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Oxidized cellulose nanofibers decorated with magnetite as efficient bioadsorbent for organic

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Abstract: This article describes the immobilization of magnetite (Fe₃O₄) nanoparticles on TEMPO-oxidized cellulose nanofiber (TEMPO-CNF) through the co-precipitation of iron salts by the alkaline medium. TEMPO-CNF and TEMPO-CNF/Fe₃O₄ were confirmed by XRD, TGA, SEM, TEM, BET, and AFM. Characterization of the samples successfully showed the preparation of cellulose nanofibers with a diameter ranging from 10-15 nm and homogenous and uniform magnetic nanoparticles with a diameter of ~ 10 nm. The ability of the synthesized nanocomposite for methylene blue (MB) adsorption, as a cationic dye model, was examined. At pH 7, the highest adsorption efficiency was observed. The isotherm, kinetic models, and enthalpic contributions were calculated to evaluate adsorption experiments. With an adsorption capacity of around 303 mg/g, pseudo-second-order, and Langmuir isotherm provided the best interpretation adsorption process. In addition, the thermodynamics parameters have been evaluated from direct measurement based on Isothermal Titration Calorimetry. The current results showed that TEMPO-CNF/Fe₃O₄ nanocomposite is a promising green bioadsorbent for organic dye removal for water purification.

Keywords: Cellulose nanofiber (CNF), Magnetite, Nanocomposites, Methylene Blue (MB), adsorption

1. Introduction

Many industries including textile, clothing, and printing produced large quantities of dyes. The majority of these dyes are toxic, carcinogenic, mutagenic, and considerably may affect aquatic life even at low concentrations. Humans and marine life can be adversely affected by toxic effluents unless they are not removed before their release. Moreover, dyestuff wastewater is not easy to be removed since its recalcitrant has strong resistance to aerobic digestion and resist oxidation

processes [1]. Dyes removal from wastewater is carried out by numerous processes such as nano-filtration, ozonation, coagulation, electrocoagulation, photocatalytic degradation, and chemical precipitation and adsorption. However, the adsorption technique appeared as a more cost-effective, efficient, feasible, and environmentally friendly adsorbent for a broad range of pollutants [2–4]. The adsorption method does not yield secondary pollution, consumes less energy, and has efficient adsorption capacity. In the case of dyes, the use of various types of materials has been successfully investigated with purely organic materials (i.e., mainly resins [5]), inorganic adsorbents (oxides [6], layered materials [7,8]), or hybrid materials such as chitosan/silica composite [9]. Composite materials which combine polysaccharides with active reagents are suitable and promising materials for adsorption especially these composite materials containing inorganic nanomaterials [10–14]. Cellulose has recently emerged as an economic and sustainable polymer for preparing composite materials suitable for organic pollutants adsorption [15,16] or photodegradation. Moreover, cellulose is economically practicable since it can be modified through various chemical processes [17,18]. Cellulose could be used as a substitute for exchanging conventional, expensive, and environmentally toxic adsorbents [19]. Modification of cellulose improves its adsorption efficiency and its application in different mediums and illustrates the good potential for the elimination of numerous organic chemicals [20,21]. Several compounds, including metals, metal oxides, organic acids, bases and oxidizing agents, etc, can be utilized for cellulose modification [22]. These techniques vary in their effectiveness for preparing efficient adsorbents. Mechanisms involved in the sorption process, and the performance of the adsorbents, mainly depend on the type of modifications and together with characteristics of the wastewater. Cellulose considered a semicrystalline polymer, consists of amorphous and crystalline parts. Cellulose nanomaterials include microcrystalline, nanocrystalline, nanowhiskers, nanofibrils, bacterial cellulose, and combinations of these material types [23,24]. Amorphous regions is reported as structural weakness regions which could be attacked by acid. The individual short monocrystalline nanoparticles known as cellulose nanocrystals are formed with a diameter of 4-10 nm and a length of 50-200 nm. Cellulose nanomaterials could be prepared from cellulose pulp through acid hydrolysis. They have shown fascinating properties such as large specific surface area, high abundance, high mechanical properties, and degree of functionality [25]. Nanocomposites have been applied as feasible and efficient technique in wastewater treatment [26–28] with the particular use of magnetic

nanoparticles showing great potential [29]. Cellulose/magnetite nanocomposites made-up through the precipitation of magnetite onto the functionalized cellulose surface can be prepared utilizing distinct inorganic and organic acids [30]. For example, TEMPO-CNF grafted acrylic acid followed by crosslinking with amino-functionalized magnetite was investigated as adsorbent for heavy metal ions [13]. Abouzeid et al. conducted a study which demonstrated that combining sodium alginate, a natural and biodegradable polymer matrix, with activated charcoal, renowned for its exceptional adsorption properties of methylene blue dye [31]. Alekseeva et al. [32] synthesized and studied the chemical, and magnetic properties of the hydroxyethyl cellulose/bentonite/magnetite nanocomposite. Moreover, the authors studied the optical, mechanical, and antifungal activity of hydroxyethyl cellulose/bentonite/magnetite films. X-ray diffraction analysis revealed that the interlayer distance expanded to 1.8 nm due to the intercalation of cellulose derivatives in clay cavities owing to the intercalation of polymer molecules. Functionalized nanofiber networks of cellulose and chitosan, packed in minicolumns were investigated for adsorption of trace quantities of metal ions such as Cd (II), and Pb (II) present in aqueous solutions. Trace metals in water were imperceptible as the concentrations were lower than identification limits. The purification process through the functionalized biosorbents in cartridges improved the recognition of the metal ions [33]. Kloster et al. [34] prepared chitosan/nano magnetite composite films by the one-step in situ co-precipitation (solvent-casting) method. It was concluded that the magnetic behavior for prepared nanocomposite was achieved at more than 2 wt% of the composite to magnetite content. F. Cesano et al., synthesized chitosan/magnetite by co-precipitation of iron oxide in the presence of chitosan which acts as both dispersant and stabilizing matrix in a one-step method [26]. It was observed that the preparation process is simple and can be effectively utilized for example to adsorb pollutants from solid and liquid media due to its exact magnetic properties. Chitosan/magnetite multifunction with polythiophene and phosphate groups was applied as careful and efficient removal of Hg (II) was studied [35]. In addition, Bezdorozhev et al. [36] reported the synthesis of magnetic properties of chitosan/magnetite nanocomposites that were developed by chemically combining magnetite nanoparticles with chitosan. They investigated the effect of different synthesis variables, including time, iron ions, and chitosan concentrations, on the nanocomposites' shape. Results showed that magnetite-chitosan nanostructures of spherical shape and particle size of (9–18 nm) were formed. The achieved magnetite-chitosan

