RESEARCH PAPER

Comparison of the Efficiency of Nanocellulose (NC) and Astragulas Plant (AS) Surfactants by the Percentage of Disperse Red (DR) Dye Removal

Haider Raad Mutar [1], ***Khawla. K. Jasim*** [2*], ***Ameena N. Seewan3, Sahar Ismail Naji*** [2], ***Zina Abdulhussain Jawad*** [3]

[1] *Ministry of Education, Directorate of Education Al-Muthanna, Iraq*

[2] *Department of Chemistry, Collage of Science, University of Al-Muthanna, Iraq*

[3] *Basic Education Collage, University of AL-Muthanna, Iraq*

ARTICLE INFO

Article History:
Received 04 April 2024
Accepted 25 June 2024
Published 01 July 2024

Keywords:
Adsorption
Astragulas plant (AS)
Disperse Red (DR)
Isotherm; Kinetic
Nanocellulose (NC)

ABSTRACT

This study aims to remove of Disperse red (DR) from aqueous solution using nanocellulose surface and astragulas plant surface and to compare the efficiency of the two surfaces in terms of absorption and application of agents. Affects adsorption such as the temperature effect, PH effect, the amount of the adsorption surface and the contact time for the efficiency of adsorption as well as knowledge of adsorption isotherms such as Frendelch and Langmuir and knowledge of thermodynamic processes to find out the free energy, enthalpy and entropy (random). Where the results of adsorption of DR dye by the surface of nanocellulose were as follows, the equilibrium time is 10 minutes, the optimum surface quantity is 0.005 grams, it works under all thermal conditions and has an acidity effect 3>7>11, which is more suitable for Freundlich's isotherm. The results of adsorption of DR dye on the NC surface were spontaneous through the negative value of Gibbs free energy (ΔG^0), and endothermic (chemical adsorption) through the positive value of enthalpy (ΔH^0) as for the adsorption of DR dye on the surface of the astragulas plant as follows, the equilibrium time is 90 minutes, the optimum surface amount is 0.02g, it works under all thermal conditions and has an acidity effect 3>7>11, which is more suitable for Freundlich's isotherm. The results of adsorption of DR dye on the AS surface were automatic through the negative value of Gibbs free energy (ΔG^0), and exothermic (physical adsorption) through the positive value of enthalpy (ΔH^0). Both surfaces had dye adsorption (DR) that was Giles (type S) classification. The kinetics of both NC&AS surfaces in the adsorption process are subject to a pseudo-second order.

How to cite this article
Mutar H., Jasim K., Seewan A., Naji S., Jawad Z. Comparison of the Efficiency of Nanocellulose (NC) and Astragulas Plant (AS) Surfactants by the Percentage of Disperse Red (DR) Dye Removal. J Nanostruct, 2024; 14(3):1000-1012. DOI: 10.22052/JNS.2024.03.028

INTRODUCTION

The term coloring is a substance that is able to transfer its color to other substances that have the ability to color [1]. Even small amounts of liquid mortars have a large impact on water [2]. The development in the field of dyes led to a change and replacement of natural dyes with synthetic dyes due to the ease of obtaining them, as they

* *Corresponding Author Email: khawla.kani@mu.edu.iq*

have distinctive properties [3]. They have been used in the textile processing industry while other synthetic dyes pose serious environmental risks to sustainability issues. Today, we need factors and influences that remove or reduce these risks [4]. The textile industry and wastewater containing dyes are major sources of severe pollution problems worldwide, and (10-25%) of textile pigments are lost. [5] Dyes are divided into several types according to the functional groups into cationic, anionic and non-anionic [6]. Contaminated water, especially wastewater, can be treated by adsorption [7]. There are materials that have the ability to absorb and are available and inexpensive, but in the future they suffer from many problems, including mechanical and thermal insulation and the relatively slow ability to absorb dyes [8]. The current development in the field of

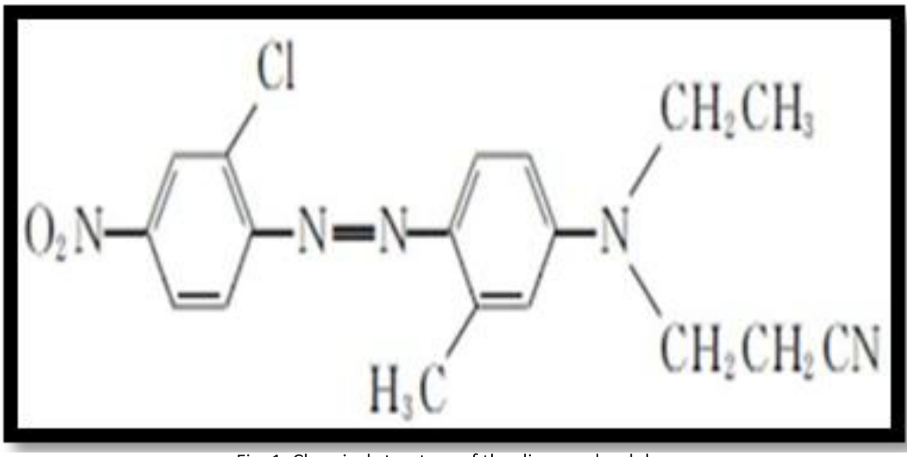

Fig. 1. Chemical structure of the dispersed red dye

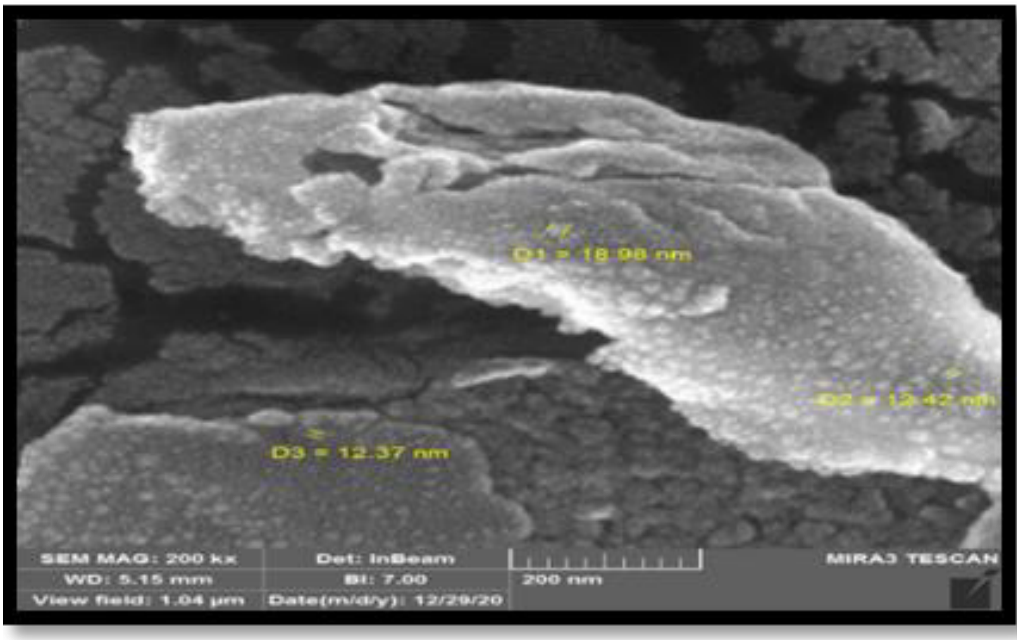

Fig. 2. The SEM image of the NC surface.

