109

Egypt. J. Chem. **Vol. 65,** No. 2 pp. 357 - 368 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Green Synthesis of copper Nanoparticles: Synthesis, Characterization and their application: About Future

Rania S. A.[a], Elshimaa H. Gomaa [b], Emam A. G.[a,b,] *, A.M. Daher [a,b,] **

[a] *PhD student , Benghazi University , Benghazi- Libya*

[b] *Chemistry Department, Faculty of Science, Al-Azhar University (Girls), Postal code: 11754 Nasr City, Cairo, Egypt.*

Abstract

In the present study copper oxide nanoparticles (CuNPs) were synthesized via simple and eco-friendly green route using black tea extract . Characterization of synthesized nanoparticles (NPs) was undertaken. The characteristic absorption peak of CuNPs was in range (352-355) nm in UV–Vis spectrum. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies revealed the morphological and structural character of green NPs. The particle size was 25-50 nm. Energy dispersive spectroscopy (EDX) showed high intense metallic peak of copper (Cu), oxygen (O), carbon (C) and low intense peaks of phosphorus (P) , calcium (Ca) , sulfur (S), potassium (K) elements due to the capping action of biomolecules of plant extract in CuNPs formation. The X-ray diffraction (XRD) pattern showed distinctive peaks corresponding to (200), (220) and (311) planes revealing the high crystalline nature of synthesized CuNPs . The dyeing behavior of green CuNPs treated fabric with Acid Black 172 (AB 172) has been studied and the build up of dye, measured as exhaustion percentage (E%). Dye adsorption rate constants according to pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic models were calculated. Moreover, the dye adsorption equilibrium data were fitted well to the Freundlich isotherm rather than Langmuir isotherm. The overall adsorption process follow pseudo-second order kinetics, Intraparticle diffusion and Elovich model. The CuNPs treatment produces a nylon fabric with advanced color fastness and antibacterial properties enabling them to improve human health care and reducing temperature, the environmental impacts, fabric damage, amount of dyestuff used and saving energy of conventional dyeing of nylon fabrics. This review focuses on green synthesis of CuNPs using environmentally benign reagents in minimal time paves the way for future studies on CuNPs toxicity without risking interference from potentially toxic reagents and capping agents. The use of this technique to treat nylon fabric may lead to new coloration technique and other functional improvement.

Keywords: green synthesis , copper nanoparticles, nylon fabric, acid black 172 , antimicrobial, dyeing process.

Introduction:

Currently, nanotechnology has gained considerable attention due to unique properties attributed to the size distribution and morphology of nanoparticles (NPs). Nanotechnology has found a wide acceptance in numerous in-vitro and in-vivo applications [1,2] . Metallic nanoparticles are multifunctional in nature, and they have been extensively used in a variety of sectors of industries and medicine including drug delivery, cancer treatment, wastewater treatment, and DNA analysis, as antibacterial agents and biosensors and in solar power generation and catalysis. Metal NPs can be synthesized using conventional or unconventional methods. Different methods such as solution, chemical/photochemical reactions, thermal decomposition, electrochemical and sonication are commonly used to synthesize the metal NPs [3,4] .However, most of the developed methods are associated with certain disadvantages such as involvement of hazardous chemicals, high energy requirements, increased the environmental toxicity, and cost uneffectiveness. Different authors suggested numerous synthesis routes using plant extracts as reducing agents in a biosynthesis or so-called green synthesis scheme for metals NPs [5,6] . Green synthesis has multiple advantages over physical and classical methods. For instance, it is cost effective,

*Corresponding author e-mail: alshimaa@azhar.edu.eg.; (Elshimaa H. Gomaa).
Receive Date: 21 July 2021, Revise Date: 05 August 2021, Accept Date: 09 August 2021
DOI: 10.21608/EJCHEM.2021.87059.4209

eco–friendly and does not require high pressure, energy, temperature or the use of toxic chemical reagents

Plants contain a vast range of secondary metabolites such as phenolics, terpenoids, polysaccharides and flavonoids, having redox capacity. Thus, ideally be used for the biosynthesis of NPs [7] . black tea is a rich source of polyphenols and its bio-molecules act as reducing and capping agents during the synthesis of metal NPs [8] . In comparison to published reports on the green production of NPs and physical and chemical properties, very limited information is available on the antibacterial properties of metal NPs. Textiles functionalized with CuNPs have become a promising option to prevent the spread of diseases due to their antimicrobial properties, which strongly depend on the structure and morphology of the nanoparticles and the method used for the functionalization process. Finally, the possible antimicrobial mechanisms that could develop in Gram-positive and Gram-negative bacteria were described [9].

Therefore, the present study was carried out on one hand to synthesize and characterize green copper nanoparticles (g-Cu NPs) using black tea leaves extracts. On the other hand, the percentage of dye exhaustion (E%) and antibacterial were evaluated. Furthermore, the mechanism of adsorption process was studied by the evaluation of adsorption isotherms models and kinetics adsorption.

Metal NPs can be synthesized using conventional or unconventional methods. Different methods such as solution, chemical/photochemical reactions, thermal decomposition, electrochemical and sonication are commonly used to synthesize the metal NPs [3,4] .However, most of the developed methods are associated with certain disadvantages such as involvement of hazardous chemicals, high energy requirements, increased the environmental toxicity, and cost uneffectiveness. Different authors suggested numerous synthesis routes using plant extracts as reducing agents in a biosynthesis or so-called green synthesis scheme for metals NPs [5,6] . Green synthesis has multiple advantages over physical and classical methods. For instance, it is cost effective, eco–friendly and does not require high pressure, energy, temperature or the use of toxic chemical reagents.

Plants contain a vast range of secondary metabolites such as phenolics, terpenoids, polysaccharides and flavonoids, having redox capacity. Thus, ideally be used for the biosynthesis of NPs [7] . black tea is a rich source of polyphenols and its bio-molecules act as reducing and capping agents during the synthesis of metal NPs [8] . In comparison to published reports on the green production of NPs and physical and chemical properties, very limited information is available on the antibacterial properties of metal NPs. Textiles functionalized with CuNPs have become a promising option to prevent the spread of diseases due to their antimicrobial properties, which strongly depend on the structure and morphology of the nanoparticles and the method used for the functionalization process. Finally, the possible antimicrobial mechanisms that could develop in Gram-positive and Gram-negative bacteria were described [9].

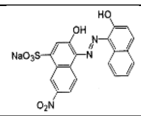
Therefore, the present study was carried out on one hand to synthesize and characterize green copper nanoparticles (g-Cu NPs) using black tea leaves extracts. On the other hand, the percentage of dye exhaustion (E%) and antibacterial were evaluated. Furthermore, the mechanism of adsorption process was studied by the evaluation of adsorption isotherms models and kinetics adsorption.