nanostructures can be utilized in numerous medical purposes. The synthesis of magnetic nanoparticle (Fe_3O_4) incorporated carboxymethyl cellulose (CMC) hydrogel nanocomposites (CMC- Fe_3O_4) using in-situ mineralization of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions in a hydrogel network was studied. The study investigated the potential of these nanocomposites in removing methylene blue (MB) from aqueous solutions by utilizing the magnetic property of the nanocomposites [37]. Novel magnetic chitosan/ Al_2O_3 /iron oxide nanoparticles were also prepared and applied as an adsorbent with high adsorption capacity in the removal of Methyl Orange. The best adsorbent amount was estimated to be 0.4 g. L⁻¹ and the adsorption method was effective in a wide pH range of 4–10. The current study aims to prepare TEMPO-CNF/ Fe_3O_4 nanocomposite through the co-precipitation technique. The prepared nanocomposite was characterized and investigated as a versatile adsorbent for the removal of cationic dyes from polluted water. Solution pH, contact time, and initial concentration were examined to identify the optimum conditions required for dye adsorption. A thermodynamic study was also carried out. A thermodynamic study based on direct calorimetric measurements was also carried out.

2. Experimental part

2.1 Materials

Bagasse fiber delivered by the Egyptian company Qena Company of Paper Industry. Sodium metaperiodite (NaIO_4), sodium bromide (NaBr), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), ferric chloride (FeCl_3) and ferrous sulfate (FeSO_4) and methylene blue (MB) were supplied from Sigma Aldrich. Other chemicals of analytical grade were used without further purification.

2.2. TEMPO-oxidized cellulose nanofiber preparation

Bleached bagasse pulp was oxidized via the TEMPO oxidation method as previously described [38]. In brief, 25 g of cellulose pulp was suspended in 2.5 L distilled water for 30 min using mechanical stirring. TEMPO (1.0 g) and sodium bromide (10 g) were combined to previous suspension followed by the addition of 300 ml of NaClO_2 (15%). The oxidized cellulose was centrifuged, and the supernatant was purified using dialysis against deionized water. Mechanical defibrillation of the TEMPO-oxidized cellulose-using Masuko grinder was done to prepare TEMPO-CNF.

2.3. TEMPO-CNF/magnetite nanocomposite preparation

TEMPO-CNF/Fe₃O₄ nanocomposite was prepared through the co-precipitation technique as previously reported by Ngenefeme et al., 2013. Shortly, 0.15 g (dry weight) of T-CNF and 5.3 g of FeCl₃ were placed in contact with 13 ml of deoxygenated and purified water [39]. Likewise, 0.2 g of T-CNF and 2.7 g of FeSO₄ were separately dissolved in 13 mL of deoxygenated water. The two solutions were stirred overnight, and after that, they were mixed and deoxygenated for 15 minutes. 2 M of ammonium solution was dropwise until the black color appears due to the precipitation of magnetite. The product that was made was washed until it was neutral. The remaining material was then freeze-dried to process complete dehydration.

2.4. Studies of batch adsorption

For removing organic dyes from wastewater, the T-CNF/Fe₃O₄ nanocomposite was made and tested. Adsorption experiments were performed at 25 °C, using an aqueous solution containing 50 mg of T-CNF/Fe₃O₄ in 50 mL distilled water. The effect of pH was calculated using 100 ppm as the initial MB concentration and 120 minutes of equilibrium time. The pH was adjusted for both 3 and 8 using hydrochloric acid or sodium Hydroxide aqueous solutions. The kinetics was evaluated also with 100 mg/L as the initial dye concentration, and at pH fixed at 7. For the determination of the complete adsorption isotherm, trials were conducted out at pH 7 and a contact time (24h). Different concentration solutions of MB (25-1000 ppm) were used. UNICO UV-2000 spectrophotometer estimated solution absorbance and MB content. **For desorption study, MB-loaded nanocomposite was agitated with 10 mL of 5% (v/v) acetic acid and methanol for 24 h. The adsorbent was dried at 60 °C and adsorption–desorption cycle was repeated three times.**

2.5. Thermodynamic study

Using a TAM III multichannel calorimetric apparatus with nanocalorimeters and a Micro Reaction System, Isothermal Titration Calorimetry (ITC) computations were performed (TA Waters). ITC tests were performed at 298 K in Hastelloy cells with 800 µL of suspension containing 2.5 mg of TEMPO-CNF/Fe₃O₄ material in water. They consist of 23 successive injections of 10 seconds with 10 µL of a 10mM MB solution. The device is supplied with a gold paddle stirrer utilized at 90 rpm to ensure the homogeneity of the mixture. Between injections, the system is allowed to stabilize for 45 minutes. Similar conditions are used to evaluate the dilution effect (without nanocomposite) and compared with the raw measurements on TEMPO-

CNF/Fe₃O₄. Experiments were done in triplicate. The heat effects were determined after suitable subtraction of the dilution effect, and then for each dose, it was correlated to the actual amount adsorbed from the isotherm. [40].

2.6. Samples Characterization

Using various methods, the prepared samples were characterized. SEM was conducted using a Model Quanta 250 FEG (Field Emission Gun) equipped with an EDX Unit (Energy Dispersive X-ray Analyses) and 20 K of accelerating voltage. On a PerkinElmer TGA thermogravimetric, thermogravimetric technique was utilized. AFM Multimode (DI, Veeco, Instrumentation Group) was done in tapping mode using multi-130 tips. Before analysis, a T-CNF suspension was mixed with water and dropped immediately on the mica surface for four hours.

