large quantity of salt are consumed causing fabric damage, pollution of rivers and streams, and upsetting the biological equilibrium. On the contrary, the treatment of cellulose fabric with inorganic nanoparticles before dying process proved to be more rapid, uniform, efficient, while also increasing the dye affinity and improving the fastness properties of cotton fabric towards washing, light, rubbing and perspiration. It is considered a better alternative to the conventional dyeing technique due to the reduction of environmental impact, and energy consumption [8].

Most of the research efforts focus primarily on highlighting the properties that the treated fabric gains from the nanomaterial's treatment stage, such as the fastness properties or the antimicrobial activity, ignoring some extent the discussion of the chemistry of the dye-fabric interaction from the viewpoint of kinetic and diffusion approaches. This work discussed all the aforementioned characteristics, and on top of that it offers a detailed description of the mechanism of the dyeing process which enables the calculation of the amount of energy that can be saved by treating the fabric. To quantify this amount of energy the kinetics and diffusion mechanisms in addition to the thermodynamic parameters had to be studied, and this by turn allowed the dyeing process to be described in depth and details [9].

Materials and Methods

Materials:

Cotton fabric

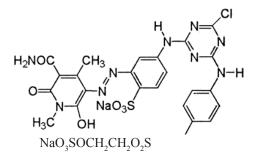Cotton fabric supplied by Misr Helwan Company was, scoured in aqueous solution containing 5% of sodium dodecyl sulfate at 50°C

for an hour to remove waxes and impurities, then rinsed thoroughly in distilled water and dried at room temperature.

Reactive dye

Reactive Yellow160 was kindly supplied by New Trend Co. Egypt the chemical structure of RY160 was shown below:

Chemicals

All chemicals used, were purchased with high purity from Merck Darmstad, Germany. Graphite fine black powder At.W.(12.01) from CDH company was used.

Experimental Techniques

Synthesis of copper oxide and graphene oxide nanostructure

Copper Oxide nanoparticles (CuO NPs) were synthesized through the simple economic aqueous precipitation method [10]. While Graphene Oxide nanoparticles (GO NPs) were synthesized according to the modified Hummer's method [11]. The synthesized Nano metal oxides will later be characterized to confirm their Nano size.

Surface modification process of cotton fabric using synthesized CuO and GO nanostructures

CuO nanostructures were applied on cotton fabric using pad- dry cure method [12]. In this method the cotton Fabric was cut to the size of 30x30 cm and was immersed in the solution containing 2% of synthesized CuO nanostructures and acrylic binder 1% for 5 mins to assist the adhesion of synthesized CuO nanostructures to cotton fabric surface. The fabric was air dried and then cured for 3 mins at 140, then was immersed for 5 mins in 2 (g/l) of sodium lauryl sulfate to remove unbound nanoparticles. Afterwards, the fabric was rinsed in distilled water at least 10 times to completely take out all the soap solution then dries simultaneously.

While the surface modification of cotton fabrics by GO nanostructures was achieved

using a dip coating approach via stirring [13]. Briefly, the cotton fabric (3x4 cm dimensions) was immersed into the solution containing 0.25 (g) of synthesized GO nanostructures in water and allowed vigorous stirring at 300(rpm) for 24 (hrs.). After that, the GO-coated fabric was taken from the solution and washed twice with distilled for removing the residual GO from the surface. The resulting fabric was allowed to dry at 35for 1 day in a vacuum desiccator.

Dyeing procedures of untreated and pretreated cotton fabrics withRY160

Untreated and pretreated cotton fabrics were dyed with RY160 by applying batch technique under the dyeing recipe: dye concentration 100(ppm), Liquor ratio (LR) 0.2: 20, Sodium Sulphate SS 50(g/L), Sodium Carbonate SC (25) g/L, pH 10, time120(min) and temperature 50,60,70,80,90 ºC.

At the end of dyeing, both the initial and equilibrium dye bath concentrations were measured with an UV-vis spectrophotometer (Model T60, United Kingdom) at $\lambda_{max} = 425nm$,to be ready for calculation of the percentage of dye exhaustion (E%) .The dyed samples were removed, and rinsed in distilled water to remove the loosely fixed dye on the surface of dyed fabric, and were allowed to dry in the open air to be ready for the determination of cotton fabric properties. The percentage of dye exhaustion (E%) was calculated by using the equation:

$$E \% = \frac{C_0 - C_e}{C_0} \times 100$$

where C_0 is the initial dye concentration, C_e is the dye concentration at equilibrium

Surface Characterization

Field Emission Scanning Electron Microscope (FE-SEM), EDX analysis, Transmission Electron Microscope (TEM), Fourier Transform Infrared-spectroscopy (FTIR) and Diffraction analysis (XRD) Measurements were used for surface Characterization

Determination of cotton Fabric Properties
  Color Fastness properties
The untreated and pretreated dyed cotton samples at dyeing recipe were tested for various fastness properties such washing, light and perspiration according to ISO standard test methods [14].