surface synthesis has opened many horizons for the disposal of pollutants [9]. Where there are many components such ass the large surface area and the large number of active sites needed to absorb and remove pollutants from wastewater [10]. Nanocellulose has unique properties and advantages that make it capable of adsorbing many dyes, due to its high surface area due to its nanoparticles and large adsorption capacity. [11]. As for the use of the raw Astragulas plant to remove pigments from the aqueous solution using the mixing method and to make use of the remains of the Astragulas plant in an environmentally friendly manner [12].

MATERIALS AND METHODS

Preparation of the Disperse Red (DR) dye solution

A stock aqueous solution of the RED (DR) dye was prepared at a concentration 500 ppm by dissolving 0.25 g of dispersed red dye in 500 mml of water. To plot the standard curve, several concentrations of RED dye were prepared from (0.75 to 50) parts per million, which were used to measure the different dye concentrations in aqueous solution.

Preparation

a-Nanocellulose

Nanocellulose (NC) is prepared by an acidified aqueous solution containing 98% sulfuric acid, 36% hydrochloric acid and water added to 1 gram of cellulose. Then leave for 8 hours with constant stirring at room temperature. The acidified aqueous solution is then neutralized with 1 M NaOH. They are then separated by centrifuge, washed, and left to dry. The Nano partial size less than 100 nm [13].

b-Astragulas plant

Astragalus (AS) was collected in Al-Salman area in the desert of Al-Muthanna Governorate. The AS was then washed with distilled-water to remove impurities, and dried in an oven at (40 °C) for three hours. The plant was then ground and sieved to a granule size (125 µm).

Batch Adsorption Study

The batch method was used in the adsorption study. To determined 1the impacts of different critical parameters such as adsorbent amount, pH levels, and adsorbate-adsorbent interaction time (or contact time). A desired weight of the (NC)and (AS) adsorbent was added to a 500ml beaker. 20 ml of the dye was taken at room temperature [14]. For proper adsorption, the solution was subjected to a magnetic stirrer and withdrawn at various times. Then put in a centrifuge (5min), to separate the sample from the adsorbent. After separation,

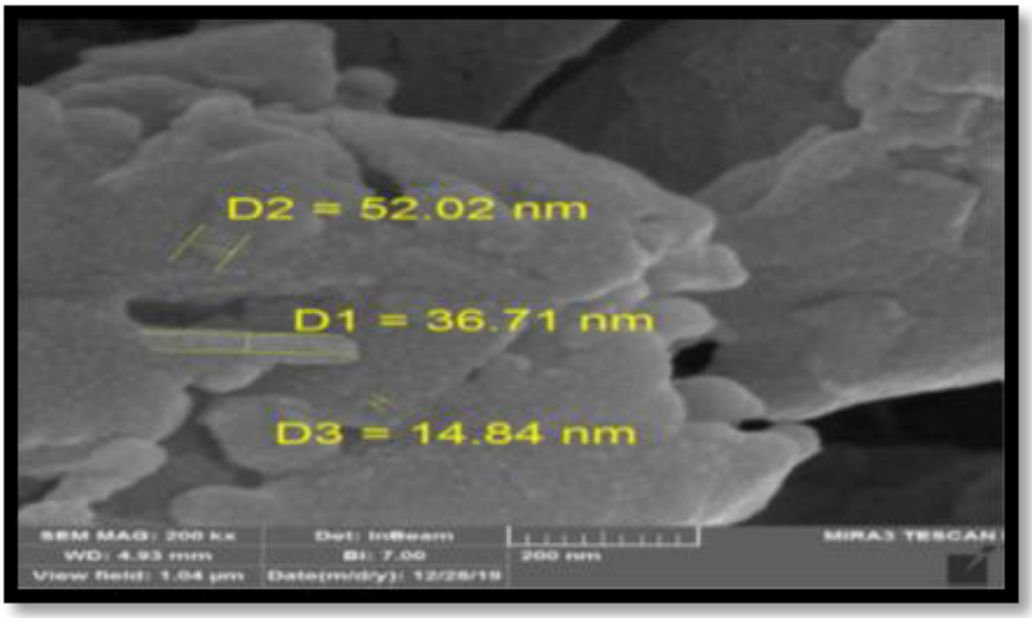

Fig. 3. The SEM image of the AS surface.

the absorbance was measured using UV-Spectrophotometer. to determine the dye uptake, some tests were carried out at different times (10-90) min and pH (3~11). A range of (0.005-0.1) g of (NC) and (0.02 to 0.5) g of (AS) adsorbent was also used. The amount of adsorption, qe(mg/g), was0 calculated using the Eq. 1:

$$qe = \frac{V(C0 - Ce)}{m} \quad (1)$$

C_0-and Ce:2the initial concentration and the

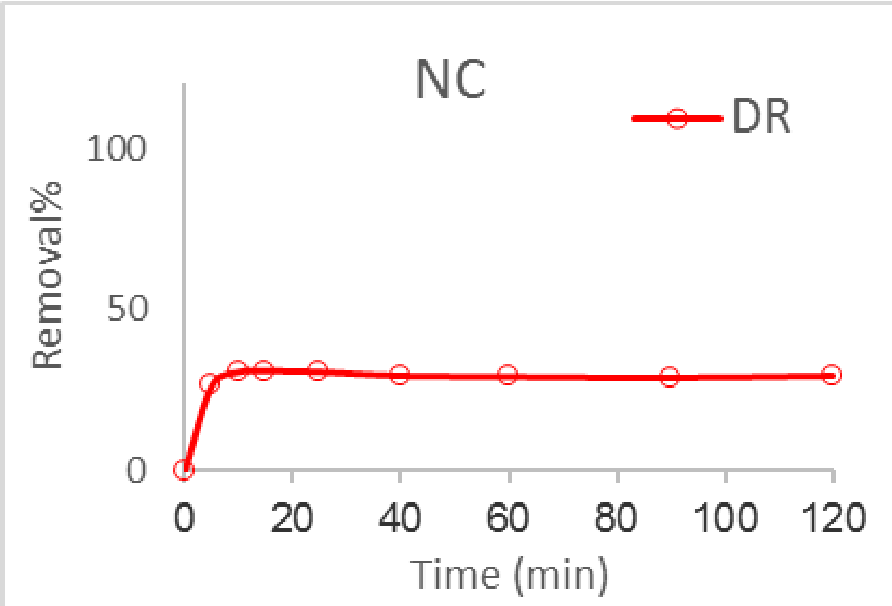

Fig. 4. Influence equilibrium time on the NC surface.