3. Results and Discussion.

3.1. TEMPO-CNFs characterization

TEMPO-CNFs were synthesized from bleached bagasse pulp, which, in comparison to other annual plants, is a good source of cellulose [25]. The morphology of TEMPO-CNFs was explored utilizing AFM. Figure 1 (a) demonstrates that the diameter of TEMPO-CNFs differs from 6 to 15 nm and the length exhibited several micrometers, these dimensions are consistent with our earlier research and provide evidence that the TEMPO-CNFs have a uniform structure [38,41]. FT-IR of TEMPO-CNFs was revealed in figure 2(b), the broad peak at 3400 cm⁻¹ assigns to stretching vibrations of OH groups. The absorption peak at 1750 cm⁻¹ is related to the C=O stretching vibration because of TEMPO oxidation. In addition to the absorbed water's O-H bending vibration, carboxylate groups also contribute to the peak at 1640 cm⁻¹. The peak at 1060 cm⁻¹ is correlated with C-O stretching vibrations. The X-ray diffraction patterns of TEMPO-CNFs, figure 2 (C), displays cellulose I with crystalline peaks at about 2θ = 18, 23, and 34.6° which refer to (110) and (200) and (004) plane. **The crystallinity index values of the samples were calculated according to Segal et al. using Equation below:**

$$C.I. (\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (2)$$

wherein I_{002} is the intensity of diffraction peak of (200) lattice plane, and I_{am} is the intensity of the amorphous background scatter measured. The crystallinity percentage of TOCNF recorded 73%.[42]. As a result of the oxidation reaction degrading amorphous regions, a greater proportion of these regions can now be found in the water-soluble fraction, leading to an increase in crystallinity.

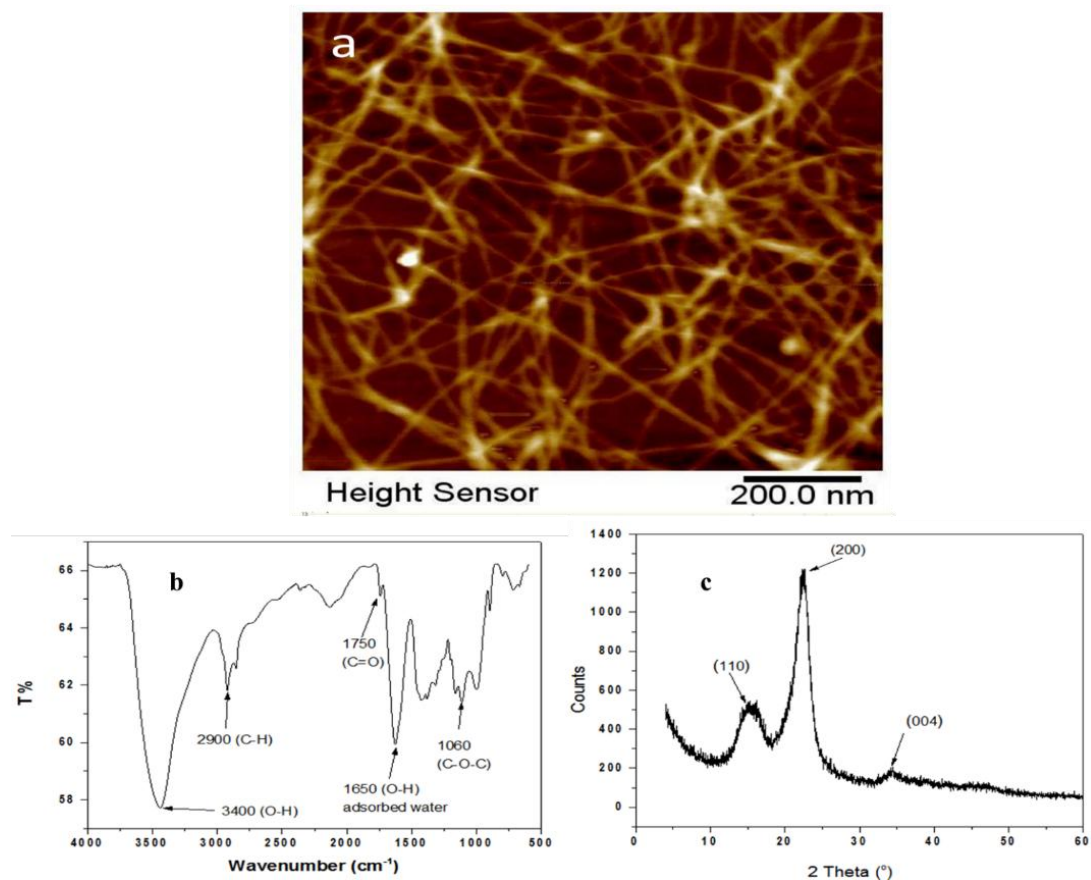


Figure 1. (a) AFM image (b) FT-IR spectrum, and (c) XRD pattern for TEMPO-CNFs.

3.2. Characterizations of TEMPO-CNF /Fe₃O₄ nanocomposite

The TEM image of the TEMPO-CNF/Fe₃O₄ nanocomposite showed that the Fe₃O₄ nanoparticles exhibit crystalline particles with spherical shapes, with diameter of 23 nm randomly distributed in the TEMPO-CNFs. Unique morphology with a smaller particle size might be due to the in-situ mineralization of Fe₃O₄ nanoparticles in the corporate of TEMPO-CNF. Moreover, TEMPO-CNF/Fe₃O₄ nanocomposite image showed uniformly dispersed Fe₃O₄ nanoparticles inside the oxidized fibers. The x-ray diffraction pattern of TEMPO-CNFs/Fe₃O₄ nanocomposite, shown in

figure 2 (b), exhibits the appearance of characteristic peaks at $2\theta = 30.3, 35.7, 43.4,$ and 63.2° relating to (2 2 0), (3 1 1), (4 0 0) and (4 4 0) planes respectively. These results were consistent with XRD for the standard Fe_3O_4 pattern (JCPDS, reference 01-075-0449) and indicate the cubic axial configuration of magnetite [43].

Figure 2 (b and d) FTIR spectrum of TEMPO-CNFs/ Fe_3O_4 nanocomposite before and after adsorption respectively. The spectra showed bands at $3410, 2980,$ and 1750 cm^{-1} which assigned to the OH, C-H, and carbonyl groups, respectively. The absorption at 600 cm^{-1} represented to the Fe-O bond's absorption vibrations. Before and after MB adsorption, the TEMPO-CNF/ Fe_3O_4 magnetite nanocomposite bands undergo significant modifications. In MB-loaded TEMPO-CNF/ Fe_3O_4 , characteristic bands are found at 1246 cm^{-1} (C-N stretching), 1487 cm^{-1} (N-H), and 1599 cm^{-1} (C=N of aromatic ring). These peaks prove that MB is absorbed by the TEMPO-CNF/ Fe_3O_4 . Additionally, the nanocomposite's characteristic bands expanded and shifted slightly. For instance, C=C stretching band shifted from 1620 to 1599 cm^{-1} and O-H stretching band shifted from 3400 to 3302 cm^{-1} . The hydrogen bonding and electrostatic interactions between the MB functional groups and the TEMPO-CNF/ Fe_3O_4 are depicted in Scheme 1. These interactions are responsible for high adsorption capacity.