Antibacterial investigation:

Six cotton samples were selected for antibacterial test. The antibacterial activity was quantitatively evaluated against Staphylococcus aureus, a Gram-positive organism, and *Escherichia coli*, a Gram-negative organism, in accordance with AATCC 100 test method using nutrient agar and an incubation period of 24 hours at 37. Colonies of bacteria recovered on the agar plate were counted, and the reduction percentage of bacteria, R (%), was calculated [15,16] using the following equation:

$$R (\%) = \frac{B-A}{B} \chi 100 \qquad (2)$$

where A is the number of bacteria colonies from treated specimen after inoculation over 24 hours contact period and B is the number of bacteria colonies from untreated control specimen after inoculation at 0 contact time.

Results and Discussions

Characterization of synthesized nanostructure materials

  Characterization of synthesized GO nanostructures

  SEM and EDX analysis
The SEM images of synthesized GO NPs, untreated cotton fabric, and pretreated GONPs-cotton fabric, were shown in figure (1 a, b, c) respectively. GO nanostructure representing the sheet like morphology. It also resembles that some of the particles look aggregated. The aggregated morphology of GO NPs may be due to the strong interaction between oxygenated functional groups in the multilayered GO NPs.

Figure (2) illustrates EDX analysis of GO nanostructure. The strong peaks observed in the spectrum related to carbon and oxygen have the weight percentages of 71.85% and 27.91%, respectively. These results confirm the successful synthesis of GO NPs.

  TEM analysis
The diameter distribution of GO NPs were evaluated by TEM analysis figure (3) .

The average particle size of synthesized GO NPs was found to be 50 nm.
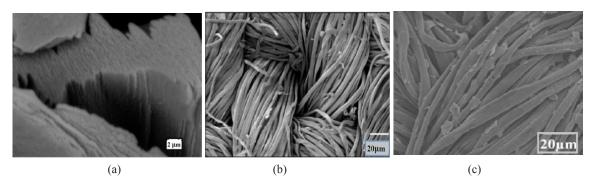
(a)   (b)   (c)

Fig. 1. SEM images of (a) Synthesized GO NPs, (b) the surface of blank cotton fabric and (c) the pretreated GONPs-cotton fabric.

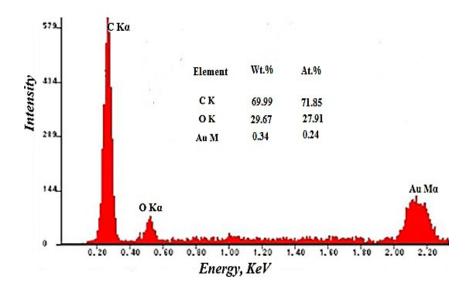| Element	Wt.%	At.%
C K	69.99	71.85
O K	29.67	27.91
Au M	0.34	0.24

Fig. 2. EDX spectrum of Synthesized GO nanostructures.

Fig. 3. EM analysis of Synthesized GO nanostructures

FTIR spectrum analysis

The various functional groups present in the GO NPs were confirmed by using Fourier transform infrared (FTIR) spectroscopy as shown in figure (4). The peak at 1600 cm−1 arises due to the C–C vibrations from the graphitic domains [17]. The relatively broad peak at 3260 cm^{-1} is due to the adsorbed water content in the surface of GO NPs [18]. The adhesion of GO NPs to the cotton fabric was recorded and compared with the untreated cotton fabrics as shown in figure (5). The FTIR spectra ensure that GO NPs were loaded onto the cotton fabric successfully [17].
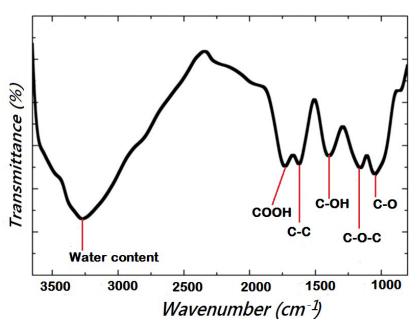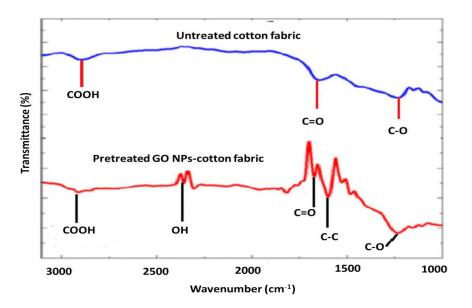

Fig. 4. FTIR spectra of synthesized GO NPs.