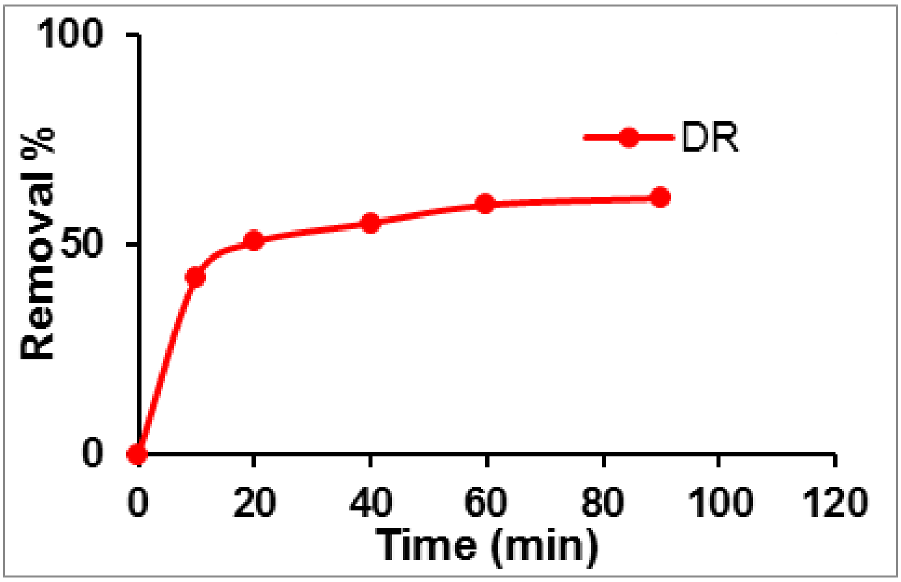

Fig. 5. Influence equilibrium time on the AS surface.

residual concentration of the dye in the solution measured (mg/L).

qe: the amount of dye absorbed, measured (mg/g).

V: represents the measured volume of dye solution (L). m: the mass of the absorbent material measured (g).

RESULTS AND DISCUSSION

Nanocellulose- morphology

The-surface of the powder (NC) was identified by scanning electron microscope as in Fig. 2. We notice the presence of light and dark regions and nanoparticles of different sizes, the average sizes of which are between 12 to 18 nanometers [15].

For the surface of astragalus plant as in Fig. 3, we observe a smooth rocky surface whose nanoparticles range from 14 to 52 nm.

Influence (equilibrium Time)

After adding (10 ml) of dye (DR) at a concentration of 50 ppm without changing the

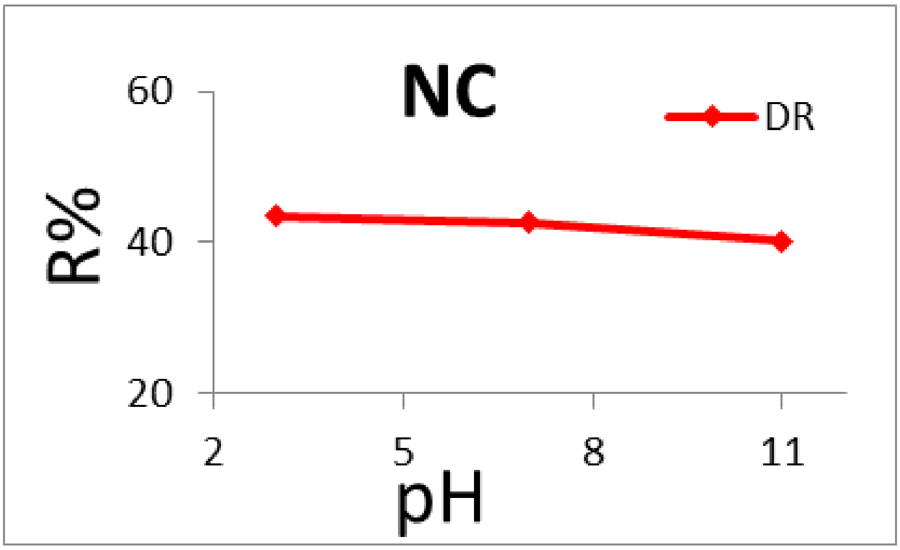

Fig. 6. Influence pH on DR dye adsorbed onto NC.

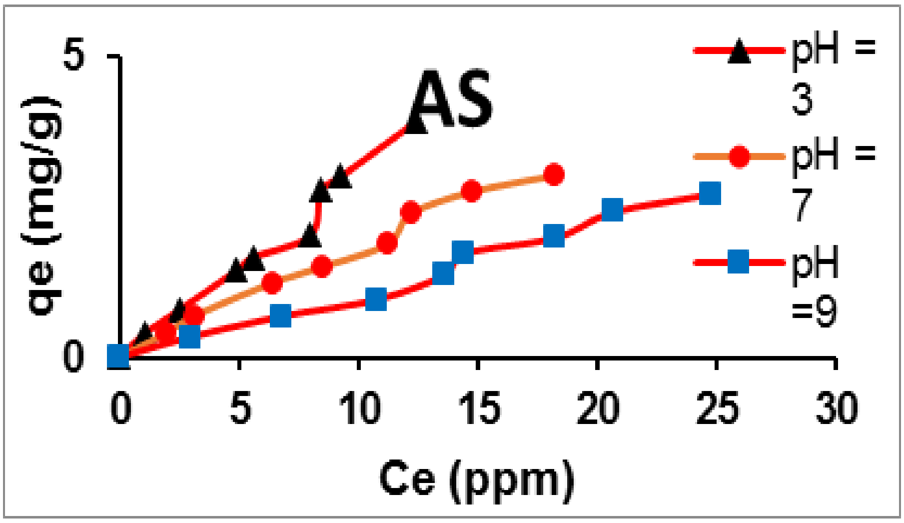

Fig. 7. Influence pH on DR dye adsorbed onto AS.

pH to 0.1 g of nanocellulose and also 0.1 g of astragalus, At different times (from 5, 10, 15, 25 40, 60, 90.120 minutes), and placed in water bath2 at room temperature and separated by centrifugation. The absorbance was measured by optical/visible spectrophotometer, and the results were as in Figs. 4.5 for two surfaces, where the equilibrium time for nanocellulose surface is 10 minutes and astragalus surface is 90 minutes [16].