2.Materials and methods :-

2.1 Materials:

Nylon fabric was supplied by El-Nasr Company, Acid Black 172 (AB172) was kindly supplied by New Trend Co. Egypt. The characteristics of the dye are listed in Table 1

Table 1: The characteristics of dye.

Dye	Molecular Formula	Molecular weight	λmax	Structure
Acid Black 172	**$C_{20}H_{12}N_3NaO_7S$**	**461.38gmol^{-1}**	**572nm**	

Black tea was purchased from local market of Sri Lanka.. All chemicals used, were purchased with high purity from Merck Darmstad, Germany. All aqueous solutions were prepared by using double-distilled water.

2.2 the methods:-

2.2.1 Preparation of black tea leaves extract

The synthesis of copper nanoparticles (NPs) was carried out using black tea leaves extracts according to previous report [10]. The leaves extract of tea were prepared separately by exactly weighing 10 g of tea leaves and transferred into 250 mL conical flask already containing 100 mL of DI-H2O.The mixtures were then heated at 80 °C for 20 min, cooled and filtered using Whatman no. 1 filter paper. Filtrates were stored at 4 °C and used within one week.

2.2.2. Preparation of green copper nanoparticles

Copper nanoparticles from black tea(g-Cu-NPs)were synthesized using CuSO4 solution with the corresponding tea leaves extract. In brief, CuSO4 (1 mmol/L) and tea leaves extract was taken in 4:1 ratio by volume and the solution was subjected to continuous stirring at 80 °C temperature for 10 min. The resulting suspensions were left at room temperature for 24 h to complete reaction and separated using the above mentioned protocol.

2.2.3. Characterization of metals nanoparticles

The structural, functional and optical properties of synthesized CuNPs were characterized using scanning electron microscope (SEM), Transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), energy-dispersive x-ray (EDX) and UV/Vis spectroscopy. The morphology and size of the synthesized CuNPs were studied using SEM and TEM analysis (Model # JSM 6380A, JEOL Ltd, Japan). The presence of functional groups or identification of chemical bonding in CuNPs was evaluated using FTIR analysis (Perkin-Elmer Inc, Waltham, MA). The spectral operational range was operated at 500–4000/cm. Elemental composition confirmation was done using EDX. Optical properties of CuNPs was analyzed using UV/Vis absorption double beam spectrophotometer (Model # UV-1700 Parma Spec., Shimadzu, Japan) within 250–700 nm wavelength range

.

2.2.4 Dyeing procedures :-

Untreated and pretreated nylon fabrics were dyed with AB 172 by applying batch technique under the dyeing recipe: dye concentration 10, 15, 25, 50 and75 (ppm), Liquor ratio (LR) 1 : 50 , time 120 (min) and different temperatures. 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 λmax = 572 nm,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 nylon fabric properties. The percentage of dye exhaustion (E%) was calculated by using the equation:

$$E\,\% = \frac{C_o - C_e}{C_o} \text{ x } 100 \qquad (1)$$

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

2.2.5 Determination of nylon 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 [11].

2.2.6 Antibacterial investigation :-

The antibacterial activity was quantitatively evaluated against Staphylococcus aureus, a Gram-positive organism, and Escherichia coli, aGram-negative organism, in accordance with AATCC 100 test method [12] using nutrient agar and an incubation period of 24 hours at 37 ºC. Colonies of bacteria recovered on the agar plate were counted, and the reduction percentage of bacteria, R (%), was calculated [13,14] using the following equation:

$$R\ (\%) = B - A\ /\ B \text{ X } 100 \qquad (2)$$

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 1 h contact time.

3.Results and discussions :-

3.1. Characterization of synthesized CuNPs

The formation of nanoparticles (NPs) was indicated by the color change in the reaction mixtures. This change in color was due to surface plasma resonance and reduction of metal ions by tea leaves extract. color of The initial blue color of the reaction mixture CuSO4/tea leaves extract solution eventually turned to dark brown color, the color change indicate the formation of NPs in the solution. The possible mechanism for the formation of NPs as mentioned below [15] :

$$nM + n(Ar - OH)n \rightarrow nM0NPs + n(Ar = O) + 3nH^+ \qquad (1)$$

Where, n is the number of groups oxidized by metals ions, M is the metal ions and Ar shows the aromatic ring. The formation of NPs was further confirmed by the change in pH of the solutions. . The pH of the NPs solution after reduction was found in the acidic range from (5.30 to 3.60) . However, the pH of sample was found to decrease during reduction and shifted to the acidic range .

3.1.1 UV-analysis :

The UV/Vis spectrums of biosynthesized CuNPs are presented in Figure 1 ,The spectra show only one sharp peak, The spectroscopic analysis of synthesized

CuNPs showed the maximum absorbance at 352 nm. This peak can be assigned to the absorption of CuNPs and confirms the formation of biosynthesized CuNPs only. This is due to the surface plasmon resonance (SPR) and proving that the protein found in the leaves acts as a template and a stabilizer in the synthesis process [16].

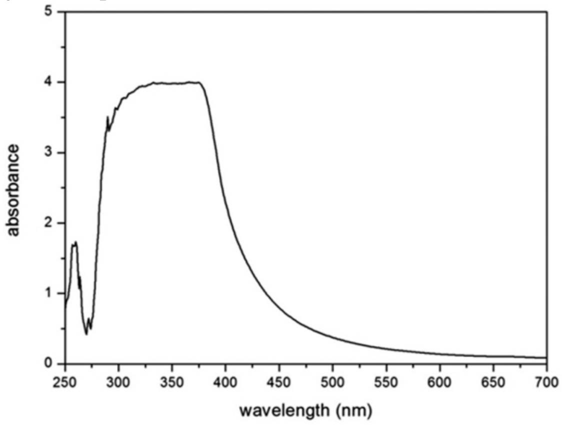


Fig. 1: Ultraviolet-visible spectrum of copper nanoparticles

3.1.2 Photographic image :

The photographic images of untreated nylon fabric and pretreated biosynthesized CuNPs nylon fabric are shown in figure 2 (a,b) . The white color of the untreated nylon fabric changed into brown color after biosynthesized CuNPs deposition confirming that the CuNPs is uniformly deposited on the nylon fabric.

