Rapid adsorption of acid dyes using Cu(II) thiourea modified cellulose complex

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Abstract

In the present work, the acid dyes namely, eriochrome cyanine R (ECR) and 2-(4-Sulfo phenyl azo)-1,8 dihydroxy-3,6 naphthalene disulfonic acid, trisodium salt (SPADNS) were effectively adsorbed by Cu(II)-thiourea modified cotton fibers (Cu(II)/Tu-MC) complex. FTIR, SEM, thermogravimetric analysis, and potentiometric titration were utilized for characterization. The impact of the fundamental adsorption parameters was systematically investigated. The results reveal that the adsorption of ECR and SPADNS acid dyes occurs via a metal-coordination mechanism. Furthermore, the adsorption process follows the 2nd order kinetic model and Langmuir model adsorption isotherm. The Cu(II)/Tu-MC shows high adsorption capacities of 0.27 and 0.22 mmol. g^{-1} for ECR and SPADNS, respectively. These findings indicate that the cationization of cellulose fibers with metal ions is a promising and efficient strategy towards enhancing the adsorption of acid dyes.

Keywords: Cotton, Eriochrome cyanine, Acid dye, Thiourea modified cellulose (Tu-MC)

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1. Introduction

Currently, and due to rapid industrialization and urbanization, water sources could be contaminated with life-threatening pollutants such as heavy metal ions and organic dyes, which cause pollution of clean water used for extensive man usages all over the world. Due to the accumulation capabilities of these pollutants within living tissues, they can cause many serious health problems within the ecosystem, which will negatively impact human and animal health even when released into the ecosystem in very limited concentrations.

Many serious diseases such as different types of cancers, renal, liver, and lung failure are strongly associated with certain heavy metals and dyes pollutants, which can be released from industrial wastes to the water sources [1-6]. Thus, the removal of these contaminations from the ecosystem became an urgent need to maintain the limited freshwater sources for human consumptions. For these reasons, novel separation techniques such as membranes, solid-phase extraction, ion exchangers, and precipitation are continuously developed to be effectively utilized in the removal of different pollutants from the different aquatic effluent [7-10]. Solid-phase extraction using various adsorbent materials such as polymeric resins, polysaccharides, and active carbon is considered as one of the most efficient and economic techniques extensively utilized for the removal of different pollutants from aqueous media [11-15].

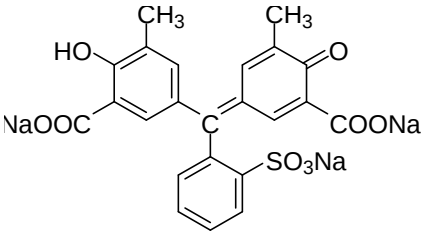
Among the aforementioned adsorbent materials, cellulose is considered as one of the most abundant natural polymers, which achieves an economic advantage. Despite this, its efficiency in capturing pollutants from water is relatively weak, which necessitates chemical modification with active functional groups that increase the ability of cellulose to scavenge pollutants quickly and efficiently. For example, the cellulose functionalization with chelating groups such as $–NH_2$, -COOH, $-SO_3H$, and succinyl groups [16-21] along with Cu(II)/EDTA functionalized cellulose were effectively employed in the removal of different water pollutants including heavy metal ions and organic dyes [22, 23].

In this study, Cu(II) ion polymeric complex based on thiourea modified cellulosic cotton fibers (Tu-MC) was synthesized and investigated for efficient adsorption of eriochrome cyanine R (ECR) and 2-(4-Sulfo phenyl azo)-1,8 dihydroxy-3,6 naphthalene disulfonic acid trisodium salt(SPADNS) acid dyes via metal ion coordination mechanism. The synthetic steps were entirely investigated using various spectral and instrumental techniques. The effect of the significant analytical parameters such as pH, contact time, temperature, initial concentration, and desorption was studied systematically.

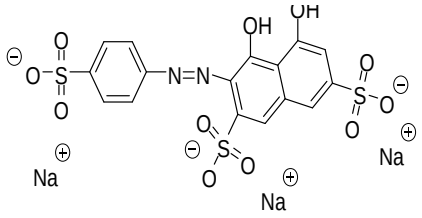
2. Experimental and methods

2.1. Materials

$CuCl_2.2H_2O$, Eriochrome cyanine R (ECR) 2-(4-Sulfo phenyl azo)-1,8 dihydroxy -3,6 naphthalene disulfonic acid, trisodium salt (SPADNS), potassium thiocyanate, potassium periodate, and ethylenediamine; were purchased from Sigma Aldrich. All these chemicals were used as received without further purification. The cellulosic cotton fibers have been obtained from a farm in Mansoura discrete in Egypt and rinsed with distilled water and ethyl alcohol before drying at 40 °C.



ECR



SPADNS

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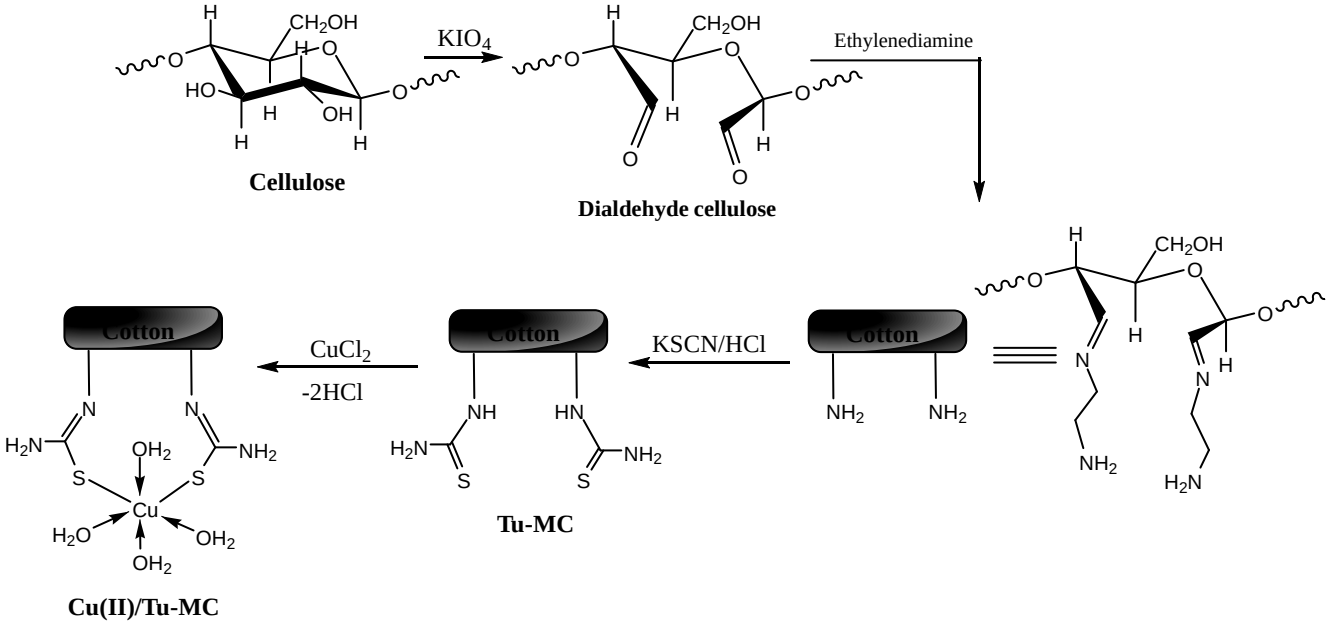
.Fig.1: Chemical structures of the investigated acid dyes