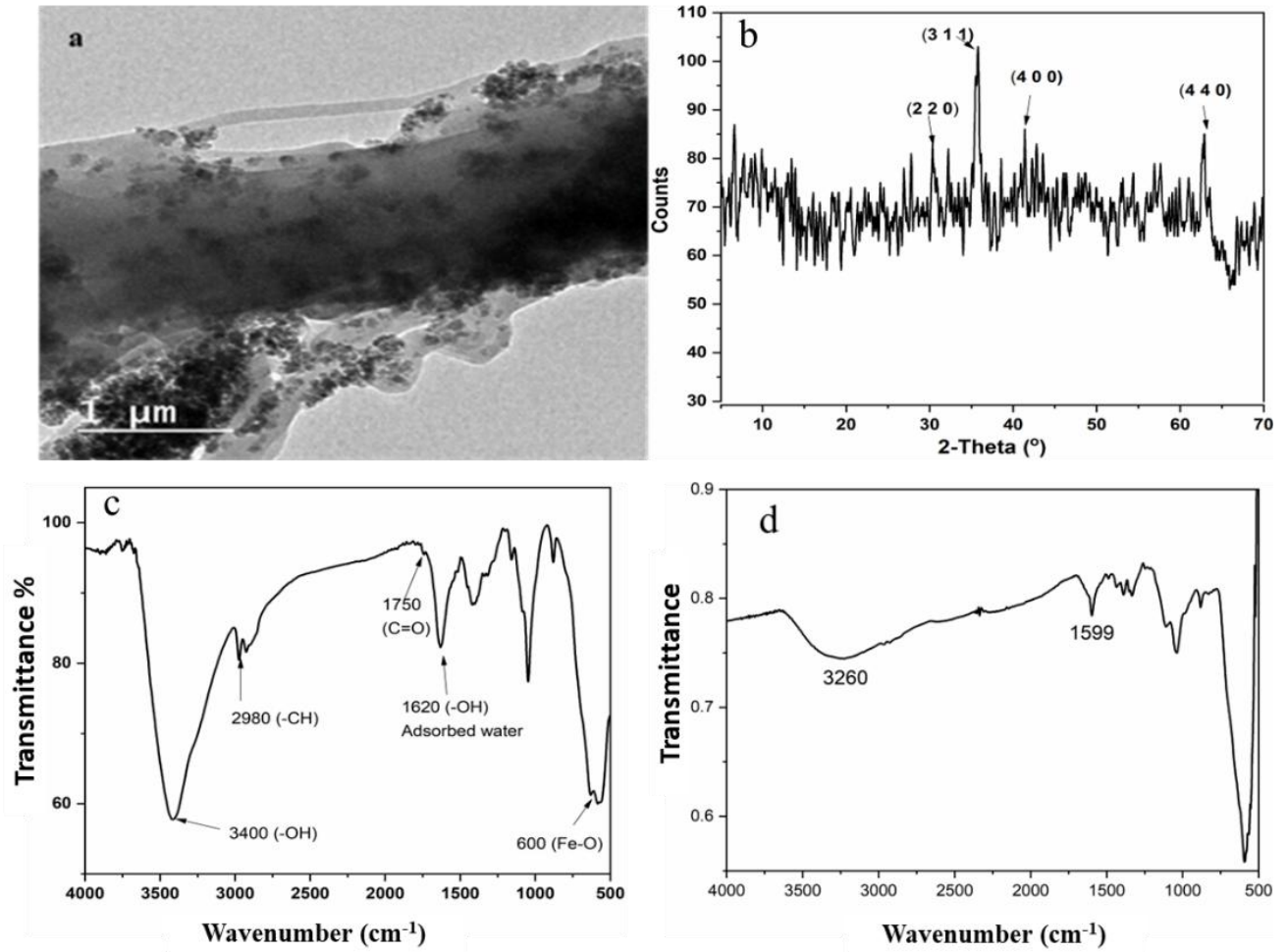
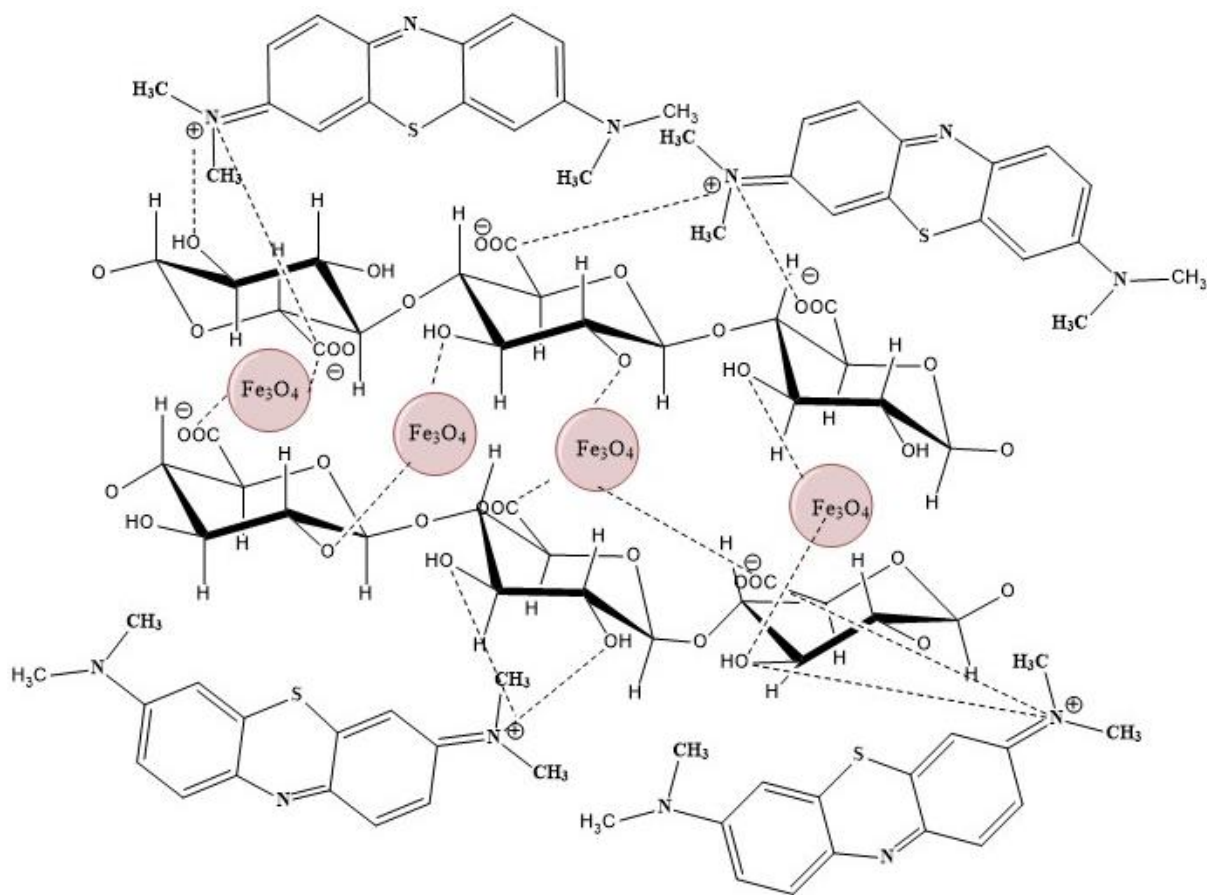