Influence of (pH)

By conducting an acidity experiment on the

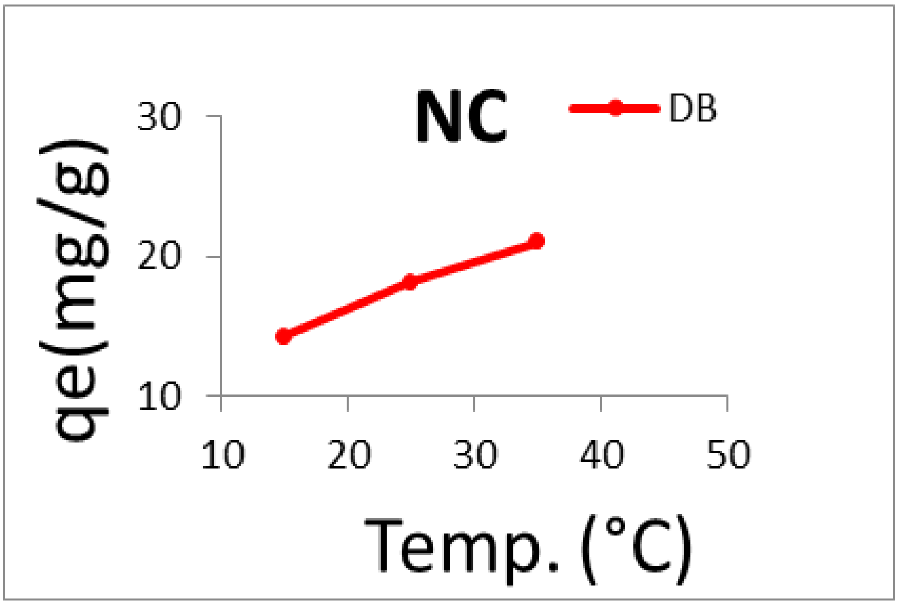

Fig. 8. Effects of Temp. of DR dye adsorbedr on to NC.

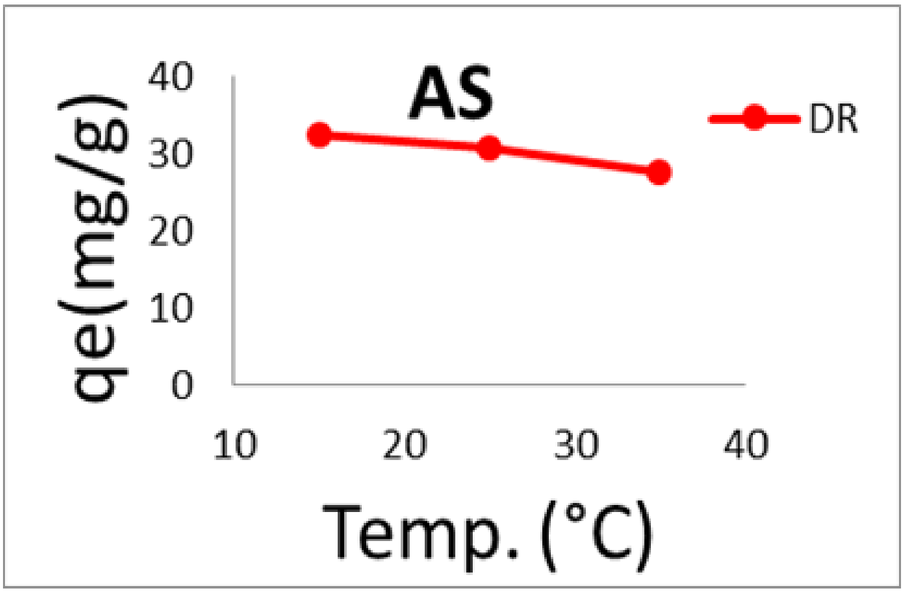

Fig. 9. Effect of Temp. of DR dye adsorbed on to AS.

surfaces of nanocellulose and astragalus plants, where acidic and basic solutions were prepared and added to the dyes, and the pH was measured at 3, 7 and 11, then 10 ml of red dispersed dye was added at a concentration of 50 ppm to 0.1g from NC and AS to complete the experiment at room temperature according to the contact time for each surface where separated by centrifugation and absorbance measurement, the following results increased the percentage of surface removal of NC & AS with pH 3>7>11 show in Fig. 6 and 7[17].

When the pH values of the solution decrease,

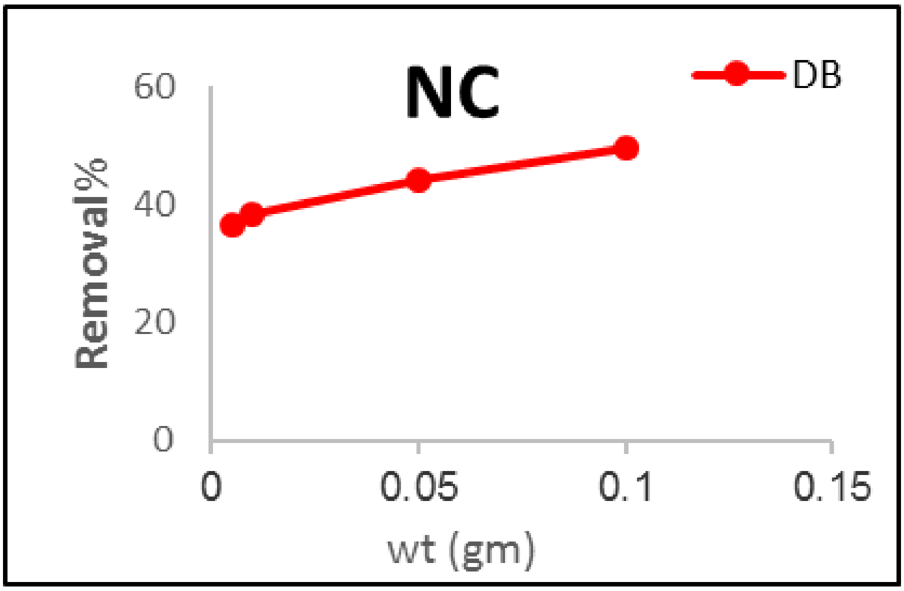

Fig. 10. Effect of adsorbent dosage for NC.