2.2. Synthesis of (Cu(II)/Tu-MC)

The synthesis of thiourea modified cellulose (Tu-MC) has been prepared according to a previous study [23]. Briefly, the aqueous KIO_4 solution (3 g/L, 100 mL) was prepared and placed in a conical flask. The clean cotton fibers (0.5 g) were immersed in the flask, which was then placed in a water bath at 50 °C and shaken for 1 h. The fibers were then taken from the flask and transferred to another one containing aqueous ethylene glycol solution (100 mL, 1% (v/v)) for 30 min to remove the excess KIO_4. The fibers were finally washed with ethyl alcohol before soaking in ethylenediamine alcoholic solution (100 mL, 10% (v/v)). The temperature of the mixture was then raised to 80 °C under reflux for 2 h. The treated fibers were then removed, washed with ethanol and distilled water before immersing in a mixture of aqueous potassium thiocyanate solution (100 mL, 10% (v/v)) and 2 mL, 0.5 M hydrochloric acid solution. The reaction flask was then connected to a reflux condenser and stirring continued at 80 °C for 2 h to finally obtain the thiourea modified cellulose (Tu-MC).

The Cu(II) ions loading was then carried out by immersing 0.5 g of the prepared Tu-MC fibers in aqueous $CuCl_2$ solution (100 mL, 150 mg/L) adjusted at pH 6 and equilibrating the mixture

for 3 h at 30 °C. The fibers were then turned green, which was taken as an indication for the reaction compellation and formation of the Cu(II) ions loaded Tu-MC (Cu(II)/Tu-MC) [24]. These reactions are schematically demonstrated in Scheme 1.



Scheme 1: Synthetic approach of Cu(II)/Tu-MC fibers

2.3. Characterization

The C, H, N, and S elemental percent composition for the untreated cotton, EDA modified cotton, and TU-MC samples were determined on a Perkin–Elmer 240 C Elemental Analytical Instrument (USA). An attenuated total reflectance (ATR) supported Perkin–Elmer Fourier-Transform Infrared (FT-IR) spectrometer (USA) was utilized to investigate the successive functionalization of the substrate cellulosic fibers until we obtain the Cu(II)/Tu-MC. A scanning electron microscope (SEM) (FEI Quanta-200 FEI Company, The Netherlands) is employed to monitor the surface morphology of the samples. The fibers were sputtered and coated with gold before examinations. Agilent's 5100ICP-OES (Agilent technologies. Melbourne, Australia) was utilized to determine the Cu(II) ions contents. Perkin-Elmer Bio UV–visible (LAMBDA XLS, USA) Spectrometer was employed in determining the residual concentrations of both ECR and SPADNS at λ_{max} = 525 and 510 nm, respectively. E53b potentio-graph connected with a 665 DOSIMAT (Metrohm, Herisau, Switzerland) was utilized in the Potentiometric measurements. Thermo analyzer Shimatzu DT40 (Japan) was used to record the TGA and DTA within a temperature range between 30 and 800 °C with 5 °C temperature break and under 20 mL/min flow rate of N_2.

2.4. Adsorption of acid dyes

The batches were prepared in plastic bottles containing 50 mg of the adsorbent Cu(II)/Tu-MC fibers immersed in the aqueous dye solutions with definite concentrations and pH values. The bottles were shaken at 200 rpm for certain predetermined periods at different temperatures. Upon the performance of the dye uptake process, the remaining concentrations of the dyes were measured to calculate the adsorbed amounts according to Eq. (1) to determine all the essential parameters including the maximum adsorption capacity, kinetics, and thermodynamic parameters.

$$q_e = \frac{(C¿¿org - C_e)V}{W}¿ \qquad (1)$$

Where q_e (mg. g^{-1}) is the adsorbed amount, C_{org}(mg. L^{-1}) and C_e (mg. L^{-1}) are the initial and equilibrium acid dyes concentrations, respectively. V (L) is the volume of the batch solution containing W (g) of the adsorbent fibers. The concentration of Cu^{2+} is determined after the adsorption process of dyes.

2.5. Fastness properties

The wash fastness of the dyed samples was evaluated according to the standard ISO 105-C06:2010 (A1S) using a neutral soap. The lightfastness test was performed under irradiation with Xenon arc fading lamp test for 40 hours according to ISO 105B02:2013 (method 5). Fading due to washing and light, and staining on a white test cloth were assessed using the grayscale.

3. Results and discussion

3.1. Characterization

3.1.1. Elemental analysis

Elemental percent composition of the natural cellulosic cotton along with the EDA-cotton and Tu-MC. Are given in Table 1. It demonstrates the C, H, N, and S elemental percent composition of the materials investigated. The N existence within both EDA-cotton and Tu-CM besides the appearance of S in Tu-CM with considerable contents could be taken as clear evidence for the successful incorporation of the thiourea units within the chemical structure of the modified cellulosic fibers with an approximate amount of 4.85 mmol/g.

Table 1

Elemental analysis of cotton, EDA-cotton, and Tu-MC.

Fibers	C(%)	H(%)	N(%)	S(%)
Cotton	43.3	6.02	0	0
EDA-cotton	50.2	9.6	19.4	0
Tu-MC	40.4	7.3	22.3	15.5

3.1.2. Infra red spectra

The successive steps that have been involved during the preparation of Tu-MC were all monitored by FTIR spectra (Fig. 1). The natural cotton displayed the well-known cellulosic peaks around 1075-1152 cm^{-1} and 1263-1415 cm^{-1} that belong to C-O stretching and O-H bending, respectively. Moreover, the O-H stretching could be recognized by the broad beak around 3500 cm^{-1} [24]. The formation of dialdehyde cellulose is also confirmed by the appearance of the characteristic aldehyde carbonyl group around 1735 cm^{-1} (Fig. 1b). In addition, the insertion of the EDA via Schiff base formation is also evidenced by the presence of the C=N peak around 1715 cm^{-1} (Fig. 1c). Furthermore, the implementation of the thiourea units could be revealed by the appearance of C=S peaks around 1293 and 865 cm^{-1} (Fig. 1d).