Figure 2. (a) Transmission electron microscope picture, (b) x-ray diffraction spectrum, (C) FT-IR for TEMPO-CNF/Fe₃O₄ nanocomposite and FT-IR spectrum of MB loaded nanocomposite (D).



Scheme 1. The possible mechanism of MB adsorption onto TEMPO-CNF/Fe₃O₄

To determine the thermal stability of the produced sample, TGA was performed. TEMPO-CNF/Fe₃O₄ magnetite nanocomposite. Figure 3 shows the TGA curve of TEMPO-CNF and TEMPO-CNF/Fe₃O₄ nanocomposite. From 50 to 200 degrees Celsius, weight loss of 10.5% and 5.3% for TEMPO-CNF and TEMPO-CNF/Fe₃O₄ was obtained, respectively, owing to the release of the water absorbed contained on the interfaces of the two samples. The cellulose backbone in TEMPO-CNF decomposes at 230°C with a maximum weight loss at 350°C. The final weight loss of TEMPO-CNF equals 887%. The weight loss behavior of TEMPO-CNF/Fe₃O₄ magnetite nanocomposite was different from TEMPO-CNF. The main weight loss was observed at 250 to 360 C corresponding to the decomposition of cellulose and the reaction of Fe₃O₄ with carbon which was the residue of the cellulose decomposition with the final weight loss of 25%.

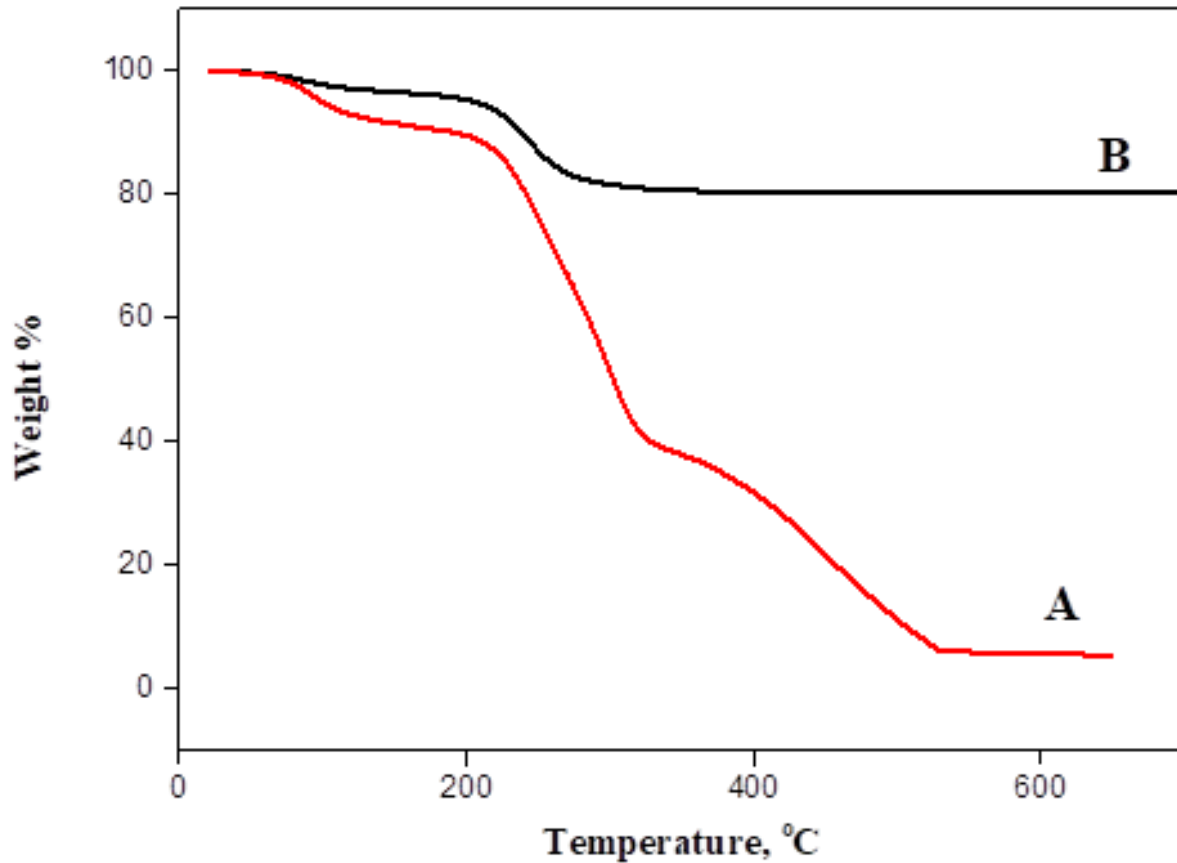


Figure 3: TGA of TEMPO-CNF and Fe₃O₄ composites (A) and (B) respectively

Using N₂ adsorption-desorption isotherms, the textural characteristics of the synthesized nanocomposites were analyzed. The specific surface area was computed utilizing the Brunauer–Emmett–Teller (BET) formula, and the pore size distribution curves were acquired utilizing the Barrett–Joy–Halenda (BJH) method. Figure 4 illustrates the N₂ adsorption-desorption isotherms of nanocomposites. The measured surface area of the TEMPO-CNF/Fe₃O₄ nanocomposite was 64.7 m²/g. The increased BET surface area of the TEMPO-CNF/Fe₃O₄ nanocomposite compared to CNF was attributable to the inclusion of TEMPO-CNF and Fe₃O₄ nanoparticles in the materials; consequently, the nanocomposite provided better access and most commonly adsorption sites. In addition, the nanocomposites' pore sizes were mainly distributed in the 12 nm range, attributed to the presence of mesopores in the materials. Consequently, these results revealed that TEMPO-CNF/Fe₃O₄ nanocomposite exhibited a more porous structure, which was

suitable towards the diffusion of the adsorbate.