Fig. 5. FTIR spectra of untreated and pretreated GO NPs- cotton fabric.

X-ray Diffraction analysis

XRD of the untreated cotton fabric and pretreated GO NPs- cotton fabric was shown in figure (6). Peaks at 16.52°, 22.82° and 34.58° correspond to cotton fabric molecular structure. The small peak corresponding to graphite (002) at 25.5° was appeared accounting the successful loading of cotton fabric by GO NPs, as clearly shown in inset and show good agreement with the previous report [19,20].

Characterization of Synthesized CuO nanostructure

SEM and EDX analysis

The SEM images of synthesized CuO nanostructures, and pretreated CuO NPS- cotton fabric are illustrated in figure (7,8) respectively. The pretreated cotton fabric presents a granular surface appearance, which might be due to the layers of copper nanoparticles coated the cotton fabrics.

The EDX analysis of CuO nanostructures was shown in figure (9). EDX results have confirmed the presence of copper and oxygen elements by the weight percentage 55.71% and 44.29%, respectively reflects the successful synthesis of the CuO NPs.

TEM analysis

The particle size of CuO NPs was obtained by TEM analysis figure (10), the distribution ranges of CuO NPs were approximately from 5 nm to 50 nm. This indicated that the synthesized CuO NPs were a narrow distribution of diameters and the average particle size approximately 50 nm was of achieved [21].
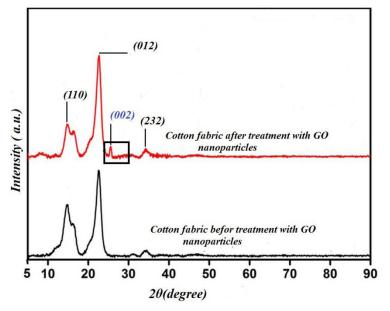

Fig. 6. XRD patterns of untreated and pretreated GO NPs-cotton fabric.
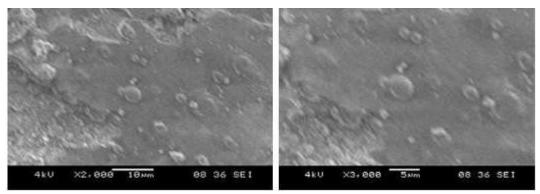

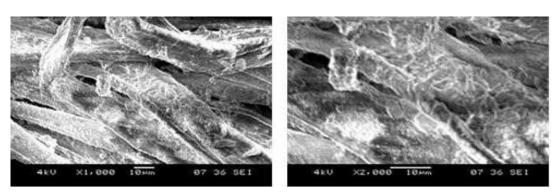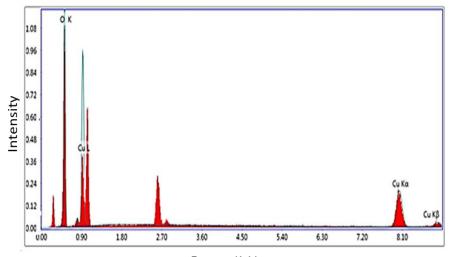**Fig. 7. SEM image of Synthesized CuO nanostructures.**

Fig. 8. SEM image of pretreated CuO NPs- cotton fabric.

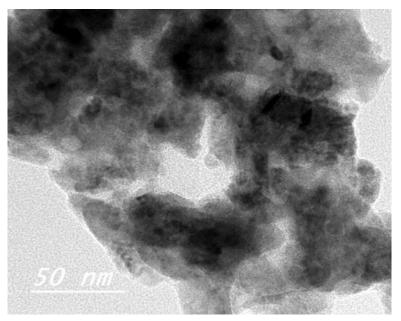**Fig. 9. EDX spectrum of Synthesized CuO nanostructure**

Fig. 10. TEM analysis of synthesized CuO nanostructures.