Scheme 2 displayed the thione-thiol tautomerism, which is a common observation with thiourea derivatives containing NH-C=S moieties [23]. As mentioned above, the Tu-MC spectrum displayed only the C=S peaks at 1293 and 865 cm^{-1} and no peaks have been noticed around 2300 and 1200 cm^{-1}, which are characteristic for S-H or C-S bonds, respectively. This finding suggested that thione is the dominant tautomer, particularly in solid-state.

The FTIR spectrum of the Cu(II)/Tu-MC fibers was also performed to investigate the coordination mechanism of Cu(II) ions and thiourea incorporated moieties. Table 2 presents a comparison of the main characteristic peaks that undergoes clear alternations upon the Cu(II) ions loading. As can be observed, during the Cu(II) ion coordination, the characteristic C=S peaks have been disappeared with the simultaneous appearance of C-S peaks around 1150 and 663 cm-1. Also, a new C=N peak around 1665 cm-1 is observed and no S-H peak can be noticed around 2300 cm-1. These findings indicated thione-thiol transformation with –SH deprotonation during the Cu(II) ions chelation.

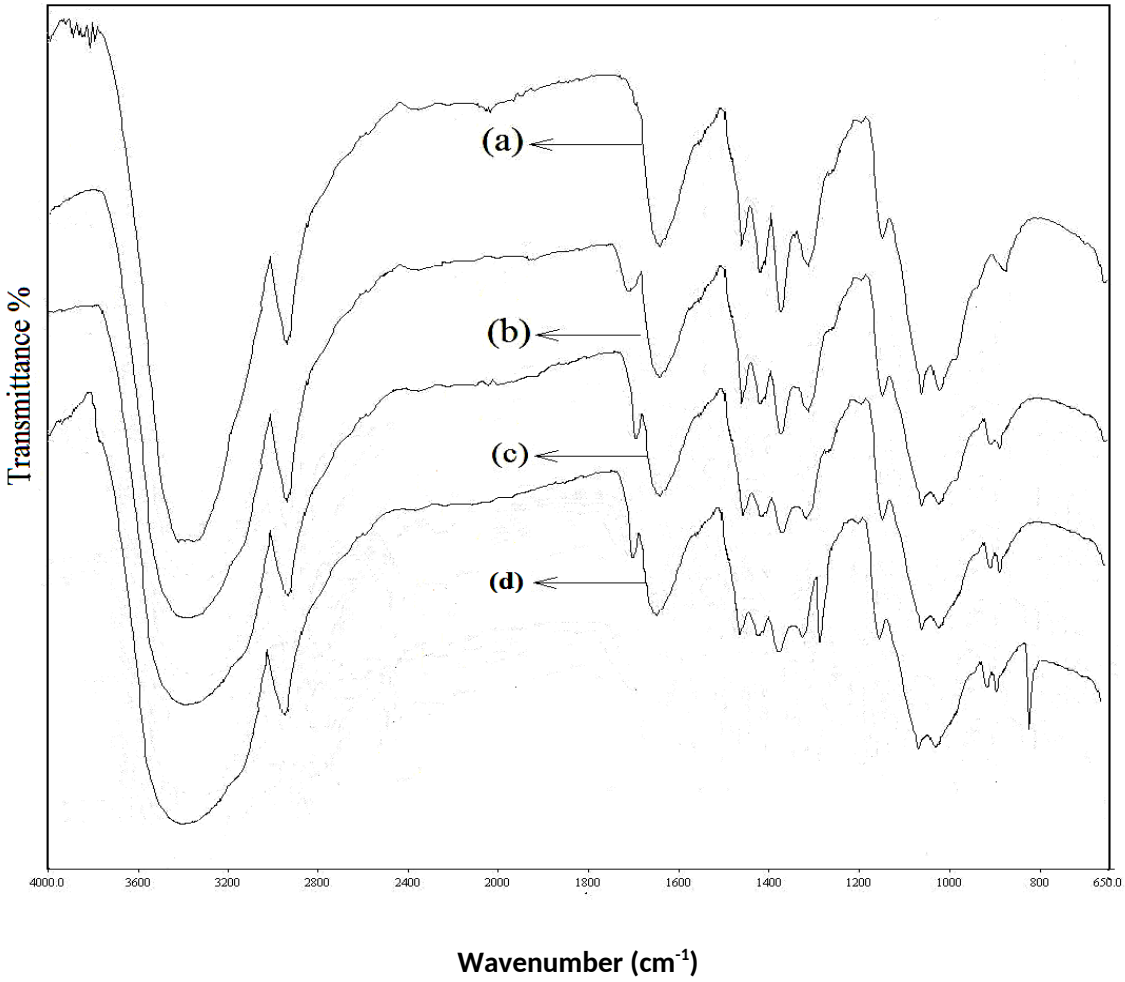
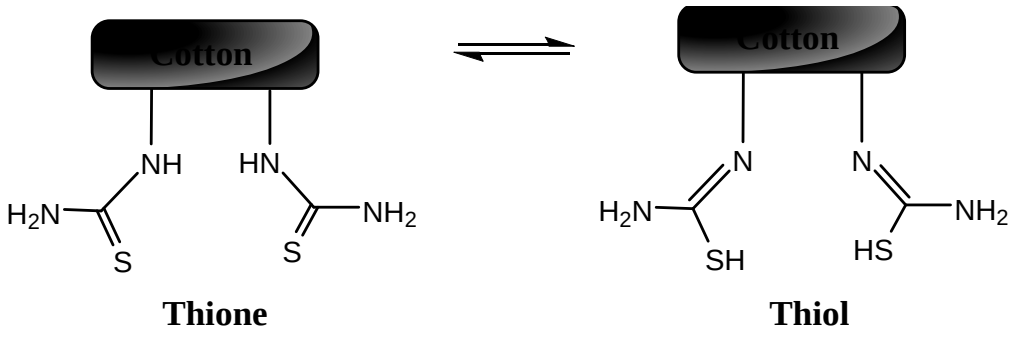


Fig. 2. FTIR spectra of (a) natural cotton, (b) oxidized cotton, (c) EDA-cotton, and (d) Tu-MC.



Scheme 2. thione-thiol tautomerism of Tu-MC

Table 2. Assignments of characteristic IR spectral peaks (cm^{-1}) of Tu-MC and Cu(II)/Tu-CM.