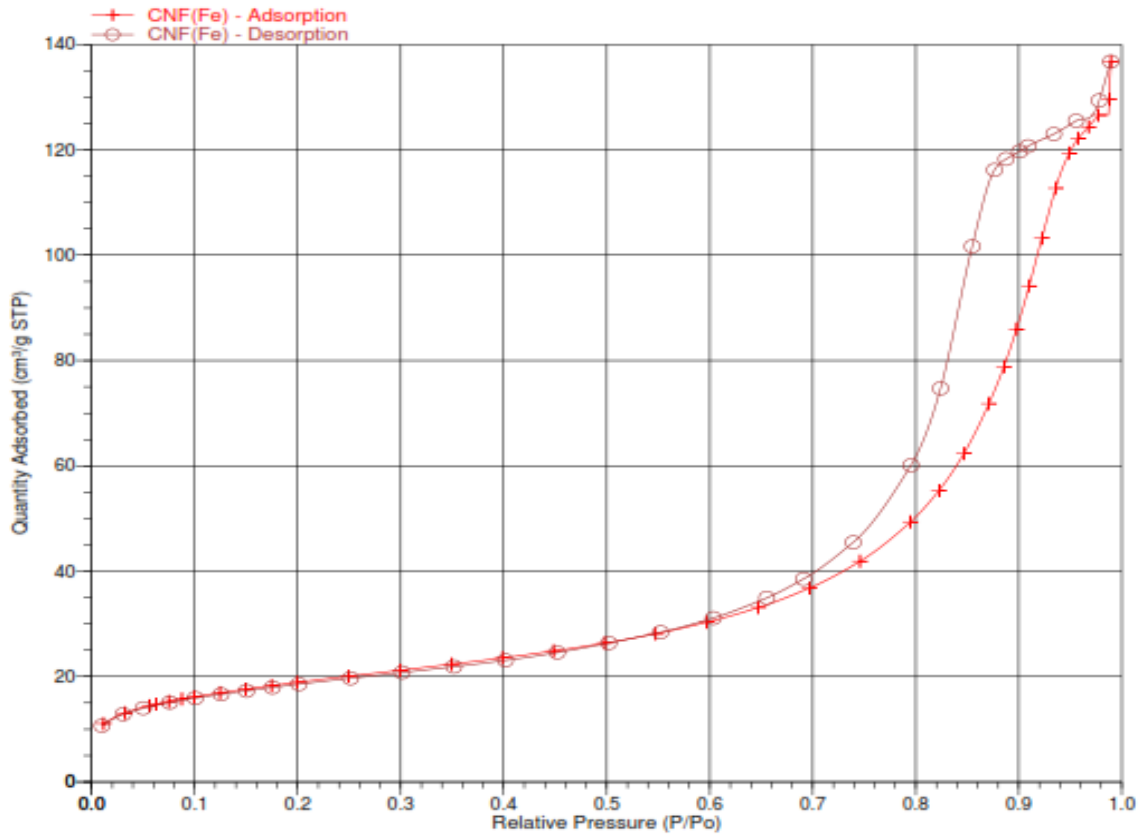


Figure 4. N₂ adsorption–desorption isotherms of TEMPO-CNF/Fe₃O₄ nanocomposite

Figure 5 illustrates the SEM study of TEMPO-CNF and TEMPO-CNF/Fe₃O₄ nanocomposite morphology. Different fiber widths are displayed in TEMPO-CNF. Furthermore, the TEMPO-CNF/Fe₃O₄ nanocomposite had a sphere shape with an approximate diameter of less than 10 nm. However, the SEM image indicates that the nanocomposite displays aggregation because Fe₃O₄ is homogeneously mixed with TEMPO-CNF. However, the SEM image signifies that the nanocomposite displays aggregation because of Fe₃O₄ homogeneously mixed with TEMPO-CNF. Additionally, Fe₃O₄ nanoparticles seem to be more distinctive and consistent. This is probably because of TEMPO-CNF and Fe₃O₄ nanoparticles interact together decreases the forces that make Fe₃O₄ nanoparticles preventing them from sticking together. After loading with MB, SEM images exhibited denser surface and EDX spectra prove the MB adsorption due to the appearance of characteristic peaks for Nitrogen and Sulphur.