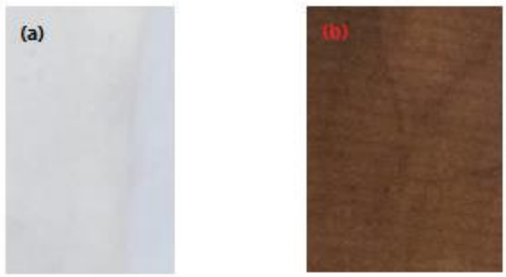


Fig. 2 :Photographic image of (a) untreated nylon fabric (b) biosynthesized CuNPs nylon fabric .

3.1.3 SEM and TEM analysis :-

The SEM images of biosynthesized CuNPs, untreated nylon and pre-treated nylon fabric CuNPs-nylon were presented in Figuer 3 (a,b). SEM images clearly showed that biosynthesized CuNPs was agglomerated and spherical shaped with a diameter ranging from 150-200 nm, However, with high magnification, further observation reveals that these Cu nanoclusters are assembled by smaller NPs, which exhibit good uniformity, and the average diameter is about 25-50 nm .It was observed that the surface of the pre-treated g-Cu NPs-nylon fabric was not as smooth as the untreated sample. The leaf contains polyphenols, caffeine and terpenoids, which have bactericidal and antioxidant activity and several other useful properties [17] . These contents in tea leaf extracts act as reducing and capping agents for the synthesis of metal NPs. Thus, plays a key role in the formation of the final structure and NPs size which adhere well with the surface of nylon fabric.

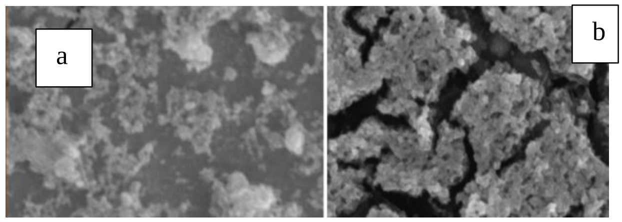


Fig.3: SEM image of (a) biosynthesized copper nanoparticles, (b) high magnification

The SEM images of untreated nylon fabric and biosynthesized CuNPs nylon fabric, were shown in figure 4 (a , b) respectively. SEM analysis shows uniformly distributed silver nanoparticles on the surfaces of nylon fabric .

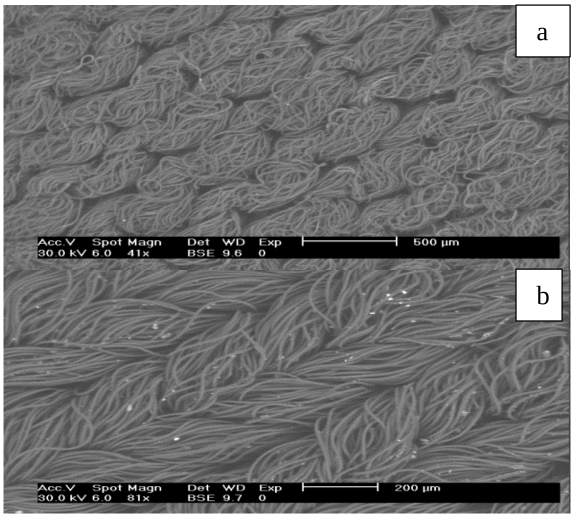


Fig. 4 : SEM image of (a) nylon fabric (b) biosynthesize CuPNs nylon fabric

3.1.4 EDX analysis :-

Figure **5** illustrates EDX analysis of green CuNPs, The spectra results showed successfully formation of NPs. However, the presence of small impurities supposed to arise from plant constituents. the strong peaks observed related to Cu have the weight percentages of 70.3 % . These results confirm the successful synthesis of biosynthesize CuNPs .

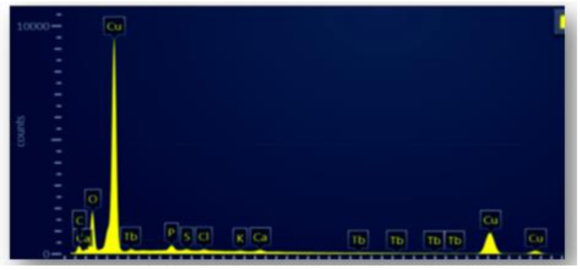


Fig. 5 : EDX image of biosynthesize CuPNs .

Table 2. Elemental composition of CuNPs by EDX analysis.

Wt %	Element
70.3	Cu
15.0	O
12.2	C
1.2	P
0.6	Ca
0.3	Cl
0.2	S
0.2	K

3.1.5 FTIR spectrum analysis :-

FTIR spectrum of biosynthesizes CuNPs is in Figure 6 .The broad peaks at 3294.38/cm and indicated the O–H groups present on the surface of the biosynthesize CuNPs. The peak at 2929/cm attributed to the symmetric and asymmetric C–H stretching vibration of flavonoids/phenolic, respectively. The peak at 1631/cm represented the un-reacted ketone group suggesting the presence of flavonones adsorbed on the surface of biosynthesize CuNPs. Whereas, the peak at 1452/cm and 1454/cm showed the C,C stretch in aromatic rings. The peaks at 1381/cm indicated the O–H bend of polyphenol, confirming the presence of an aromatic group. The absorption peaks at 1087/cm were assigned for C–O–C and secondary –OH of the phenolic group in biosynthesize CuNPs, respectively.

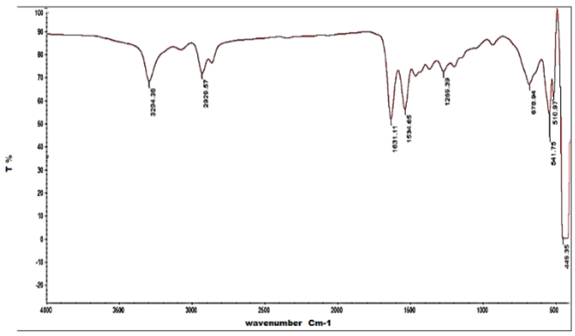


Fig. 6 : FTIR spectra of biosynthesize CuPNs .

3.1.6 XRD analysis :

X-ray diffraction analysis was used to investigate the crystallographic behavior , figure 7,8 shows XRD patterns for biosynthesize CuNPs . The Four main characteristic diffraction peaks for Cu were observed at 2θ = 38.45, 46.35, 64.75 and 78.05, which correspond to the (111), (200), (220) and (311) crystallographic planes of face-centered cubic (fcc) Cu crystals, respectively (JCPDS 00-004-0783). No peaks from any other phase were observed showing that single phase Cu with cubic structure nanoparticles have been obtained directly. The peak intensity of the (111) planes was very high due to the preferential adsorption of the Cu atom on that plane during the growth process. Moreover, there were no impurities evident , which indicated that the nano-copper generated by this method had a cubic crystal structure [18]. Also , the sharp peaks suggest the formation of highly crystalline copper particles .