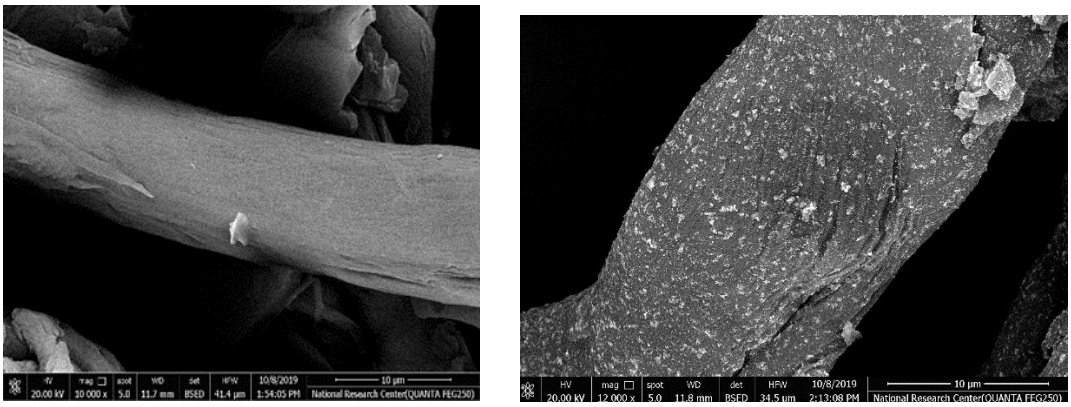
Fibers	*ν*(C=N)[a]	*ν*(C=N)[b]	*ν/δ*(C=S)	*ν/δ*(C-S)
Tu-MC	1715	-	1293, 865	-
Cu(II)/Tu-CM	1712	1665	-	1150, 663

[a]Azomethine

[b]New

3.1.3. Scanning electron microscope

The morphological appearances of both Tu-MC and Cu(II)/Tu-MC have been visualized using SEM and the images are displayed in Fig. 2. The Cu(II) ions loaded fibers exhibited a rough surface with an irregular appearance compared to the Cu(II) ions free fibers. This could be attributed to the morphological alternation that may take place within the fiber structure during the chemical interaction with Cu(II) ions. This difference is also clarified by the color of each fiber. As can be seen, the Cu(II) free fibers displayed a pale yellow color while Cu(II)/Tu-MC fibers were green, which can imply the formation of a polymeric Cu(II) ions complex [24].



(a) (b)

Fig. 2: SEM micrographs of (a) Tu-MC, (b) Cu(II)/Tu-MC

3.1.4 Thermal studies (Thermogravimetric analysis)

The obtained Tu-MC and Cu(II)/Tu-MC along with the natural cotton fibers were also investigated by thermal analysis, TGA and DTA, in a temperature range of 30-800 °C, and the thermograms are presented in Fig. 3. It is obvious that upon the chemical modification and Cu(II) ions coordination, the used modified cotton fibers displayed a different decomposition pattern with four consecutive decomposition steps compared to the natural cotton, which displayed only two steps during the thermal degradation [25]. Moreover, the residual weight formed from the Cu(II) ions containing fibers attains around 15%, which is higher than that obtained from that of the Cu(II) ions-free Tu-MC fibers (4%).

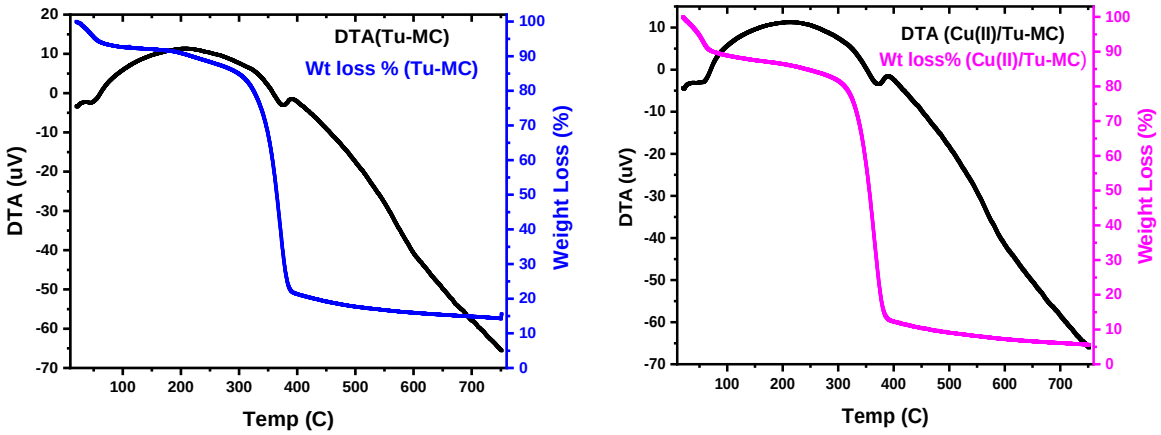


Fig.3. Thermal gravimetric analysis of (a) Tu-MC and (b) Cu(II)/Tu-MC

3.1.5. Potentiometric characterization

The coordination nature of the Cu(II) ions with the thiourea units implemented within the structure of the Tu-MC fibers was clarified using potentiometric titrations and the curves are shown in Fig. 4. As can be noticed, the Tu-MC presents two expected inflection points related to both amino and –SH protons. The stepwise deprotonation of the two groups is indicated with pK_1 = 7.65 and pK_2 = 9.4. In presence of Cu(II) ions, the titration curve displayed a right shift with different pK values revealing the liberation of the protons during the formation of the Cu(II) ions polymeric complex as previously reported [24].