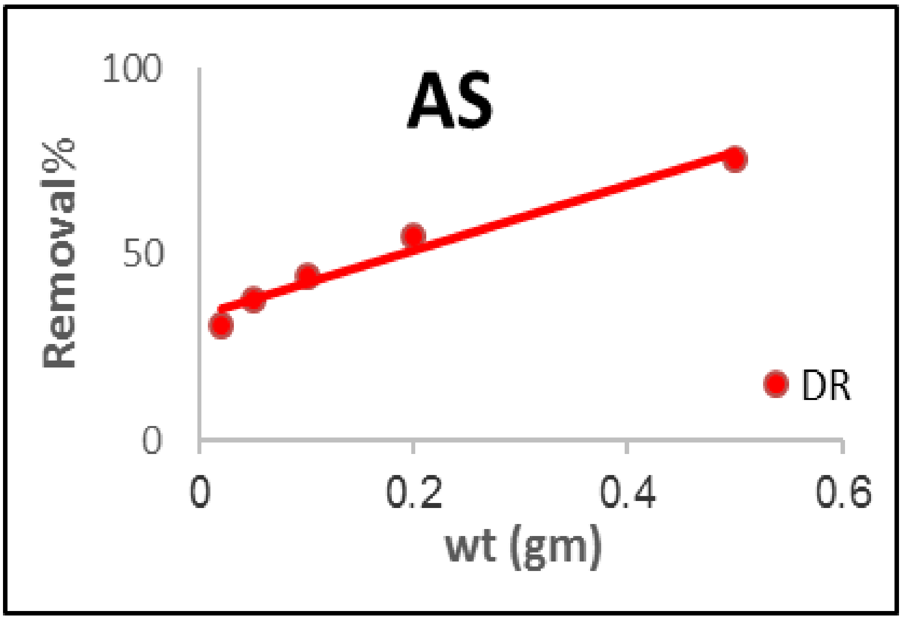

Fig. 11. Effect of adsorbent dosage for AS.

the positive charges control the adsorbent surface, since the positively charged surface will cause hydrostatic attraction to the absorbent material and the DR dye. In this case, a slight interaction such as a dipole charge can be suggested. The attractive force increases the adsorption of DR dye molecules on the surface of the absorbent material. When the pH of the system increases further, the adsorbed surface tends to become negative, which avoids DR dye adsorption due to electrostatic repulsion [18].

(qe): Calculate the amount of dye absorbed as in Eq. 2. (R%): The percentage of the pigment removed as in Eq. 3 is as follows:

$$qe = \frac{V(C0 - Ce)}{m} \quad (2)$$

$$R\% = \frac{(C0 - Ce)}{C0} * 100 \quad (3)$$

Influence of (Temperature)

The experiment was conducted at three different temperatures, 15, 25, 35. Where 10 ml of the dispersed red dye was taken at a concentration of 50 ppm with no change in pH and added to the surface of the 0.1g Nanocellulose and the surface of the astragalus plant and then at the mentioned degrees remained in the water bath. According to the ideal time for each surface, then the surface was separated by a centrifuge and the absorbance was measured. The following results appear in Figs. 7, 8 and 9 where the adsorption capacity increases relative to the nanocellulose surface with increasing temperature. Otherwise, it was the surface of the astragalus plant, where the adsorption capacity decreases with increasing temperature [19].

Influence of amount of adsorbent

The experiment of different weights is done by taking three different weights from the surface of the nanocellulose and the surface of the Astragalus plant and adding to it 10 ml of dispersed red dye at a concentration of 50 ppm and then placing it in the water bath at the optimum temperature and according to the equilibrium time for each surface, we will get the results as in Figs. 10, 11 Where it shows that the adsorption capacity increases with increasing weight because it leads to an increase in the active sites [20].

Adsorption Isotherm

The study of adsorption provides important

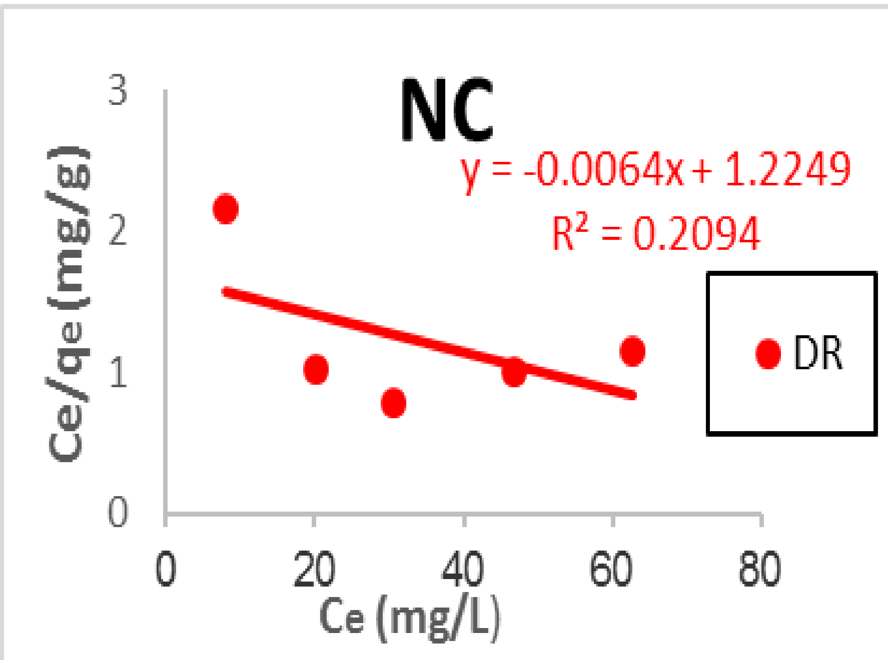

Fig. 12. Langmuir’s equation for DR dye adsorption on the surface of NC.

information about the method and energy of adsorption. The results were applied to two types of isotherms, Langmuir and Freundlich, for nanocellulose and astragalus surfaces. Freundlich isotherms absorb from a liquid to a solid surface and have multiple layers and energies [21]. Fig. 12 and 13 Multiple concentrations of DR dye were taken and adsorbed on the surface of NC & AS, then by drawing The linear equation of Freundlich isotherms, having the constants (Kf, n), gives us information about the amount of adsorption and the quality of the surfaces (homogeneous