The two peaks situated at 2θ values of 20.92° and 23.60° for nylon fabric [19] , still present after the treatment with CuNPs. This observation suggests that the grafting of CuNPs on nylon fabric did not change the basic structure of the treated nylon fabric.

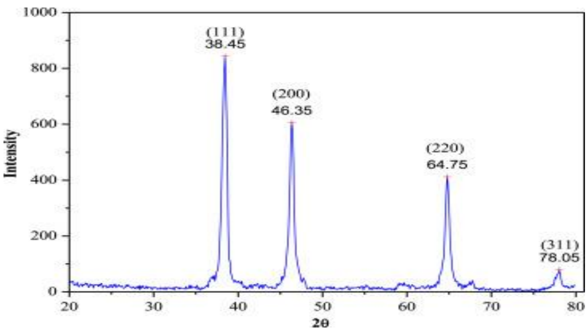


Fig. 7. XRD analysis of biosynthesize CuNPs .

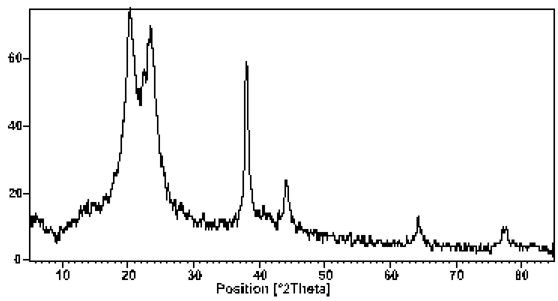


Fig. 8. XRD analysis of biosynthesize CuNPs nylon fabric .

3.2 Dyeing kinetics :-

The biosynthesize CuNPs nylon fabric was dyed with AB 172 and compared with the untreated nylon fabric .It is observed from figure 9, that the E%

values of the CuNPs pre-treated nylon are higher than those of the corresponding untreated nylon fabric. The higher E% values of nano-treated nylon indicate that the presence of nano metal particles increases the dye affinity (from 70.88 % to 97.78 %) towards the fabric. The negatively charged dye anions get attracted towards the fabric probably due to the polarity developed in the metal particles by induction which results in better bonding between the dye and the fabric. . The biosynthesize CuNPs are small size can enter in between the polymer molecules and perhaps act as filler or crosslinking agent which also contribute to the load sharing phenomenon during load application to the fabric [20] . The CuNPs treatment produces a nylon fabric with confirmed color enabling them to reducing temperature, fabric damage, amount of dyestuff used and saving energy of conventional dyeing of nylon fabrics

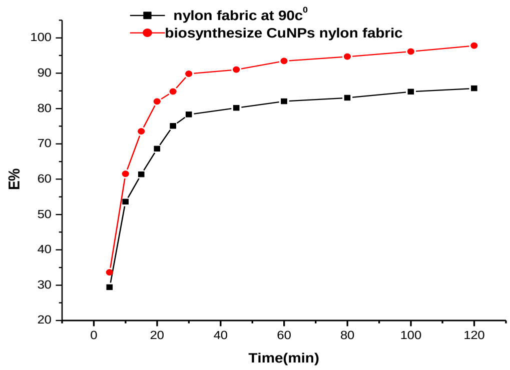


Fig. 9: Time-Exhaustion isotherms of AB 172 dye adsorption onto untreated and pre- treated nylon fabric with green CuNPs . [dyeing recipe: LR 1:50, 25 ppm, 90⁰C].

3.3 kinetic of adsorption:-

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 AB 172 in absence and presence of synthesized nanostructured materials are expressed, respectively, as follows:

A simple kinetic analysis of adsorption is the Lagergren equation [21,22], a pseudo-first-order type, written as follows:

$$\text{Log}\,(q_e - q_t) = \log q_e - k\,t\ /2.303 \qquad (3)$$

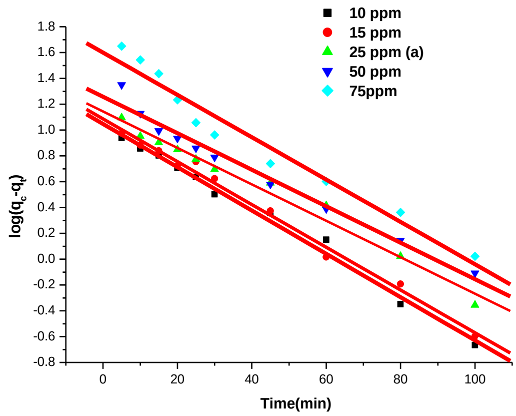
where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at contact time t (mg/g), k_1 is the pseudo-first order rate constant (min-1). A plot of log (q_e-q_t) versus t gives a linear line Figure 9 (a,b) from which the values of k_1 and q_e were determined from the slope and intercept respectively and presented in Table 3.

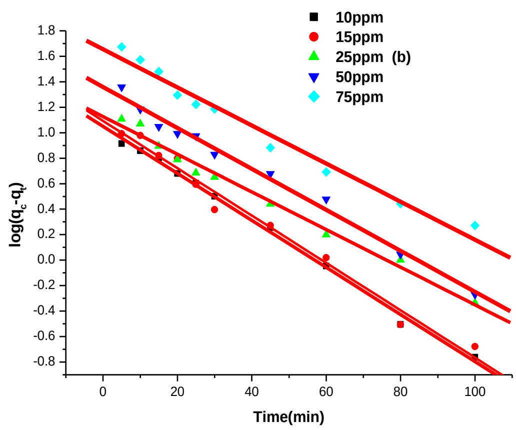
The pseudo-second-order kinetic model is another important model to investigate the kinetic of adsorption of dyes on textile fabrics [23,24]. The pseudo-second order kinetic model can be expressed in linear form as follows:

$$t/q_t = 1/\ k_2\, q_e^2 + t\ /q_e \qquad (4)$$

where k_2 is the rate constant of pseudo-second order adsorption (g/mg min). A plot of t/q_t versus t gives a linear relationship Figure 8(c,d), from which qe and k_2 were determined from the slope and intercept of the plot respectively and presented in Table 3.

The correlation coefficients R^2 higher than 0.99 suggest that adsorption of AB 172 onto untreated and biosynthesize CuNPs nylon fabric predominantly follows the pseudo-second order kinetic model .The pseudo-second order rate constants for adsorption of AB 172 onto the untreated and biosynthesize nylon fabric show a steady increase with an increase in the solution concentration.