FTIR spectrum

FTIR spectrum of the CuO NPs and pretreated CuO NPs -cotton fabric is given in figure (11). The spectrum (b) of the CuO NPs-cotton fabric contains the peak stretches found in the cotton fabric confirming the presence of CuO NPs in the cotton fabric [22].

X-Ray Diffraction analysis

The XRD spectrum of pretreated CuO NPs -cotton fabric was shown in **figure (12),** the three peaks situated at 43.38°, 50.52°, and 74.25° are observed. Those peaks are assigned to the diffraction of the (111), (200), and (220) lattice planes of the Cu. This statement suggests that

the grafting of CuO NPs on cotton fabric did not change the basic structure of the treated cotton fabric.

Dyeing kinetics

Time-exhaustion isotherm of pretreated CuO NPs-cotton fabric using RY160 was shown in figure (13). The figure shows that the exhaustion% of RY160 onto pretreated CuO NPs- cotton fabric (78.85%) is generally better than that obtained by using untreated sample (72.32 %) under the same conditions. This may be attributed to the ability of CuO NPs to form a thin layer onto cotton fabric during pre-treatment stage [23].
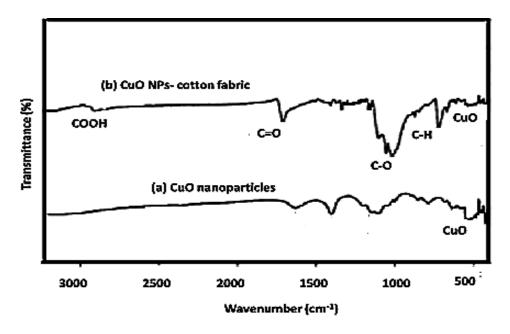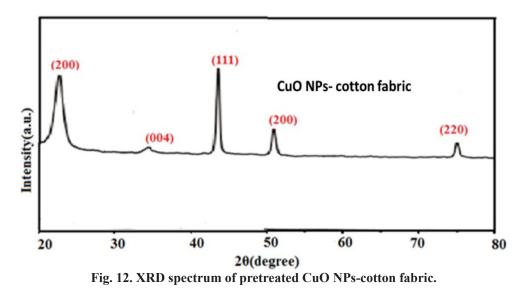

Fig. 11. FTIR spectrum of synthesized CuO nanoparticle and pretreated CuO NPs-cotton fabric.

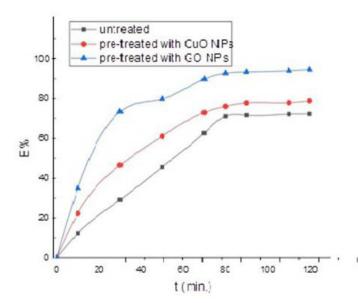**Fig. 12. XRD spectrum of pretreated CuO NPs-cotton fabric.**

Fig. 13. Time-Exhaustion isotherms of RY160 dye adsorption onto untreated, pretreated CuO NPs-cotton fabric and pretreated GO NPs-cotton fabric. [dyeing recipe: LR 0.2:20, 100ppm, pH = 10, SS 50 (g/l), SC 25 (g/l), 90°C].

The figure also shows that the E% of RY160 onto pretreated GO NPs-cotton fabric is noticeably better scoring 94.50% as compared to that obtained by using both untreated sample 72.3 % and pretreated CuO NPs-cotton fabric 78.85 % under the same conditions of the selected dye recipe. This is generally attributed to the successful coverage of the surface area of cotton fabric by Nano GO sheets which result in rising both the loading amount and degree of exfoliation-dependent hydrophobicity that enlarged present in the rose petals and lotus leaf on the textile substrate, which maximizes and accelerate the adhesion of the dye to the cotton fabric surface [24-26].

In order to examine the mechanism and rate-controlling step in the overall adsorption process, three kinetic models, pseudo-first-order, pseudo-second-order and intra-particle diffusion, are adopted to investigate the dyeing kinetics of cotton fabric with RY160 in absence and presence of synthesized nanostructured materials at different temperatures.

Pseudo-First-Order kinetic model
A simple kinetic analysis of adsorption is the Lagergren equation [27,28], a pseudo-first-order type, written as follows:

$$Ln(q_e-q_t) = lnq_e - k_1t \quad (3)$$

Where, k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), q_e and q_t were the amount of dye adsorbed on cotton fabric (mg/g) at equilibrium and at time t

The parameter can be calculated at different temperatures from the slopes of the plots of ln (q_e-q_t) versus t, and listed in table (1), its corresponding $R^2 < 0.90$. This suggests that the pseudo-first-order kinetic model is not suitable to describe the adsorption process.