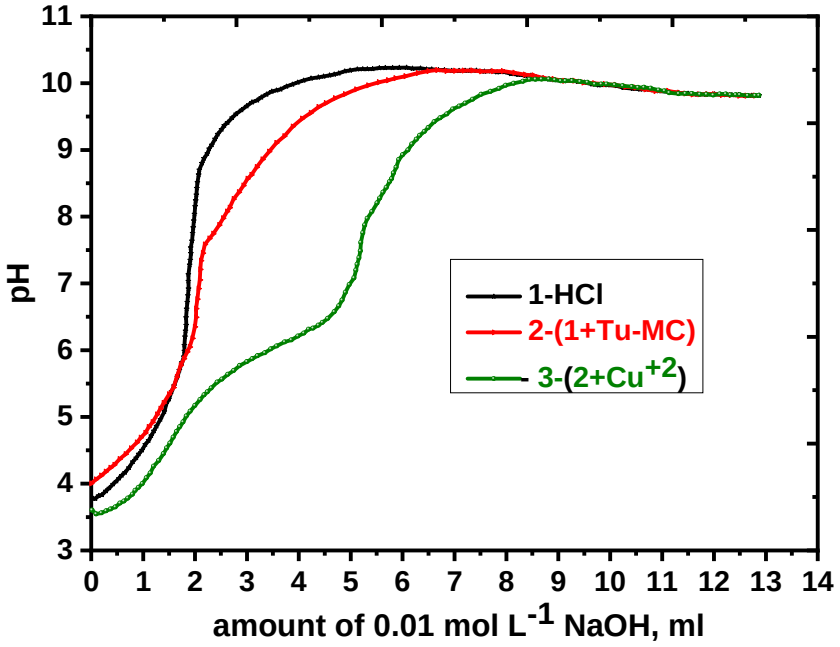
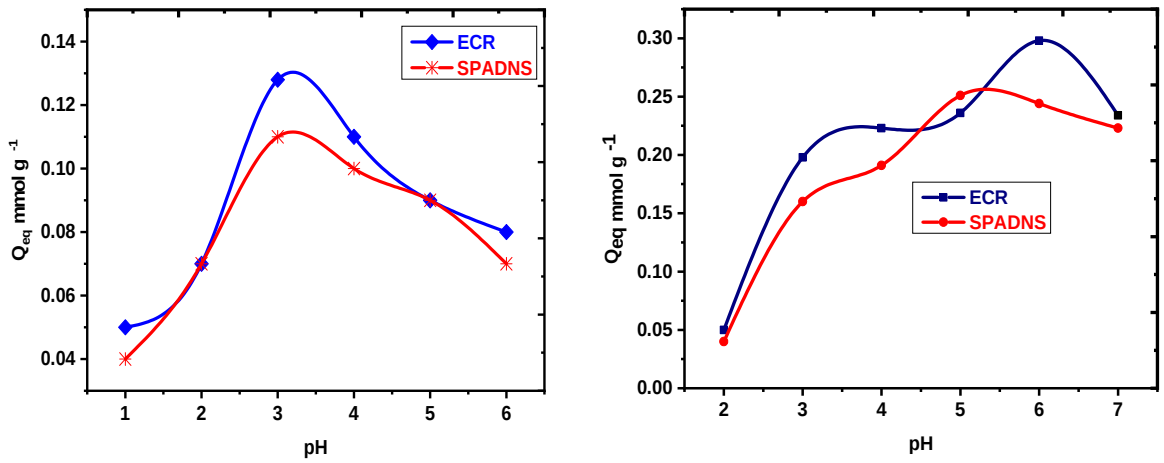


Fig.4. The pH metric titrations of (a) HCl, (b) [HCl + Tu-MC] and (c) [HCl + Tu-MC + Cu(II)] against 0.01 mol L^{-1} NaOH].

3.2. Adsorption of ECR and SPADNS by Cu(II)/Tu-MC fibers

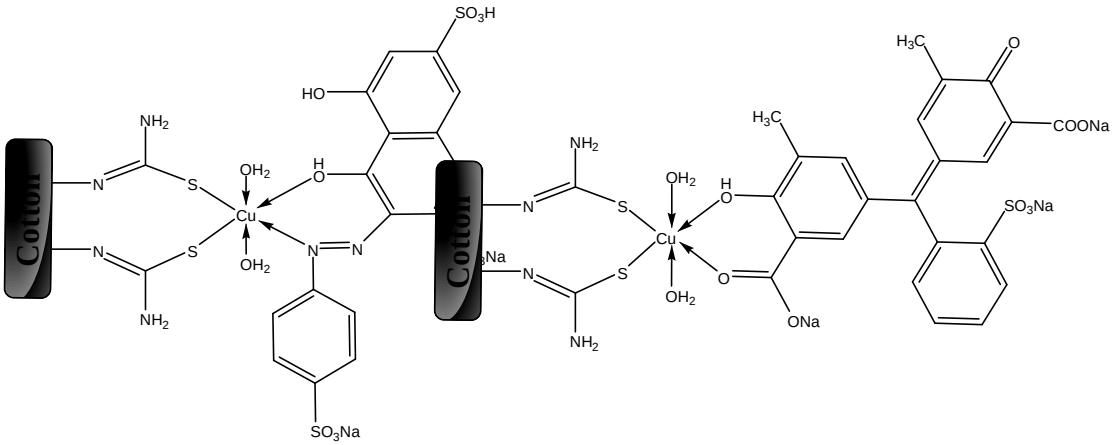
3.2.1. Effect of pH

The uptake of the organic acid dyes ECR and SPADNS by the modified Tu-MC and Cu(II)/Tu-MC fibers were investigated as a function of the initial pH of the working batch solution under pH range 1-7. The obtained results are shown in Fig. 5 and as can be noticed, the Tu-MC fibers adsorbed considerable amounts of ECR at pH 3 and SPADNS at pH 4. However, the affinity toward both dyes was dramatically reduced at higher pH values, which could be attributed to the inevitable decrease of the protonation degree of the inserted functional groups that could interact with anionic sulfonate groups of the dyes and consequently, decrease the adsorption capability of the Tu-MC fibers [26]. On the other hand, the Cu(II) ion containing Cu(II)/Tu-MC fibers displayed different behaviors and exhibited relatively higher uptake values for both ECR and SPADNS at pH values 5 and 6 (Fig. 5b), which indicates the important role played by the coordinated Cu(II) ions in enhancing the dye uptake capabilities via coordination mechanism [27,28] as schematically suggested in Scheme 3.



(a) (b)

Fig.5. Effect of pH on the uptake of ECR and SPADNS using (a) 0.04 g cotton fibers Tu-MC and (b) 0.04 g Cu(II) / Tu-MC in a series of flasks containing 40 ml (0.3 mmol L^{-1}).



(a) (b)

Scheme 3. Proposed coordination mode of Cu(II)/Tu-MC with (a) ECR and (b) SPADNS.

The digital photographs of modified cotton fibers Cu(II)/Tu-MC after adsorption of ECR and or SPADNS dyes are shown in Fig.S1. The bluish violet and brilliant red colors of Cu(II)/Tu-MC after adsorption of ECR and SPADNS ensure the complete penetration and adsorption of both dyes within the modified fibers.

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3.2.2. Thermodynamics

The uptake of ECR and SPADNS by Cu(II)/Tu-MC was studied under different temperatures to evaluate the thermodynamic functions including standard free energy (ΔG^{o}_{ads}), enthalpy (ΔH^{o}_{ads}), and entropy of adsorption (ΔS^{o}_{ads}). As can be seen in Fig. 7a, both dyes displayed a noticeable uptake lowering by increasing the temperature, which may give a clue about the exothermic nature of the dye-fibers interaction. The following series of mathematical equations are utilized to determine the aforementioned thermodynamic parameters.