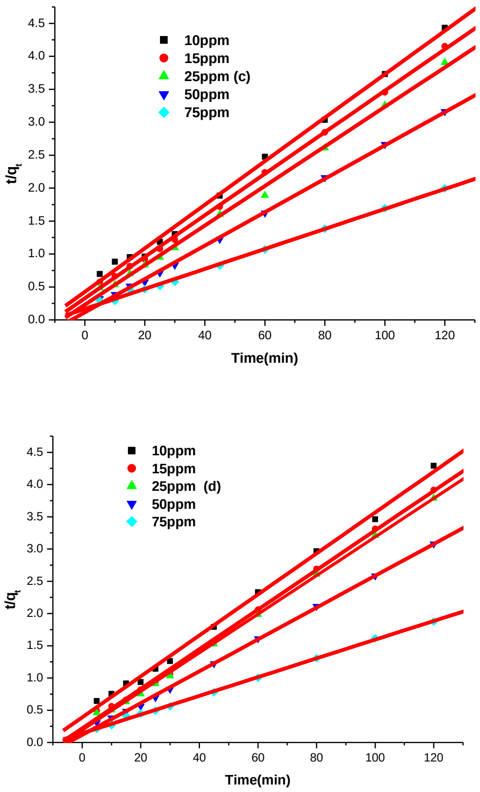


Fig. 10 : Kinetic plot for the adsorption of AB 172 onto nylon fabric at 90 ^{0}C .

a. Pseudo-first order of untreated nylon fabric.
b. Pseudo-first order of biosynthesize CuNPs nylon fabric.
c. Pseudo-second order of untreated nylon fabric.
d. Pseudo-second order of biosynthesize CuNPs nylon fabric.

3.4 Diffusion mechanism :-

The two models above cannot identify the diffusion mechanism during the adsorption process, so the experimental data are tested by the intra-particle and Elovich diffusion models.

3.4.1 Intra-particles diffusion

Intra-particle diffusion can be expressed by following equation:

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

Where q_t (mg/g) is the amount of AB 172 adsorbed at time t, K_P (mg/g min$^{1/2}$) is the intra-particle diffusion rate constant obtained from the slope, of the plot q_t versus t $^{1/2}$shown in figures 9 . 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 [25]. The intra-particle diffusion rate constant k_p and C are given in table 3 . The intra-particle diffusion rate constants k_p increase with rising concentration because increasing concentration results in an increase of the driving force, which will increase the diffusion rate of AB 172 [26]. 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 rat-limiting step [27].

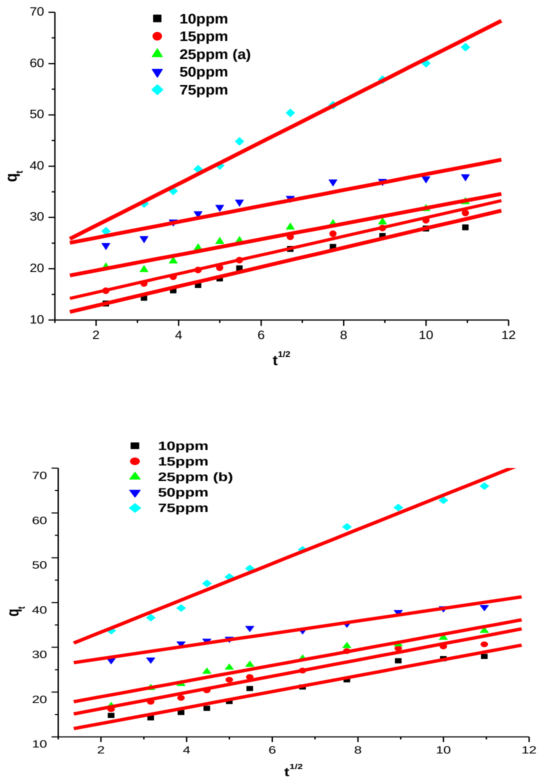


Fig. 11: Intra-particle diffusion kinetics of AB 172 into (a) untreated nylon fabrics (b) biosynthesize CuNPs nylon fabrics at various concentrations.[Dyeing recipe : LR 1:50, 90 ^{0}C].

3.4.2 Elovich diffusion

The Elovich equation was first applied to the chemisorptions kinetics of gases on solids [28] it has also been successfully used in recent years to describe the adsorption of the solutes from a liquid solution. The linear form of the Elovich equation is given as

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \qquad (6)$$

Where α is the initial adsorption rate constant (mg/(g min) and the parameter β is the desorption constant(g / mg) . The constant can be obtained from the slope and the intercept of the plot of q_t versus ln t at different concentrations, as shown in figure10. The value of β decreases while that of α increases as the concentration rises as shown in Table 3 .

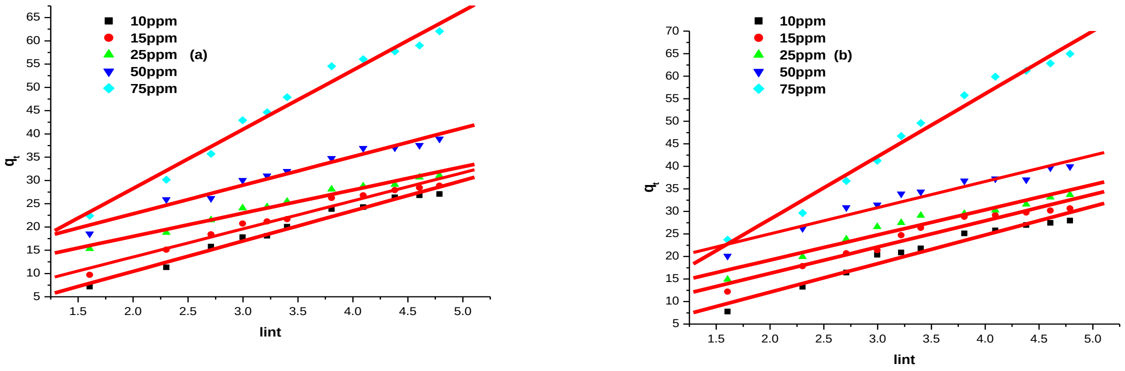


Fig.12 :Elovich diffusion kinetics plots of adsorbed AB 172 into (a) untreated nylon fabrics (b) biosynthesize CuNPs nylon fabrics at various concentrations.[Dyeing recipe : LR 1:50, 90 ^{0}C].

Table (3) : Kinetic parameters of the dyeing process of AB 172 onto untreated and biosynthesize CuNPs nylon fabrics at different concentrations .