Pseudo-Second-Order kinetic model
The pseudo-second-order kinetic model is another important model to investigate the kinetic of adsorption of dyes on textile materials.

The pseudo-second order kinetic model can be expressed in linear form as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 \, q_e^2} + \frac{t}{q_e} \quad (4)$$

where (g/mg min) is the pseudo-second-order rate constant. The values can be obtained from the slopes and the intercepts of plots of t/q_e versus t, which are listed in table (1). The correlation coefficients R^2 higher than 0.99 suggest that adsorption of RY160 onto untreated and pretreated cotton fabric predominantly follows the pseudo-second order kinetic model [29].

The pseudo-second order rate constants for adsorption of RY160 onto the untreated and pretreated cotton fabric show a steady increase with an increase in the solution temperature from 323 to 363 K as shown in table (1). In conventional physisorption systems, increasing the temperature usually increases the rate of approach to equilibrium.

Intraparticle diffusion model

Intra-particle diffusion can be expressed by following equation:

$$q_t = k_p t^{1/2} + C \qquad (5)$$

Where (mg/g) is the amount of RY160 adsorbed at time t, (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant obtained from the slope, of the plot of versus/shown in figure (14). The plots were linear over a detectable time range but with marked deviation from the origin; this indicates that the intra-particle diffusion is not only the rate controlling step, but also some other processes may control the rate of dye adsorption [30]. The intraparticle diffusion rate constant k_p and C are given in table (1). The intra-particle diffusion rate constants k_p increase with rising temperature because increasing temperature results in an increase of the driving force, which will increase the diffusion rate of RY160.[31]. . While the C value gives an indication of the thickness of the boundary layer. The larger C shows greater boundary layer effect that account greater contribution of the surface sorption in the rate-limiting step [32].

Diffusion coefficients and activation energy of diffusion

The dyeing process is a solid/liquid phase process, which commences by the movement of the dye molecules from liquid phase to the solid surface of the fabric by virtue of their affinity, and then diffusion takes place inside the fabric. Therefore, the first process would be a rapid adsorption-controlled process where the dye molecules get into the fabric, the second slow process, which is diffusion controlled, starts to take place. [33]. From Hill's equation, (6), the diffusion coefficients were calculated.

$$D = (\pi r^2/16t)(C_t/C_e)^2 \qquad (6)$$

Where C_t and C_e represent the dye concentrations in solution at time t and at equilibrium respectively; r is a radius of the cylindrical fabric (cm)

It can be concluded from data in table (1) that as the temperature of dyeing increases, the diffusion coefficient also increases which reflects the capability of fabrics to hold dye molecules within its polymeric matrix at higher temperatures. The appreciable high values of diffusion coefficients of RY160 onto pretreated GO NPs - cotton fabric for all temperature range may be due to the amphiphilic property of synthesized GO that impart both hydrophilic and hydrophobic functional groups to the cotton fabric sheets that facilitates the diffusion of RY160 into it.[34]

The activation energy of diffusion of RY160 into untreated and pretreated cotton fabrics was calculated by equation (7).
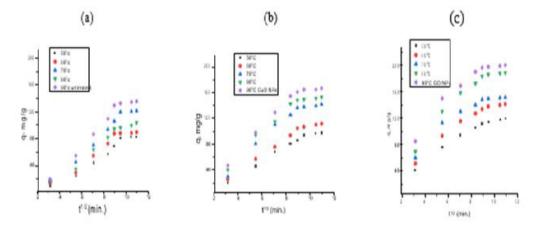
$$\ln D = \ln D_o - (E_D/RT) \qquad (7)$$

Fig. 14. Intra-particle diffusion kinetics of of RY160 into (a) untreated cotton(b) pretreated CuO NPs – cotton fabric (c) pretreated GO NPs – cotton fabrics at various temperatures. [Dyeing recipe: LR 0.2:20, pH=10, 100 ppm, SS 50(g/l) , SC 25(g/l].

TABLE 1. Kinetic, thermodynamic and diffusion parameters of the dyeing process of RY160 onto untreated, pretreated CuO NPs and pretreated GO NPs -cotton fabrics at different temperatures.