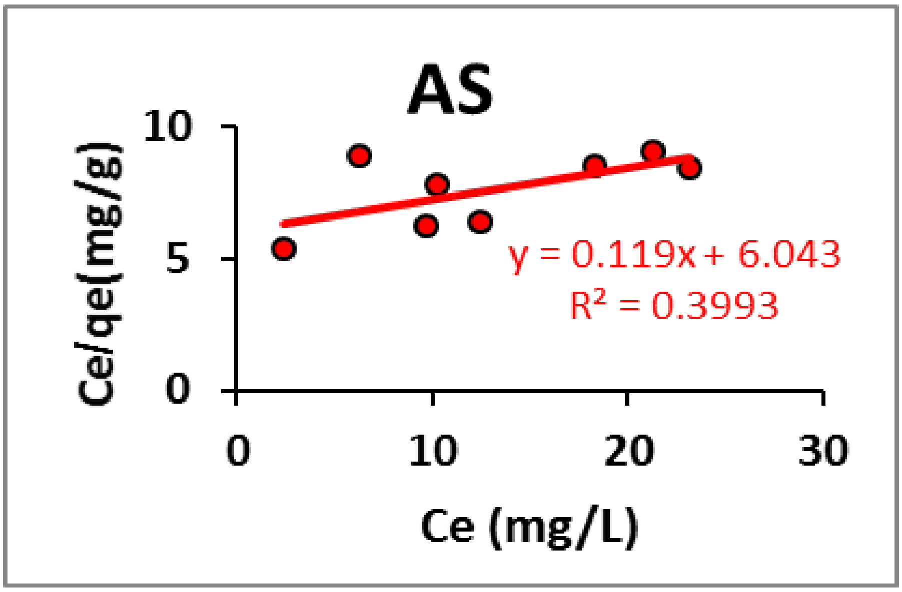

Fig. 13. Langmuir's equation for DR dye adsorption on the AS surface.

Table 1. Values of Langmuir and Freundlich Constants on the NC & AS Surface.

	Langmuir		
NC	qm	be	R2
	166.6	0.8169	0.209
	Freundlich		
NC	Kf	n	R2
	1.598	0.871	0.932
	Langmuir		
AS	qm	be	R2
	8.403	0.816	0.399
	Freundlich		
AS	Kf	n	R2
	5.662	1.168	0.949

or heterogeneous). Also, Langmer's constant was calculated by taking multiple concentrations of DR dye and drawing the linear relationship as in Figs. 14 and 15, and calculating Langmer's constant (b) and (qm) and the maximum absorption capacity of the two surfaces NC & AS by linear equations as follows:

The Langmuir linear equations (Eq. 4):

$$\frac{Ce}{qe} = \frac{1}{qm} * b + \frac{(Ce)}{qm} \quad (4)$$

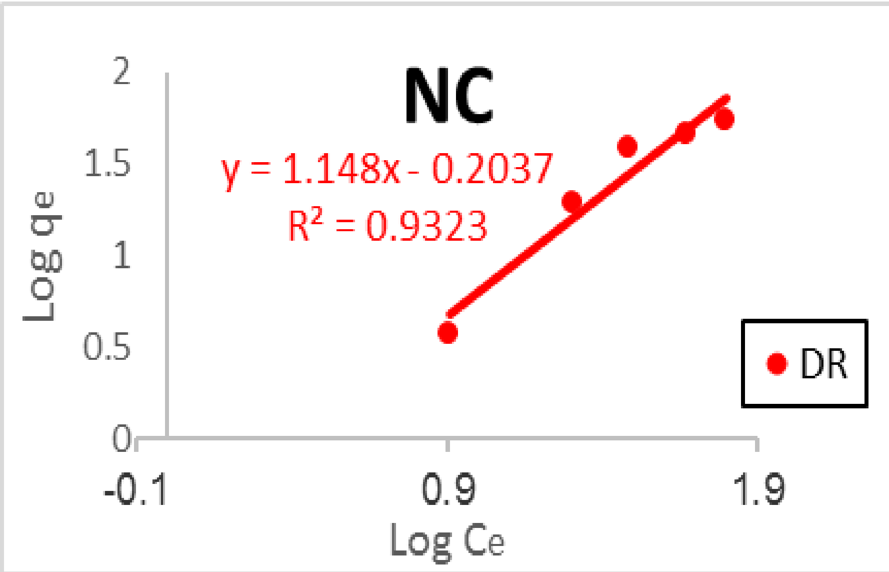

Fig. 14. Freundlich's equation for DR dye adsorption on the NC surface.

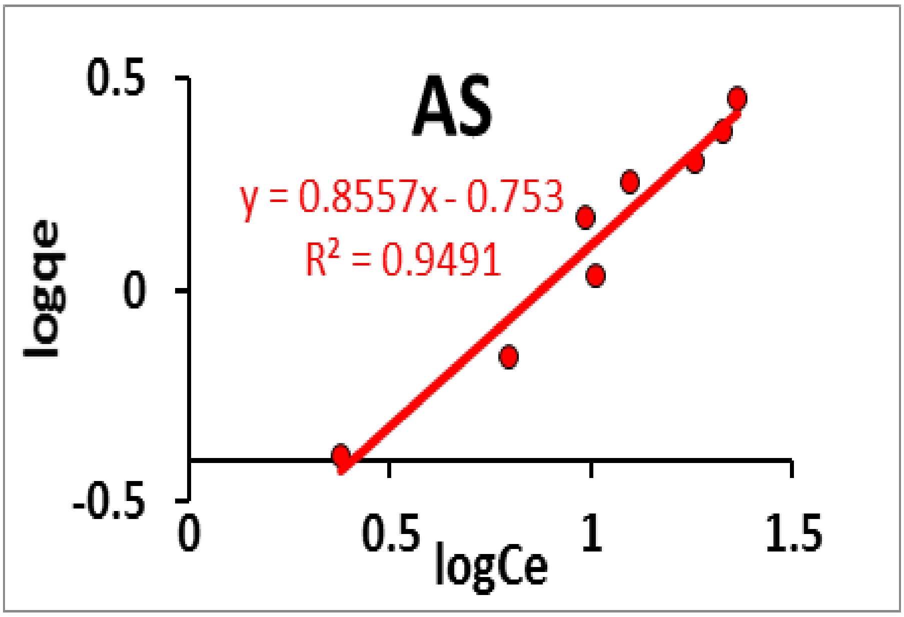

Fig. 15. Freundlich's equation for DR dye adsorption on the AS surface.