Conc. of dye (ppm)	First-order kinetic model			Second-order kinetic model			Elovich			Intraparticle diffusion		
	qe,cal (mg/g)	k_1 (1/min)	R^2	q_e,cal (mg/g)	k_2 x10^{-4} (g/mg min)	R^2	β(g/mg)	α x10^{-3} mg/g min)	R^2	ki (mg/g min$^{1/2}$)	Cx 10-3	R^2
Nylon fabric												
10	22.04	0.063	0.85	26.83	37	0.99	0.14	1.85	0.86	1.66	2.89	0.85
15	39.80	0.066	0.87	29.57	39	0.97	0.13	1.93	0.87	1.79	4.87	0.84
25	42.18	0.071	0.87	31.90	41	0.98	0.12	2.03	0.88	1.85	7.03	0.86
50	50.03	0.074	0.88	39.49	43	0.97	0.11	2.34	0.87	2.01	16.99	0.88
75	55.97	0.077	0.87	62.92	45	0.98	0.087	2.51	0.88	3.77	17.79	0.85
Biosynthesize CuNPs nylon fabric												
10	32.15	0.066	0.82	28.47	42	0.97	0.12	3.28	0.95	2.16	9.06	0.97
15	37.72	0.069	0.80	32.58	43	0.99	0.11	3.79	0.96	2.35	13.79	0.99
25	41.47	0.072	0.84	33.41	45	0.98	0.10	4.13	0.96	2.81	15.42	0.96
50	49.90	0.076	0.88	39.50	47	0.98	0.098	4.95	0.97	3.69	22.06	0.98
75	68.21	0.079	0.85	64.66	49	0.99	0.061	8.47	0.99	5.45	25.75	0.99

3.5 Adsorption isotherm :-

Adsorption isotherm models are widely used to describe and investigate mechanisms of adsorption. The equilibrium data was analyzed by the Langmuir and Freundlich isotherm model.

3.5.1 Langmuir adsorption isotherm

The Langmuir model describes monolayer sorption on distinct localized adsorption sites.It indicates no transmigration of the adsorbate in the plane of the surfaces and assumes uniform energies of monolayer sorption onto the sorbent surface [29]

The linear form of Langmuir equation can be written as follows:

$$C_e / q_e = 1/q_m \ K_L + C_e /q_m \qquad (7)$$

where C_e (mgL^{-1}) is the concentration of AB 172 at equilibrium, q_e (mgg^{-1})is the amount of AB 172 adsorbed by the fabric at equilibrium, q_m (mgg^{-1}) is the maximum adsorption capacity corresponding to monolayer coverage, and K_L (L/mg) is the Langmuir constant. The values of q_m and K_L can be calculated from plotting C_e /q_e versus C_e . The Langmuir plots for AB 172 adsorption onto the fabric are obtained in figure 11, and the parameters are shown in Table 4 . The values of the correlation coefficient for the Langmuir plots changed in the range 0.74 to 0.83 . This suggests that the adsorption of AB 172 onto the fabric did not follow the Langmuir model .

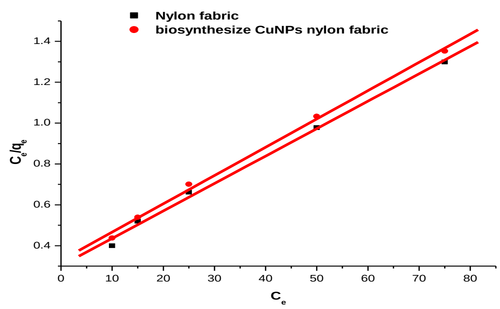


Fig .13: Langmuir adsorption isotherm of AB172 onto untreated and biosynthesize CuNPs nylon fabric at [LR 1:50, 90 ^{0}C].

3.5.2 Frendlich adsorption isotherm

The Freundlich isotherm is used to describe adsorption processes that occur on heterogeneous surfaces and active sites with different energies based on multilayer adsorption and equilibrium [30].
The linear form of Freundlich equation is given as:

$$\log q_e = \log K_F + 1/n \log C_e \qquad (8)$$

where q_e is the AB 172 concentration on the fabric at equilibrium, C_e (mgL^{-1}) is the concentration of AB 172 in solution at equilibrium, and K_F ($dm^3\ g^{-1}$) and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively .Freundlich constants are calculated from the slope and the intercept in figure 12 , and are given in Table 4. The correlation coefficients ($R^2 > 0.99$) reflect that the experimental data agree well with the Freundlich model. The values of 1/n (0.37 and 0.41) are smaller than 1, so they represent the favorable adsorption conditions [31].

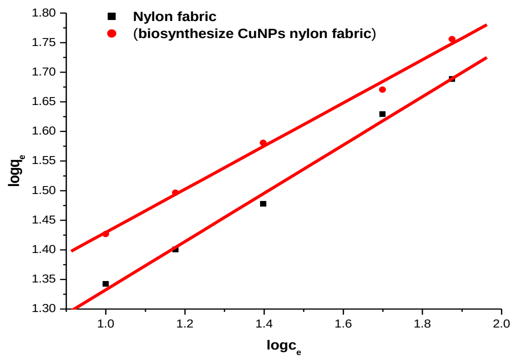


Fig.14:Freundlich adsorption isotherm of AB172 onto untreated and biosynthesize CuNPs nylon fabric at [LR 1:50, 90 ^{0}C].

Table (4) : Langmuir, Freundlich isotherm constants of the dyeing process of AB 172 onto untreated and biosynthesize CuNPs nylon fabrics at [LR 1:50, 90 ^{0}C].

Fabric type	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q_{max} (mg g^{-1})	K_L x10^{-4} (dm^3 mg^{-1})	R^2	K_F (dm^3 g^{-1})	n/1	R^2
Nylon fabric	**69.11**	**43.60**	**0.74**	**8.40**	**0.37**	**0.99**
Biosynthesize CuNPs nylon	**72.62**	**49.82**	**0.83**	**11.29**	**0.41**	**0.99**

3. 6 Determination of nylon fabric properties :-

3.6.1 Color fastness properties

The effect of green copper (CuNPs) treatment on physical properties has been studied. The dye and nanoparticles should have penetrated into the Nylon fabric, but stay mostly on the internal side of the surface since dyed fabrics possess very good crocking fastness. However lower washing fastness was achieved Table 4, which can be due to the polymeric structure of polyamide fabrics because they have high crystallinity and low swelling ability in water in comparison to other polymeric fabrics, such as wool and cellulose**.** 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 nylon fabric with nanomaterials that became a smart treatment applied as a novel approach to textile dyeing and finishing [32,33] .

Table (4): Fastness properties of untreated and biosynthesize CuNPs of nylon fabric in presences of various AB172 dye concentration at 90^{0}C.