Sample	Temperature °K	Pseudo first-order model		Pseudo second-order model		Intraparticle Diffusion model			Thermodynamic parameters					$D \times 10^{-6}$ (cm²sec⁻¹)	ED (KJ mol⁻¹)
		$k_1 \times 10^2$ min⁻¹	r^2	$K_2 \times 10^4$ g cotton/ mg min	r^2	Kp mg (g min)⁻¹	C mg g⁻¹	r^2	ΔH^0 (kj/mol)	ΔS^0 (KJ/mol)	ΔG^0 (kj/mol)				
Untreated cotton fabric	323	2.34	0.86	0.57	0.99	9.03	-5.78	0.98			10.79			3.24	
	333	2.59	0.80	0.60	0.99	12.79	-24.67	0.99			10.89			3.32	
	343	2.76	0.08	0.64	0.99	15.33	-25.88	0.99	7.56	-10.16	10.99			3.38	7.58
	353	3.05	0.86	0.75	0.99	15.84	-30.96	0.99			11.09			3.90	
	363	3.83	0.89	0.78	0.99	18.90	-36.93	0.98			10.19			4.14	
Pretreated CuO NPs-cotton fabric	323	3.23	0.84	2.01	0.99	10.33	-3.31	0.99			7.59			4.22	
	333	3.81	0.85	3.02	0.99	13.02	-6.16	0.99			7.69			4.56	
	343	4.00	0.82	3.75	0.99	16.55	-10.36	0.98	6.29	-4.22	7.79			4.75	6.33
	353	4.54	0.86	4.57	0.99	18.19	-8.549	0.99			7.89			5.35	
	363	4.64	0.86	7.20	0.99	20.53	-16.37	0.99			7.99			5.76	
Pretreated GO NPs-cotton fabric	323	4.03	0.84	1.84	0.99	12.50	4.00	0.99			2.58			7.05	
	333	4.08	0.86	4.44	0.99	15.90	8.63	0.99			2.68			7.40	
	343	4.66	0.83	9.03	0.99	17.50	17.82	0.99	1.61	-3.41	2.78			9.34	4.24
	353	4.76	0.88	9.51	0.99	20.06	26.46	0.97			2.88			9.51	
	363	4.78	0.83	9.991	0.99	22.23	35.64	0.99			2.98			9.57	

Where D_0 is a constant, E_D is the activation energy of diffusion (kJ mol^{-1}), R is the gas constant 8.314 (J mol^{-1} K^{-1}) and T is the absolute temperature (^{0}K).

The activation energy of the diffusion was obtained from the slope of the linear relationship of ln D against 1/T for the three cotton fabric samples, figure (15). The activation energy of diffusion of RY160 into pretreated GO NPs-cotton fabric was the least saving 44.06% of the energy required for conventional dyeing completion table (1), reflecting the successful grafting of the surface of cotton fabric with these nanostructures and the economic benefits of the treatment process of cotton fabric.

Dyeing Thermodynamics

To establish a criterion for determining the feasibility or spontaneity of the dyeing process the chemical thermodynamic parameters had been examined.

The enthalpy ΔH^0 and entropy ΔS^o were calculated using equation (8)

$$\ln Kc = \Delta S^o/R - \Delta H^o/(RT) \quad (8)$$

where the values of ΔH^o and ΔS^o can be determined from the slope and intercept of the plot of ln Kc versus 1/T figure (16) **.**

Gibbs free energy change, ΔG^0, can be calculated in terms of enthalpy and entropy as in the following equation (9) [35]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

As can be seen from the data in table (1), all magnitudes of enthalpy change indicate that the adsorption is physical in nature. In addition, the enthalpy change had a positive value indicate the endothermic nature of the overall dyeing process. The entropy change shows negative values, indicates that the adsorbed dye RY160 become more ordered within cotton fabric sheet than the dye in solution [36]. The data also show that the positive ΔG^0 values suggest that the adsorption of RY160 dye onto untreated and pretreated cotton fabrics require energy to achieve the dyeing process accounting the endothermic and spontaneous nature of the overall dyeing process.