The equilibrium constant K_C was first calculated using Eq. 2

$$K_C = C_{ads}/C_{eq} \qquad (2)$$

where C_{ads} (mg/g) is adsorbed ECR or SPADNS amounts by the Cu(II)/Tu-MC and C_{eq} (mg/L) is the equilibrium concentration of the dyes in the solution.

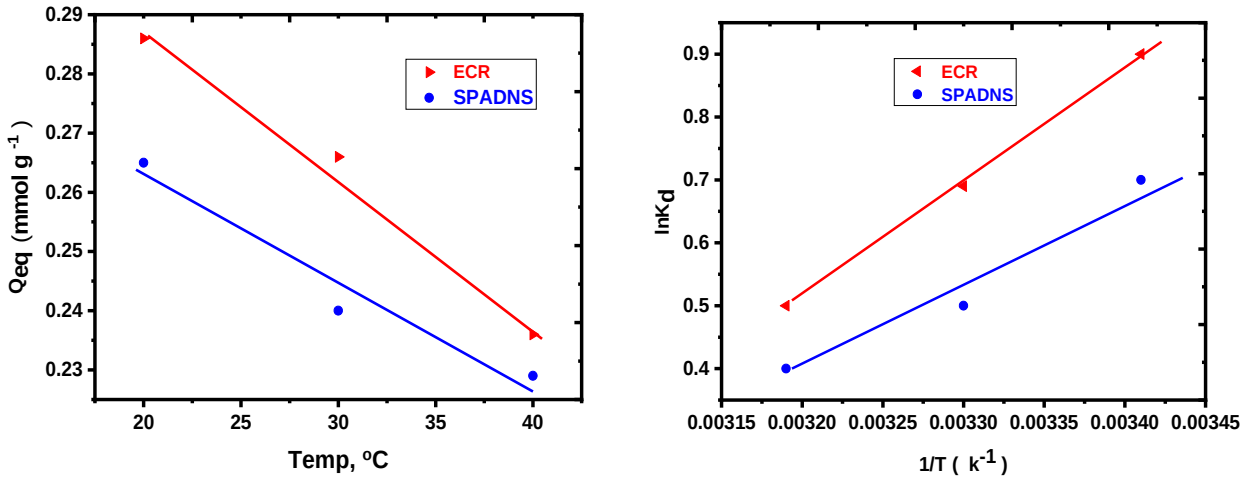
The corresponding ΔG^{o}_{ads} can be evaluated using the previously determined K_C values according to Eq. (3).

$$-\Delta G^{o}_{ads} = nRT \ln K_C \qquad (3)$$

where R is the universal gas constant R (8.314 J/mol K).

Both ΔH^{o}_{ads} and ΔS^{o}_{ads} are determined by plotting the estimated lnKc values against 1/T (Fig. 7b) following Eq. 4. The values of the intercept and the slop were used to determine ΔS^{o}_{ads} and $\Delta H^{o}_{ads,}$ respectively.

$$\ln K_C = (\Delta S^{o}_{ads}/R) - (\Delta H^{o}_{ads}/RT) \qquad (4)$$



(a) (b)

Fig.7. Effect of temperature on the uptake of ECR and SPADNS dyes on Cu(II)/Tu-MC (a) The plot of $\ln K_d$ of dyes against 1/T (b).

The determined thermodynamic functions were demonstrated in Table S1. The observed ΔG^{o}_{ads} exhibited negative values under all studied conditions, which implies the spontaneous uptake of both ECR and SPADNS by the adsorbent Cu(II)/Tu-MC fibers. Moreover, ΔS^{o}_{ads} values were found to be negative, which is expected in such type of uptake process that usually decreases the randomness of the system over the aggregation of the dyes molecules onto the adsorbent fibers surface. Finally, the exothermic nature of the dye uptake process was confirmed by the calculated ΔH^{o}_{ads} values.

3.2.3. Contact time

The kinetics of ECR and SPADNS uptake by the modified Cu(II)/Tu-MC were investigated by monitoring the adsorbed dye amounts within predetermined time intervals from 60 to 240 min and the resulted are presented in Fig. 8. As can be seen, the uptake of the dye demonstrated an initial rapid profile, and the equilibrium was reached within around 190 min in both ECR and SPADNS. After 4 h, the color of the solution of ECR dye almost changed to be colorless in the case of ECR and slightly changed to faint red in the case of SPADNS. The obtained kinetic data were employed to understand the nature and mechanism of the uptake of the dye by Cu(II)/Tu-MC by treatment with both pseudo 1st order model and pseudo 2nd order mathematical equations Eq. (5) and Eq. (6), respectively [16, 29].

$$\ln(q_e - q_t) = \ln q_{e1} - k_1 t \qquad (5)$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_e} \qquad (6)$$

where *t* is the contact time (min), q_t (mmol/g) is the extracted dyes amounts by Cu(II)/Tu-MC fibers after *t* min and q_e (mmol/g) is the extracted dyes amounts after the equilibration. k_1 (min^{-1}) is the rate constant related to the pseudo 1st order model and k_2 (g $mmol^{-1}$ min^{-1}) is the rate constant of the 2nd order model.

The obtained constants and parameters of the kinetic moles are collected in Table S2 and as expected the experimental values found are much more closer to the calculated values obtained from the 2nd order model with a greater R^2 value suggesting that the uptake of both ECR and SPADNS by the developed Cu(II)/Tu-MC fibers involve chemical interactions via coordination mechanism [30].