Conc. of dye (ppm)	Nylon fabric				Biosynthesize CuNPs nylon fabric			
	Washing	Light	Perspiration		Washing	Light	Perspiration	
			acid	Alkali			Acid	Alkal i
10 PPm	3-4	3-4	3-4	3-4	4	4-5	4-5	4-5
15 PPm	3-4	3-4	3-4	3-4	4	4-5	4-5	4-5
25 PPm	4	3-4	3-4	3-4	4	5-6	4-5	4-5
50 PPm	4	4	4	4	4-5	6	4-5	5
75 PPm	4	4	4	4	4-5	6	5-6	5-6

3.6.2 Evaluation of antibacterial activity of nylon fabric :-

The quantitative results for the evaluation of antibacterial activity of nylon fabric samples are shown in figure 13 . It is easily noticed that the untreated nylon sample 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 nylon sample exhibits slightly higher antibacterial activity scoring 45.60 % and 48.70 % R % values against the Gram- negative and Gram-positive bacteria, respectively. This may be attributed to the presence of various functional groups in AB 172 dye which can act as bacterium cells [34].The experimental results reveal that the R% values of pre-treated nylon fabric towards Gram-positive bacteria and Gram-negative bacteria are 95.48% and 93.28% respectively. The biosynthesize CuNPs nylon dyed fabric , higher values of antibacterial activity scoring 96.58 % and 98.13 % against E. coli and S. aureus were recorded when compared to the untreated fabric samples. This may be due to the fact that metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered the part of the oxygen in the air or water is turned into active oxygen by means of catalysis with the metallic ion, there by dissolving the organic substance to create a sterilizing effect [35]. CuNps is very reactive with proteins. When contacting bacteria , it adversely affects cellular metabolism and inhibits cell growth. Furthermore, it inhibits the multiplication and growth of those bacteria which cause infection, odor, itchiness and sores. The green CuNPs treatment produces a nylon fabric with preceding antibacterial properties enabling them to improve human health care .

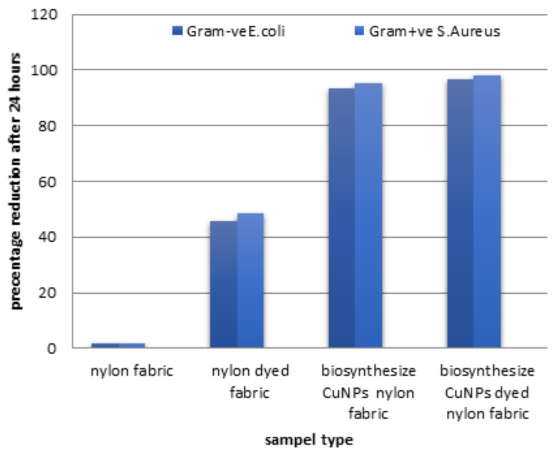


Fig. 13 : Antibacterial activity of nylon fabrics towards E.coli and S. Aureus.

4. Conclusion

The researchers discovered that metal nanoparticles (NPs) can be easily made from black tea leaves extracts. This is a straightforward, dependable, environmentally friendly, low-cost, and cost-effective biological approach that could help promote the industrial production of metal NPs without the use of toxic reducing, capping, or dispersion agents. XRD, FTIR and EDX patterns and also SEM images confirmed the successful synthesis of copper nanoparticles . The nano treatment on the nylon fabric also improved some other fabric properties due to the cross linking action of nano-copper between the polyamide chains of nylon. Further, antibacterial properties of the treated fabric against *S. aureus* and *E. coli* bacteria . Equilibrium studies showed the favorability of the freundlich isotherm model by synthesized CuNPs, indicating multilayer adsorption process. Whereas, kinetic data showed that the synthesized CuNPs followed pseudo second order model. As a result of their stable nature and associated antibacterial capabilities, these nanoparticles could be useful in a variety of biomedical applications.

Conflicts of interest

"There are no conflicts to declare".

Formatting of funding sources

No funding sources

5. References :

[1] Chinen A. B., Guan C. M., Ferrer J. R., Barnaby S. N., Merkel T. J., Mirkin C. A., Nanoparticle probes for the detection of cancer biomarkers, cells, and tissues by fluorescence. Chemical Reviews , 115 , 10530–10574 (2015).

[2] Vaseeharan B., Ramasamy P., Chen J. C., Antibacterial activity of silver nanoparticles (AgNps) synthesized by tea leaf extracts against pathogenic Vibrio harveyi and its protective efficacy on juvenile Feneropenaeus indicus., Letters in Applied Microbiology, 50(4), 352–356 (2010).

[3] Rajput N., Methods of preparation of nanoparticles – a Review. , International Journal of Advances in Engineering & Technology, 7(4), 1806–1811 (2015).

[4] Sutradhar P., Saha , M., Maiti D. , Microwave synthesis of copper oxide nanoparticles using tea leaf and coffee powder extracts and its antibacterial activity., Journal of Nanostructure in Chemistry , 4(1) , 1–6 (2014).

[5] Nakhjavani M., Nikkhah V., Sarafraz M. M., Shoja S., Sarafraz M. , Green synthesis of

silver nanoparticles using green tea leaves: Experimental study on the morphological, rheological and antibacterial behaviour. ,Heat and Mass Transfer, 1–9 (2017).

[6] Senthilkumar S. R., Sivakumar T., Green tea (Camellia sinensis) mediated synthesis of zinc oxide (ZNO) nanoparticles and studies on their antimicrobial activities., International Journal Pharmacy and Pharmaceutical Sciences , 6(6), 461–465 (2014).

[7] Sun Q., Cai X., Li J., Zheng M., Chen Z., Yu C. P., Green synthesis of silver nanoparticles using tea leaf extract and evaluation of their stability and antibacterial activity., Colloids and Surfaces a: Physicochemical and Engineering Aspects, 444 , 226–231 (2014).

[8] Shah R. K., Boruah F., Parween N. , Synthesis and characterization of ZnO nanoparticles using leaf extract of Camellia sinesis and evaluation of their antimicrobial efficacy., International Journal of Current Microbiology and Applied Sciences, 4(8), 444–450 (2015).

[9] Luz E. R. , Enrique D. , Gomez , José L. S., Mónica M. , Antibacterial Cotton Fabric Functionalized with Copper OxideNanoparticles., Molecules , 25(24) , 5802 (2020)

[10] Huang L., Weng X., Chen Z., Megharaj M., Naidu R., Green synthesis of iron nanoparticles by various tea extracts: Comparative study of the reactivity. , Spectrochimica Acta a: Molecular and Biomolecular Spectroscopy, 130, 295–301 (2014).