Determination of cotton Fabric Properties
Color Fastness properties

The results in tables (2) indicate very good to excellent color fastness grade for cotton pretreated with GO NPs; good for the cotton pretreated with CuO NPs and poor for untreated sample towards washing, light and perspiration. The data assist the important requirement for comfort properties which base the fundamental of medical fabrics. In general, the results give very good indication for enhancement the functionality of cotton fabric with nanomaterials that became a smart treatment applied as a novel approach to textile dyeing and
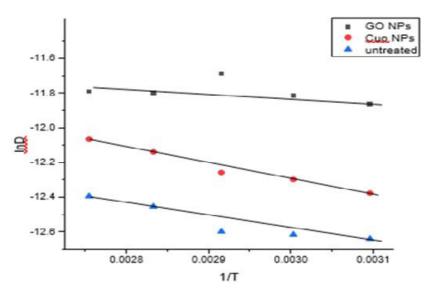

Fig. 15. Relation between lnD and 1/T for determination of activation energy of RY160 diffusion into untreated, pretreated CuO NPs and pretreated-GO NPs cotton fabric.
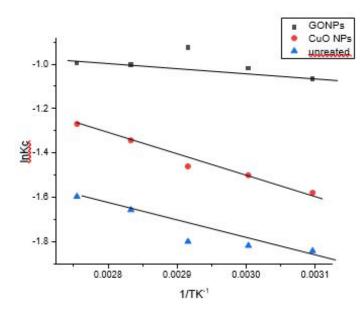
Fig. 16. Variation of ln K$_c$ with 1/T (^{O}K^{-1}) for estimation of the enthalpy and entropy of RY160 onto untreated, pre-treated CuO NP sand pretreated GO NPs-cotton fabrics.

finishing [37].

Evaluation of antibacterial activity of different cotton fabric samples:

The quantitative results for the evaluation of antibacterial activity of the six cotton fabric samples are shown in figure (17). It is easily noticed that the untreated cotton sample (sample 1) shows clear growth of bacteria, which reflects that almost all the bacteria were alive after 24 hours with zero R %. On the other side, the dyed untreated cotton sample (sample 2) exhibits slightly higher antibacterial activity against the Gram- negative and Gram-positive bacteria, respectively. This may be attributed to the presence of various functional groups in RY160 dye which can act as bacterium cells in acidic medium [38]. Withrespect tosamples3and4, higher values of antibacterial activity against*S. aureus* and *E. coli*were recorded when compared to the untreated fabric samples, 1and 2. This is because of the improved bioactivity due the higher surface area to volume ratio of the smaller CuO nanoparticles that generates larger number of active oxygen species fromCuO onto the surface of the colony, which kills bacteria more effectively [39].

The antibacterial activity of the GO-coated fabric samples shows outstanding toxicity towards Gram-positive bacteria compared to the Gram-negative ones with different nature of their cell walls [40] Furthermore, the chemical composition of GO nanoparticles, which contain several oxygenated functional groups such as carbonyl, carboxyl, and epoxy groups on their surfaces, facilitates their binding to the bacterial cell walls and damage them. Last but not least, the role of reactive oxygen species product by GO when exposed to UV and/or VIS, contributes to the antibacterial activity of the GO-coated cotton fabrics along with the excess action of the dye RY160 functional groups

Conclusion

This research was conducted to examine the effect of treating cotton fabric with CuO NPs and GO NPs, prior to the dyeing process, on producing functionalized cotton fabrics. CuO and GO nanostructures were successfully coated onto the cotton fabrics using a facile method, which is confirmed from the data of characterization analysis. Comparing the results, the dyeing of nanoparticles-pretreated cotton fabrics with RY160 at different temperatures can be regarded as an eco-friendly alternative to conventional dyeing without

TABLE 2. Fastness properties of untreated and NPs-treated dyed cotton fabric at various temperatures.

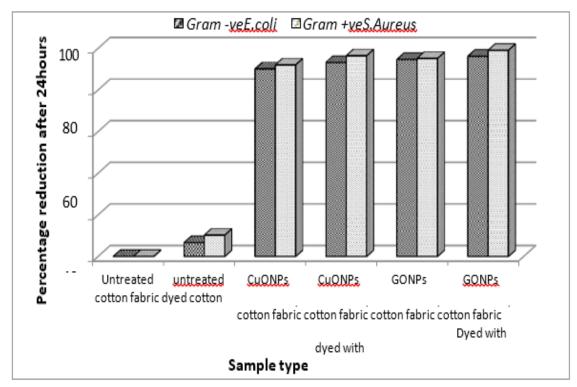| Temp °C	Untreated Cotton Fabric				Pretreated CuO NPs-cotton fabric				Pretreated GO NPs-cotton fabric			
	Washing	Light	Perspiration		Washing	Light	Perspiration		Washing	Light	Perspiration	
			Acid	Alkali			Acid	Alkali			Acid	Alkali
50 °C	3	4	3	3	4	4-5	4-5	4-5	4-5	5	4-5	4-5
60 °C	3-4	4	3-4	3-4	4-5	5	4-5	4-5	4-5	5	4-5	4-5
70 °C	4	4-5	3-4	3-4	4-5	5	4-5	4-5	4-5	5-6	4-5	4-5
80 °C	4	4-5	4	4	4-5	5	4-5	4-5	5	6	5	5
90 °C	4	4-5	4	4	4-5	5-6	4-5	4-5	5	6	5	5