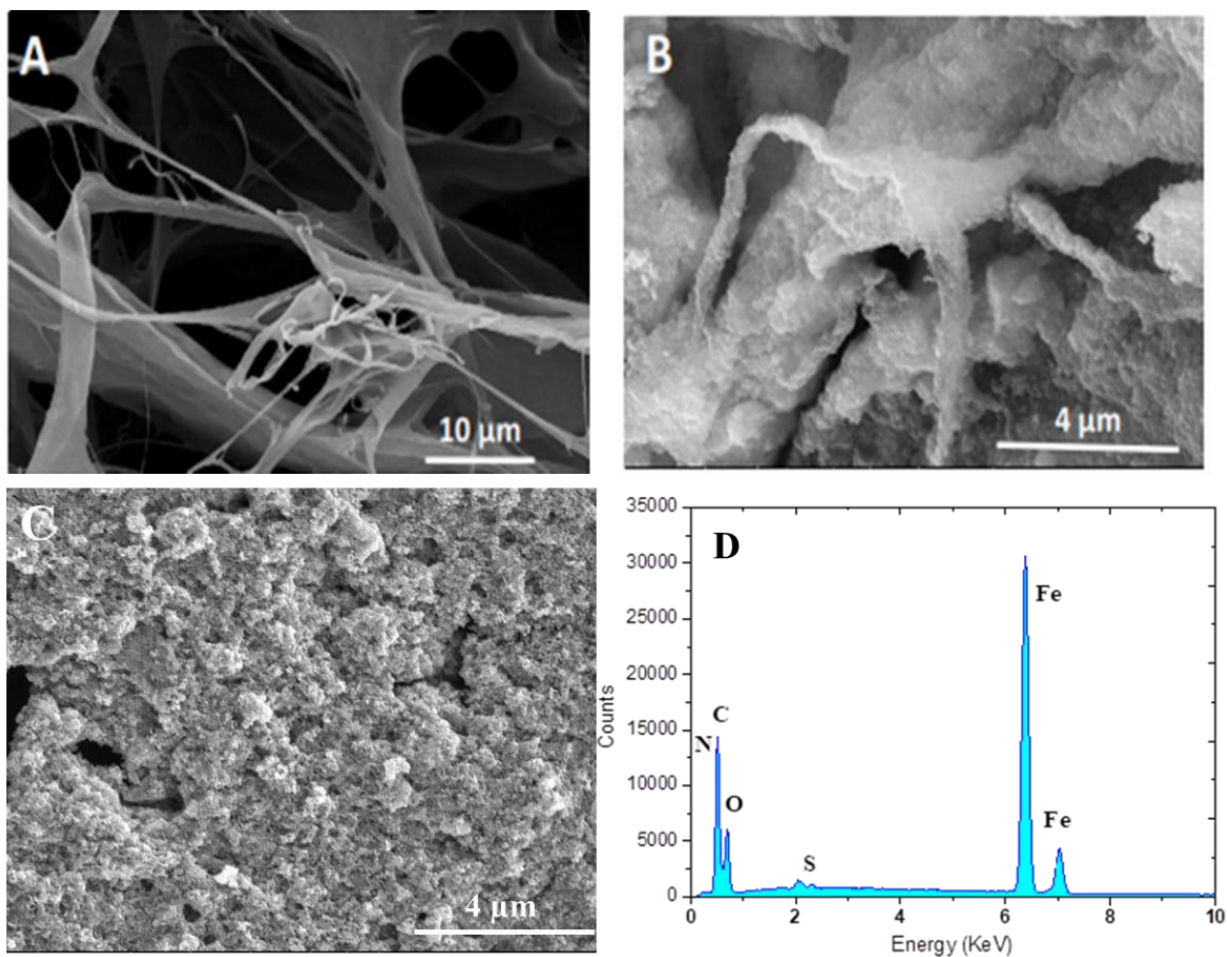


Figure 5. SEM images of TEMPO-CNF (A), TEMPO-CNF/Fe₃O₄ before (B) and after (C) MB adsorption, and EDX of TEMPO-CNF/Fe₃O₄ nanocomposite loaded MB (D).

3.2. MB absorption using TEMPO-CNF/Fe₃O₄ nanocomposite.

The obtained TEMPO-CNF/Fe₃O₄ nanocomposite was subjected to organic dye removal from effluent. To better understand the behavior of the current nanocomposite, using TEMPO-CNF/Fe₃O₄ as an adsorbent, various factors such as pH, contact time, and dye concentration were investigated.

3.2.1. Effect of pH

Figure 6 illustrates the influence of pH on the absorption rate of TEMPO-CNF/Fe₃O₄ nanocomposite. The results demonstrate that the adsorption of MB increased slightly to achieve the optimal value of 79.5 mg/g at pH 7. At a low pH, TEMPO-CNF/Fe₃O₄ functional groups were protonated and showed as positive charge groups. Electrostatic repulsive force for both MB

and protonated groups may inhibit uptake [44]. This demonstrated the function of Fe_3O_4 nanoparticles in enhancing the adsorption performance of the prepared nanocomposites, which possesses extra sites for ionic attraction with cationic dye. The pH study suggests that the adsorption efficiency of the TEMPO-CNF/ Fe_3O_4 nanocomposite is improved in neutral conditions. Increasing the capability of adsorption of cationic dyes with pH has been recorded in previous work [45].

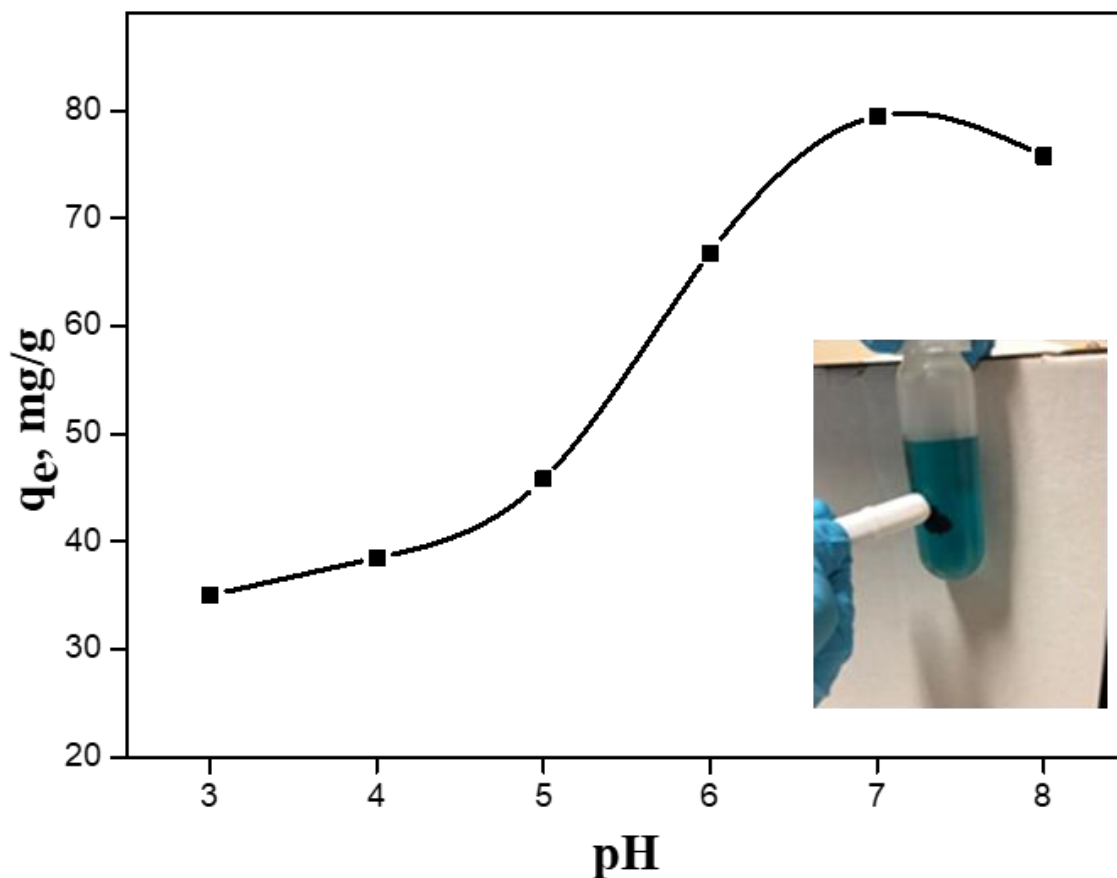


Figure 6: Influence of different pH on the MB adsorption capability of nanocomposite TEMPO-CNF Fe_3O_4 .