The Freundlich linear equations (Eq. 5):

$$\log qe_q = \log Kf + \frac{1}{(n \log Ceq)} \qquad (5)$$

From Table 1, we note that the values of the correlation coefficient (R) for both Langmuir and Freundlich, where the values of Freundlich R2 are greater than the others, the Freundlich model is more suitable 0to perform the adsorption of DR dye from an aqueous solution on the surface of NC and AS. It is a multi-layer adsorption (more than

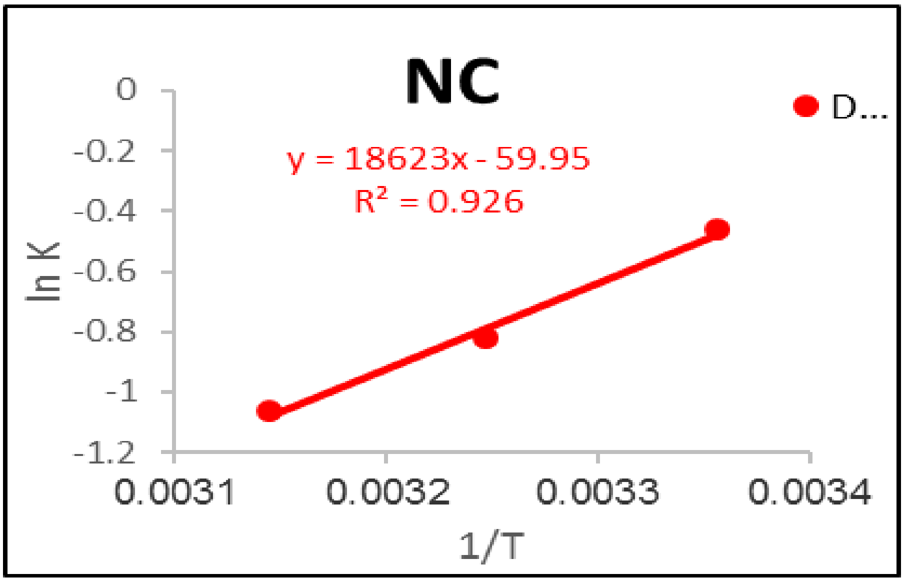

Fig. 16. lnK vs. (1/T) for the DR dye on the surface of the NC.

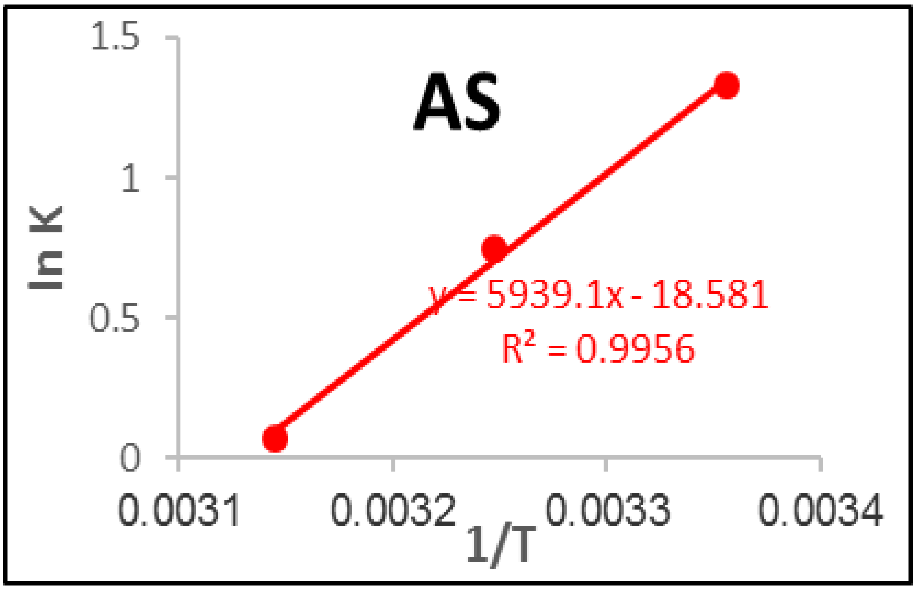

Fig. 17. lnK vs. (1/T) for the DR dye on the surface of the AS.

Table 2. Thermodynamic value of DR dye on NC & AS.

(NC)		
$\Delta\mathbf{H}$- (K.J.mol^{-1})	$\Delta\boldsymbol{G}$°u (J.mol^{-1})	$\Delta\boldsymbol{S}$°v (J.mol^{-1} K^{-1})
154.8316	-2103.26	-498.424
	(AS)	
$\Delta\mathbf{H}$ (K.J.mol^{-1})	$\Delta\boldsymbol{G}$°y (J.mol^{-1})	$\Delta\boldsymbol{S}$° i(J.mol^{-1} K^{-1})
-49.3768	-1924.16	-154.474

one layer) [22].

Thermodynamics

We have studied the dynamic kinetics of adsorption and find out the type of adsorption. We work at temperatures (from 298 to 318) measured in Kelvin to find out the change in adsorption entropy (ΔS^0), the changes in Gibbs freee energy (ΔG^0), and the standard enthalpy change (ΔH^0), according to the Eq. 6 [23]:

$$\Delta G^0 = - R\ T\ \ln k \qquad (6)$$

Variables must be specified and constants such as: (ΔG^0): is the change in Gibbs free energy, measured in (KJ.mol^{-1}).

T (is the absolute temperature of the solution, measured in Kelvin).

R: (is the general gas constant for the measured gases (8.314 g $^{-1}$. K $^{-1}$)).

K: (is the thermodynamic equilibrium constant for absorption).

The value of (K) was calculated by the Eq. 7:

$$K = \frac{(qe\ m)}{(Ce\ v)} \qquad (7)$$

Enthalpy standard change (ΔH^0) determined using lnk values versus the reciprocal of temperature (1/T) according to the Van't Hoff - Arrhenius equation (Eq. 8):

$$\ln k = \frac{(\Delta S°)}{R} - \frac{(\Delta H°)}{RT} \qquad (8)$$

From the line plots, show in Figs. 16, and 17 The results are shown in Table 2 for thermodynamic analysis from the calculation of (ΔS/R) and (-H/R) values. That the DR dye adsorption on the surfaceuof NC was spontaneous and endothermic (chemical adsorption). The DR dye adsorption on the AS surface was spontaneous and exothermic (physical adsorption) [24,25].