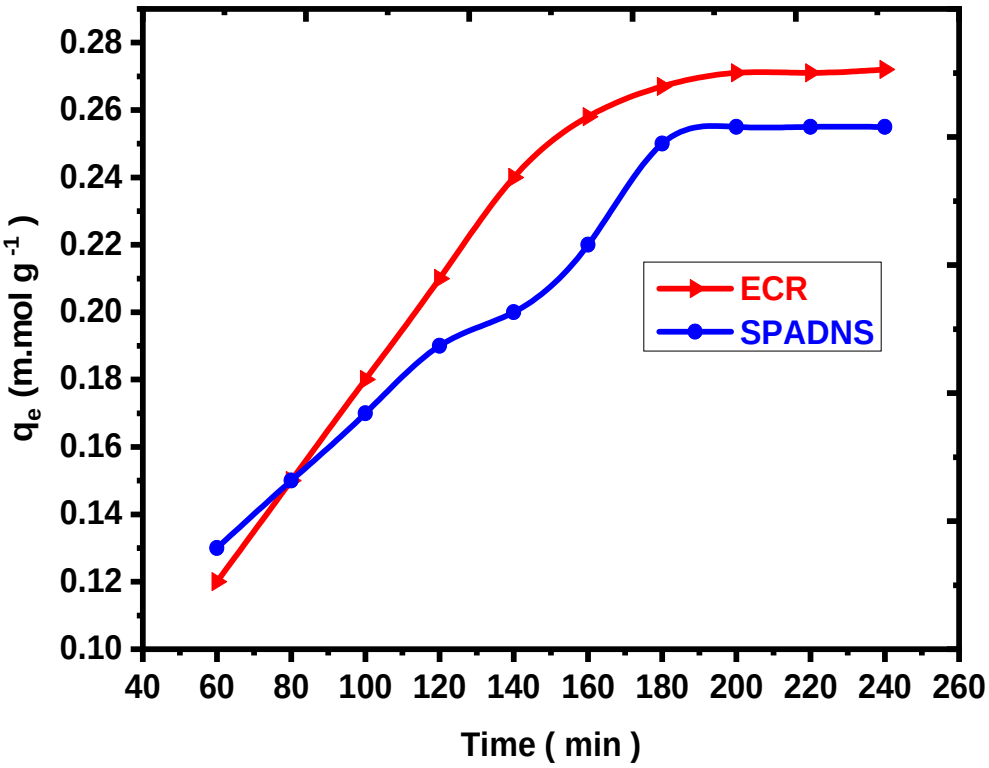


Fig. 8: Effect of contact time on the uptake of both ECR and SPADNS by Cu(II)/Tu-MC

3.2.4. Isotherm studies

The uptake of ECR and SPADNS using Cu(II)/Tu-MC was monitored in a series of batches containing different initial dye concentrations to evaluate the nature of the dye interaction with the modified fibers and determine the maximum capacity related to each dye. The isotherms are presented in Fig. 9, which displayed a noticeable raising of the Cu(II)/Tu-MC capacity toward both ECR and SPADNS by raising the dye concentration in the adsorption batch. As the dyes were contentiously adsorbed on the Cu(II)-Tu-MC fibers, the concentration of the dyes around the surface of the fibers became less than that in the bulk of the solution, which can enhance the adsorption capacity at equilibrium under the developed mass transfer force. Furthermore, the mathematical analysis of the isotherms was carried out by the well-known Langmuir and Freundlich models that are shown by Eq. (7) and Eq. (8), respectively [31-33].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (7)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (8)$$

where C_e (mmol/L) is the equilibrium ECR and SPADNS concentration after equilibration; q_e (mmol/g) is the adsorbed ECR and SPADNS amounts by Cu(II)/Tu-MC; q_m (mmol/g) is the calculated maximum capacity of ECR and SPADNS by the Cu(II)/Tu-MC adsorbent fibers; K_L (L/mmol) is the Langmuir model constant; K_F and n are Freundlich model constants.

The values of the parameters resulted from the above equations are collected in Table 5. It can be observed that the results are consistent with the Langmuir model more than the Freundlich model with the observed higher R^2 values suggesting the uptake of the ECR and SPADNS dyes in monolayer pattern over the Cu(II)/Tu-MC adsorbent fibers that contain energetically equivalent chelating sites. A comparison of the proposed modified adsorbent with the other cited adsorbents is given in table S4

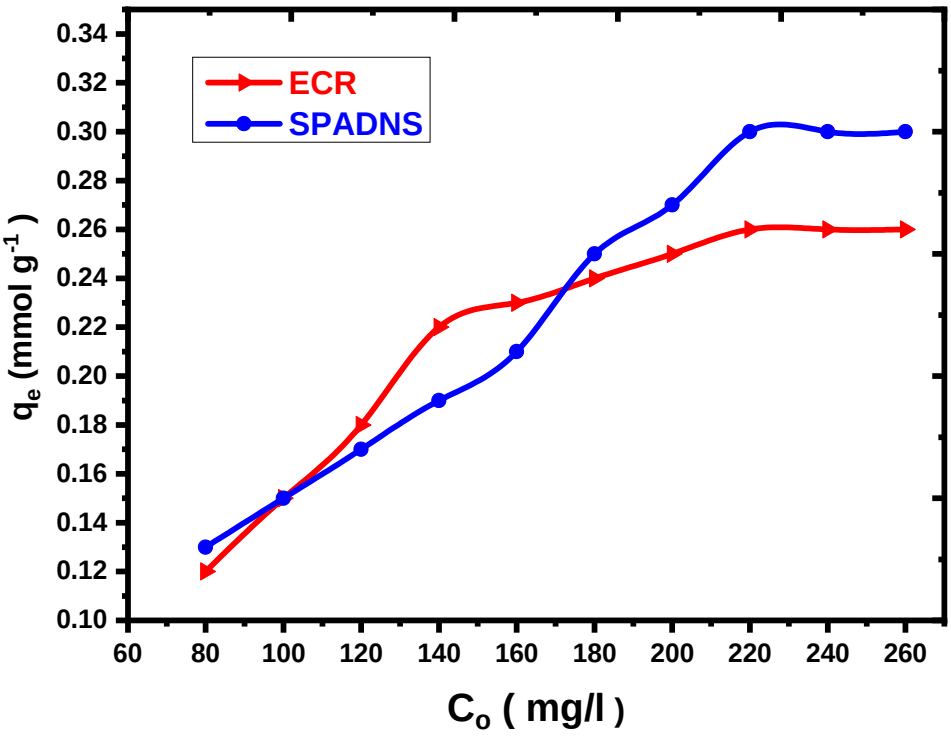


Fig.9. Adsorption isotherms of (ECR, SPADNS) dyes by Cu(II)/Tu-MC sorbent initial concentrations, sorbent (0,040 g), at pH 6.0, and shaking rate 150 rpm, at 25°C.

Table 5. Physicochemical adsorption of organic dyes (ECR and SPADNS) by Cu(II)/Tu-MC sorbents.