Fig. 17. Antibacterial activity of cotton fabrics towards *E. coli* and *S. Aureus.*

adding any polluting auxiliary agents.

Detailed description of the dyeing adsorption mechanism was investigated by the evaluation of some kinetic parameters, such as pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models, and was further verified by saving 21.20% and 41.95% from the activation energy required for dyeing the untreated cotton when CuO NPs and GO NPs were employed for coating cotton fabrics, respectively.

In conclusion, the dyeing process was determined to be endothermic with a physical nature, which is supported by the positive values of the enthalpy change. Moreover, the nanostructure materials-finished cotton fabric demonstrated proper fastness properties and antimicrobial activity.

To sum up, the pretreatment of cotton fabric using CuO NPs and GO NPs is a very promising, simple, and practical method for achieving textile with great resistance to bacterial infection and excellent to very good fastness properties.

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استخدام بعض تراكيب المواد النانوية المحضرة لتحسين الخواص الوظيفية لنسيج القطن للتطبيقات الممكنة

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تتلخص النتائج التي تم التوصل اليها الي :

تم دراسة قدرة بعض اكاسيد المواد النانونية المحضرة مثل اكسيد النحاس واكسيد الجرافين لتحسين خواص نسيج القطن عند صباغته بالصبغه النشطه الصفراء ١٦٠ ولهذا الغرض تم تحضير اكسيد النحاس النانوميتري بطريقة الترسيب المائي من كلوريد النحاس ثنائي جزيئات الماء كمصدر لأيونات النحاس, وهي عملية سهلة ومنخفضة التكلفه بينما تم تحضير اكسيد الجرافين النانوميتري بطريقة هامر المعدلة. تلي ذلك توصيف المواد النانونيه المحضرة باستخدام تقنيات متعدده منها الميكرسكوب الإلكتروني الماسح والميكرسكوب الإلكتروني النافذ وتحليل الطاقة المشتت بالأشعة السينية وتحليل قياسات الطيف المرئي بالإضافه لقياسات التحليل بإستخدام الأشعة تحت الحمراء.

تمت معالجة نسيج القطن بالأكاسيد النانونيه المحضره كلا على حده ثم صباغته بالصبغه النشطه الصفراه ١٦٠ ومقارنة نسب استنفاذ الصبغه لعينات الأقمشه القطنيه المعالجه بالقيم المقابله لها والتى تم الحصول عليها من خلال الصباغه التقليديه للقطن الغير معالج وتم حساب ثوابت معدل أدمصاص للصبغه ومدى تطابقها مع معدلات التفاعل الرتبه الاولى الكاذبه ,والرتبه الثانيه الكاذبه ومعادلة انتشار   intraparticle. علاوه على ذلك تم حساب معاملات الانتشار وطاقة تنشيط الصبغه داخل نسيج القطن قبل وبعد معالجته قيمة طاقة تنشيط الانتشار للصبغه النشطه الصفراء ١٦٠ داخل نسيج القطن المعالج بأكسيد الجرافين النانونى كانت الاقل توفير فى الطاقه بنسبة ٤٤,٠٦ من الطاقه الازمه لأستكمال الصباغه التقليديه . تطابقت عملية الأدمصاص مع تفاعلات الرتبه الثانيه الكاذبه وميكانيكية الأنتشار.   intraparticle

تم حساب الدوال الديناميكيه الحراريه وهى (الأنثالبى - الأنتروبى – طاقة الحبس الحره) للنسيج القطنى غير المعالج ومقارنته مع النتائج التى تم الحصول عليها للأقمشه القطنيه المعالجه بعد التعديل السطحى بالمواد النانونيه . تنتج المعالجه النانونيه نسيجا قطنيا ذو ثبات للألوان وخصائص مضاد للبكتريا مما يمكنهم من تحسين الرعايه الصحيه للأنسان وتقليل الأثار البيئيه وتلف النسيج.