CONCLUSION

A comparison was made from an applied and practical point of view between two surfaces of NC and AS, in which we obtained the following results.

Nanocellulose (NC):

1. The surface preparation of nanocellulose is cheap and widely available. It has a high adsorption capacity for dyes.

2. Adsorption with respect to the surface of nanocellulose is preferred at pH = 3.

3. The adsorption amount of DR dye increases with the increase in the amount of adsorbent surface due to the increase of NC surface active sites. The results also indicate preferably, the higher the temperature, the higher the adsorption capacity of the NC surface.

4. The surface is multi-layered by conforming to the Friendlich isotherm.

5. The adsorption of DR dye on the NC surface is spontaneous and endothermic (chemical adsorption).

6. The equilibrium time is 10 minutes.

Astragalus plant (AS):

1. The surface preparation of astragalus is cheap and widely available in Al-Salman area in Al-Muthanna governorate. It has a high absorption capacity of dyes

2. Adsorption is preferred with respect to the surface of astragalus at pH =3

3.The adsorption of DR dye increases with the increase in the amount of surface AS due to an increase in the active sites of AS. This adsorption is preferred at lower temperatures as the adsorption capacity of the DR dye increases.

4. The surface is multi-layered in accordance with the temperature of Friendlich.

5. That the adsorption of DR dye on the AS surface is spontaneously exothermic (physical adsorption).

6. The equilibrium time is 90 minutes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Pavithra KG, P SK, V J, P SR. Removal of colorants from wastewater: A review on sources and treatment strategies. Journal of Industrial and Engineering Chemistry. 2019;75:1-19.
2. Adegoke KA, Bello OS. Dye sequestration using agricultural wastes as adsorbents. Water Resources and Industry. 2015;12:8-24.
3. Radhakrishnan S. The Sustainable Apparel Coalition and the Higg Index. Textile Science and Clothing Technology: Springer Singapore; 2014. p. 23-57.
4. Shahid ul I, Mohammad F. Natural Colorants in the Presence of Anchors So-Called Mordants as Promising Coloring and Antimicrobial Agents for Textile Materials. ACS Sustainable Chemistry and Engineering. 2015;3(10):2361-2375.
5. Carmen Z, Daniel S. Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview. Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update: InTech; 2012.
6. Sen TK. Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents. Journal of Chemical and Process Engineering. 2013.
7. Nounou MN, Nounou HN. Multiscale estimation of the Freundlich adsorption isotherm. International Journal of Environmental Science and Technology. 2010;7(3):509-518.
8. Mahmoodi NM, Maghsoodi A. Kinetics and isotherm of cationic dye removal from multicomponent system using the synthesized silica nanoparticle. Desalination and Water Treatment. 2015;54(2):562-571.
9. Mahmoodi NM. Synthesis of Amine-Functionalized Magnetic Ferrite Nanoparticle and Its Dye Removal Ability. J Environ Eng. 2013;139(11):1382-1390.
10. Jin L, Sun Q, Xu Q, Xu Y. Adsorptive removal of anionic dyes from aqueous solutions using microgel based on nanocellulose and polyvinylamine. Bioresour Technol. 2015;197:348-355.
11. Phanthong P, Guan G, Ma Y, Hao X, Abudula A. Effect of ball milling on the production of nanocellulose using mild acid hydrolysis method. Journal of the Taiwan Institute of Chemical Engineers. 2016;60:617-622.
12. Wang J, Xu J, Zhu S, Wu Q, Li J, Gao Y, et al. Preparation of nanocellulose in high yield via chemi-mechanical synergy. Carbohydr Polym. 2021;251:117094.
13. Ribeiro RSA, Pohlmann BC, Calado V, Bojorge N, Pereira N, Jr. Production of nanocellulose by enzymatic hydrolysis: Trends and challenges. Eng Life Sci. 2019;19(4):279-291.
14. Mao H, Gong Y, Liu Y, Wang S, Du L, Wei C. Progress in Nanocellulose Preparation and Application. Paper and Biomaterials. 2017;2(4):65-76.
15. Nasihin ZD, Masruri M, Warsito W, Srihardyastutie A. Preparation of Nanocellulose Bioplastic with a Gradation Color of Red and Yellow. IOP Conference Series: Materials Science and Engineering. 2020;833(1):012078.
16. Islam MT, Alam MM, Patrucco A, Montarsolo A, Zoccola M. Preparation of Nanocellulose: A Review. AATCC Journal of Research. 2014;1(5):17-23.
17. Henrique MA, Flauzino Neto WP, Silvério HA, Martins DF, Gurgel LVA, Barud HdS, et al. Kinetic study of the thermal decomposition of cellulose nanocrystals with different polymorphs, cellulose I and II, extracted from different sources and using different types of acids. Industrial Crops and Products. 2015;76:128-140.
18. Yu H, Qin Z, Liang B, Liu N, Zhou Z, Chen L. Facile extraction of thermally stable cellulose nanocrystals with a high yield of 93% through hydrochloric acid hydrolysis under hydrothermal conditions. Journal of Materials Chemistry A. 2013;1(12):3938.
19. Suneetha M, Sundar BS, Ravindhranath K. Removal of fluoride from polluted waters using active carbon derived from barks of Vitex negundo plant. Journal of Analytical Science and Technology. 2015;6(1).
20. Annadurai G, Juang R, Lee D. Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. J Hazard Mater. 2002;92(3):263-274.
21. Khattri SD, Singh MK. Removal of malachite green from dye wastewater using neem sawdust by adsorption. J Hazard Mater. 2009;167(1-3):1089-1094.
22. Shimizu N, Ogino C, Dadjour MF, Murata T. Sonocatalytic degradation of methylene blue with TiO2 pellets in water. Ultrason Sonochem. 2007;14(2):184-190.
23. Zhou J, Tang C, Cheng B, Yu J, Jaroniec M. Rattle-type Carbon–Alumina Core–Shell Spheres: Synthesis and Application for Adsorption of Organic Dyes. ACS Applied Materials and Interfaces. 2012;4(4):2174-2179.
24. Coles CA, Yong RN. Use of equilibrium and initial metal concentrations in determining Freundlich isotherms for soils and sediments. Engineering Geology. 2006;85(1-2):19-25.
25. Bartell FE, Thomas TL, Fu Y. Thermodynamics of Adsorption from Solutions. IV. Temperature Dependence of Adsorption. The Journal of Physical Chemistry. 1951;55(9):1456-1462.