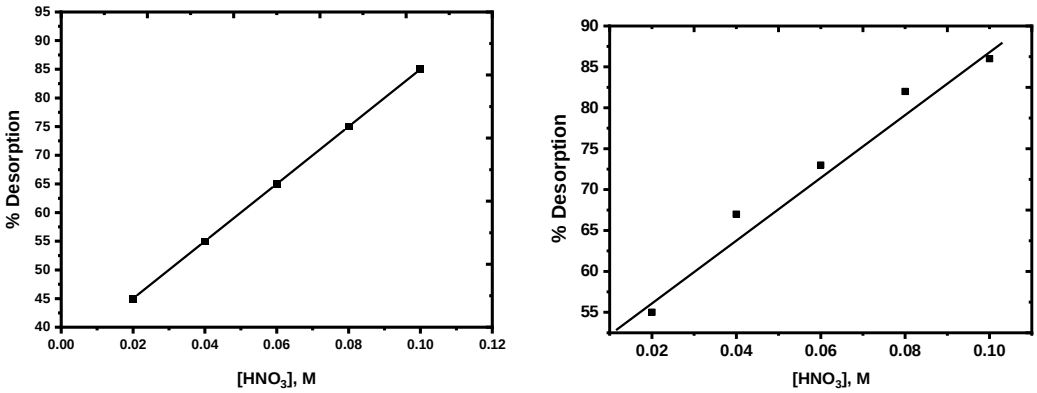
Dyes	Langmuir isotherm constants			Freundlich isotherm constants		
	K_L(L/g)	q_m (mmol g^{-1})	R^2	K_F	n	R^2
ECR	$19x10^{-2}$	0.27	0.998	14.424	2.1	0.898
SPADNS	$12x10^{-2}$	0.22	0.978	25.395	1.7	0.910

3.2.5. Sorbent reusability

To check the economic feasibility of the adsorption process, it is important to carry out the adsorption and regeneration studies. 0.15 M HNO_3 was used as eluent in the case of ECR and 0.1 M HNO_3 in the case of SPADNS. The results showed that maximum recovery of ECR was observed when 0.15 M HNO_3 was used as eluent Fig.12a, b.

The results obtained showed about a 5% drop in the adsorption capacity after the first regeneration cycle. This decrease in adsorption capacity might be attributed to decomposition caused by 0.15 M HNO_3 to certain adsorption sites of Cu(II)/Tu-MC. In the

case of SPADNS the decrease in the adsorption capacity is 10% after the first regeneration cycle.



(a) (b)

Fig.12: Desorption of (a) ECR and (b) SPADNS at different concentration of HNO_3

3.2.6. Mechanism

The organic dyes were known for their capacity of metal ions due to the presence of donor atoms in their structure that leads to complexation to occur by using the metal ions loaded on the fiber [34-40]. The mode of interaction between the proposed adsorbent and the acid dyes is presented in scheme 3.

3.2.7. Fastness properties

Modified cotton fiber (Cu(II)/Tu-MC) has shown a high color wash fastness when compared with untreated cotton fiber (Table S3). The high affinity of the modified cotton fiber is due to the presence of cationic copper ions in the cotton which improved the binding of the dyes to the fiber, increasing the wash fastness and this is consistent with recently published papers. [41, 42]

4. Conclusions

From the results obtained, the following conclusions can be derived:

1-The morphological appearance of the fibers was visualized by SEM and the effect of treatment was detected.

2- The mode of Cu(II) ions chelation by the functionalized Tu-MC fibers was confirmed using FTIR spectroscopy along with the potentiometric analysis.

3-Various essential parameters including optimum pH, temperature, contact time, and isotherms were studied and the best condition through which these dyes can be adsorbed on the surface of the fibers were evaluated.

4- The optimum pH for the uptake of the dye was found to be 6 and the process of both ECR and SPADNS uptake by the modified fibers was spontaneous under the different studied temperatures.

5- Kinetic studies showed that the uptake followed the pseudo 2nd order model and the isotherms confirmed the monolayer adsorption profile with both dyes by following the Langmuir model.

6- The dyes were also showed a considerable fastness on the developed fibers under different environmental conditions confirming the economic feasibility of the performed process.

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Supporting Information

Rapid adsorption of acid dyes using Cu(II) thiourea modified cellulose complex

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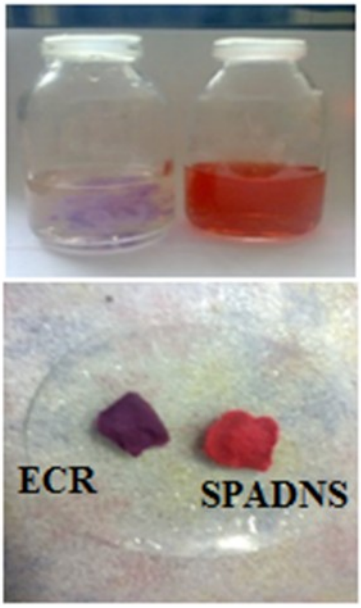

Fig. S1. Digital photographs of Cu(II)/Tu-MC fibers upon uptake of ECR and SPADNS dyes.

Table S1**.** Thermodynamic parameters for the uptake of ECR and SPADNS on Cu(II)/Tu-MC fibers.

Dye	K_c			$-\Delta G^o_{ads}$ (kJ/mol)			ΔH^o_{ads} (kJ/mol)	ΔS^o_{ads} (J/mol K)
	293 K	303 K	313 K	293 K	303 K	313 K		
ECR	76.52	53.78	39.23	10.56	10.03	9.55	-12.76	-29.8
SPADNS	66.65	47.63	35.42	10.23	9.73	9.28	-10.7	-13.5

Table S2. 1st order kinetic equilibrium for dye adsorption by Cu(II)/Tu-MC.

Dye	First-order model		
	k_1 (min^{-1})	q_{e1}(mmol/g)	R^2
ECR	58.65	0.24	0.933
SPADNS	45.32	0.2	0.943
Adsorbent	Second-order model		
	k_2 (g/(mmol min))	q_{e2} (mg/g)	R^2
ECR	52.65	0.27	0.9998
SPADNS	43.23	0.22	0.9987

Table S3. Colour fastness of the dyed cotton fiber with ECR and SPADNS

	Wash fastness		Light fastness
	Colour change	Staining on cotton	
Untreated cotton	2	4-5	1-2
Cu(II) / Tu-MC and ECR	3-4	4-5	3
Cu(II) / Tu-MC and SPADNS	2-3	5	2

Table S4. Comparison of maximum sorption capacity of some dyes by proposed method with newly published method

Dyes	Adsorbent	q_e (adsorption capacity) mg/g	Reference
Congo red and methylene blue	cotton fibers	and 102.7 350.8	[43]
methyl orange and methyl red	composite of cobalt ferrite and Tragacanth gum	336 and 387	[44]
methylene blue	cellulose-acetate	42	[45]
anionic Brilliant Red and cationic Methylene Blue	cellulose-based materials	25.25 and 454.54	[46]
Telon Fast Red ER	The amidoximated Jute fibers	185	[47]
methylene blue	Wheat straw	16.21	[48]
Congo red and methylene blue	Raw cotton	<10 and <10	[49]
methylene blue	Pistachio hull waste	66.5	[50]
ECR and SPADNS	cotton fibers	144.8 and 125.4	Present work

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