[11] Gomaa S.H., Nora M. H., Elsisi A.A., Emam A.G., Rania M.A. , Utilizing Some Synthesized Nanostructured Materials to Improve The Functional Properties of Cotton Fabric for Possible Applications., Egypt. J. Chem., 63 (7) , 2493 - 2509 (2020).

[12] Grabowska E. L., Gryglewicz G., Adsorption Characteristics of Congo Red on Coal-Based Mesoporous Activated Carbon., Dyes Pigments,74, 34–40 (2007) .

[13] Adriana M., Constantin T. , Elena C., Mircea R., Mihai V., Ioan S. , Graphene-based Materials Used as the Catalyst Support for PEMFC Applications materials-today-proceedings, 2(6), 3797-3805 (2015) .

[14] Khan M. N., Lin H., Li M., Wang J., Mirani Z. A., Khan S. I., et al. , Identification and growth optimization of a Marine Bacillus DK1-SA11 having potential of producing broad spectrum antimicrobial compounds. , Pakistan Journal of Pharmaceutical Sciences, 30(3), 839–853 (2017).

[15] Keihan A. H., Veisi H., & Veasi H. , Green synthesis and characterization of spherical copper nanoparticles as organometallic antibacterial agent. Applied Organometallic Chemistry., (2016) http://dx.doi.org/10.1002/aoc.3642.

[16] Ashajyothi C., Kudsi J., Kelmani C.R., Biosynthesis and characterization of copper nanoparticles from *Enterococcus faecalis.*, Int. J. Pharm. Bio .Sci ., 5(4) , 204-211 (2014) .

[17] Sivamani S., Jyothi S., Joseph B., Gunalan B., Venkatesh B., Kar B. , Synthesis of antibacterial Ag nanoparticles from tea powder., International Journal of NanoScience and Nanotechnology, 4(1) , 9–17 (2013).

[18] Samar Fatma , Kalail,A P , Ernestr. , Renganathans. ,
Green Synthesis of Copper NanoParticel from *Passiflora foetida* leaf extract and its antibacterial activity., *Asian. J .Pharm. Clin .Res., 10(4), 79-83 (2017).*

[19] Montazer M., Allahyarzadeh V. , Electroless Plating of Silver Nanoparticles/Nanolayer on Polyester Fabric Using $AgNO_3$/NaOH and Ammonia.,Ind. Eng. Chem. Res. , 52(25) , 8436-8444 (2013) .

[20] R. Perumalraj , Effect of Sliver Nanoparticles on Wool Fibre.,ISRN Chemical Engineering**.,** (2012) .

[21] Ru-Ling T. , Pin-Hsueh W. , Feng-Chin W., Ruey-Shin J., A convenient method to determine kinetic parameters of adsorption processes by nonlinear regression of pseudo-nth-order equation.,Chemical Engineering Journal., 237, 153–161 (2014).

[22] Yiyong C., DejinZ. , Adsorption kinetics, isotherm and thermodynamics studies of flavones from Vaccinium Bracteatum Thunb leaves on NKA-2 resinChemical., Engineering Journal, 254, 579-585 (2014) .

[23] Talal S. , Sorption kinetics: Obtaining a pseudo-second order rate equation based on a mass balance approach., Journal of Environmental Chemical Engineering., 2(2), 1001–1006 (2014).

[24] Nahali L., Miyah Y., Assila O., EL Badraoui A., EL Khazzan B., Zerrouq F., Kinetic and thermodynamicstudy of the adsorption of twodyes:brilliant green and eriochrome black T using a natural adsorbent "sugarcane bagasse". , Mor. J. Chem. , 7 (N°4) , 715-726 (2019).

[25**]** Grabowska E.L. , Gryglewicz G. **,** Adsorption Characteristics of Congo Red on Coal-Based Mesoporous Activated Carbon., Dyes Pigments. 74 (1), 34-40 (2007).

[26] Agnes P., Eliazer B.N.,Augustine E.O., Intraparticle diffusion of Cr(VI) through biomass

and magnetite coated biomass: A comparative kinetic and diffusion study., 32, 39- 55 (2020).

[27] Poot V.J.P., McKay G., Healy J.J. , Removal of Basic Dye from Effluent Using Wood as an Adsorbent., J. Water Pollut. Control Fed., 50 (5), 926-935 (1978).

[28] Yuan X., Xia W., An J., Yin J., Zhou X., Yang W., Kinetic and Thermodynamic Studies on the Phosphate Adsorption Removal by Dolomite Mineral**.,** J. Chem., 1–8 **(** 2015**).**

[29] Balouch A., Kolachi M., F. N. Talpur, Khan H., Bhanger I.M., Sorption Kinetics, Isotherm and Thermodynamic Modeling of Defluoridation of Ground Water Using Natural Adsorbents., Am. J. Anal. Chem. , 4 , 221–228 (2013).

[30]S. A. Shama , M. A. Gad , Removal of heavy metals ($Fe^{3+,}$ Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+} and Cd^{2+}) from Aqueous Solutions by using Hebba Clay and Activated Carbon., Portugaliae Electrochimica Acta , 28 (4) , 231-239 (2010) .

[31] Boujelben N., Bouhamed F., Elouear Z., Bouzid J., Feki M., Removal of phosphorus ions from aqueous solutions using manganese-oxide-coated sand and brick Water Treat., Desalination and Water Treatment. 52, 2282-2292 (2013) .

[32] Elizabeth R.G., Ricardo L.M., Marcos M.L., Isaias H.P., Maria J.V., Ana M.M., Adsorption of azo- dye orange ll from aqueous solutions using a metal-orangic framework material: iron-benzentricarboxylate., J. Materials ., 7 , 8037-8057 (2014).

[33] Cai J.F. , Jiang H., Cui Z., Chen W., *N*-Sulphonatoalkyl indophenine derivatives: Design, synthesis and dyeing properties on wool, silk and nylon fabrics., Coloration Technology., 137 (2) , 181-192 (2021).

[34] Shereen O.B., Dyeing of cotton fabric with reactive dye using infrared heating technique., Egypt. J. Agric. Res., 97 (1), 407-417 (2019)

[35**]** Farouk R. , Youssef Y. , Mousa A., Ibrahim H., Simultaneous Dyeing and Antibacterial Finishing of Nylon 6 Fabric Using Reactive Cationic Dyes., World Applied Sciences Journal, 26 (10), 1280- 1287 (2013).

[36] Devagi P., Suresh T.C. , Sandhiya R.V. , Sairandhry M., Bharathi S., Velmurugan P., et al., Actinobacterial-mediated fabrication of silver nanoparticles and their broad spectrum antibacterial activity against clinical pathogens., *J. Nanosci. Nanotechnol.* , 20, 2902–2910 (2020) .