3.2.2. Effect of contact time and adsorption kinetics.

The rate of MB adsorption is dependent on the amount of time that TEMPO-CNF/ Fe_3O_4 nanocomposite is in touch with the dye solution. The adsorption of MB on TEMPO-CNF/ Fe_3O_4

nanocomposite presents a trend of rapid increase through the first 90 minutes and then reaches equilibrium after 120 minutes as displayed in figure 7.

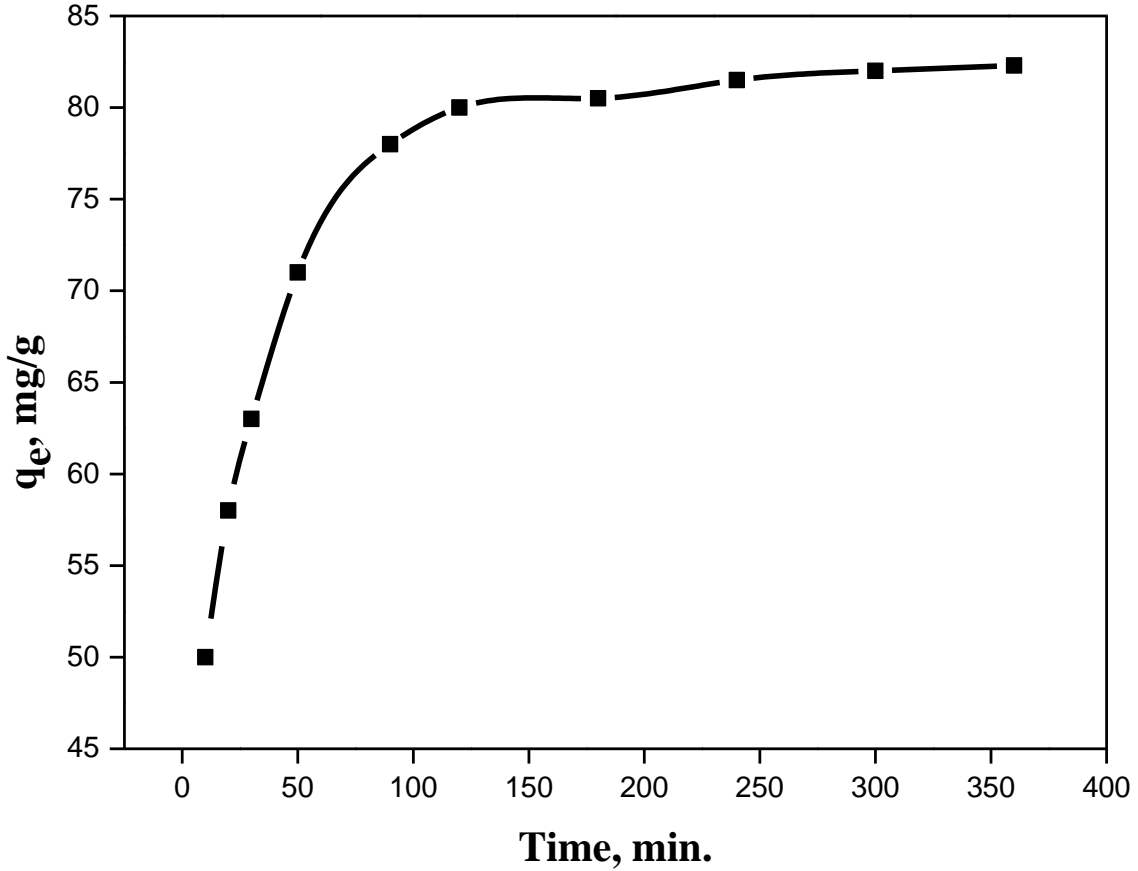


Figure 7: Effect of time on the adsorption of TEMPO-CNF/Fe₃O₄ nanocomposite and the pseudo-second-order kinetic model that was applied.

In formulae 1 and 2, the pseudo-first- and -second-order models are illustrated, respectively.

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \frac{K_1}{2.303} t \quad (1)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (2)$$

Table 1 illustrates the characteristics of TEMPO-CNF/Fe₃O₄ kinetic. In the case of the 1st order, the coefficient of determination is relatively low, and the calculated q_e is far from the experimental one. From pseudo second order models, the coefficient of determination (R^2) is nearly 0.99, and the calculated q_e (87.7 mg/g) is close to the experimental q_e (82.3 mg/g). This

signifies that the kinetic data were better fitted with the pseudo-second-order model. The pseudo-second-order kinetic model assumes that the rate-limiting process is chemisorption-related. This chemisorption assumption based on the kinetics result will be confronted with the enthalpic data.

Table 1. Kinetic characteristics for MB adsorption by nanocomposite TEMPO-CNF/Fe₃O₄

Pseudo first order-model				Pseudo second- order model		
$q_{e, \text{exp}}$	$q_{e, \text{cal}}$	K_1	R^2	$q_{e, \text{cal}}$	K_2	R^2
(mg g^{-1})	(mg g^{-1})	(min^{-1})		(mg g^{-1})	($\text{g mg}^{-1}\text{min}^{-1}$)	
82.3	69	0.0032	0.63	84.7	$1.47 * 10^{-3}$	0.99

3.2.3. Effect of MB concentration and equilibrium isotherm.

Figure 8 illustrates the adsorption characteristics of TEMPO-CNF/Fe₃O₄ at different MB concentrations. The maximum rate of MB removal is 234 mg/g at a concentration of 300 ppm. Higher concentrations tend to level off the adsorption ability.

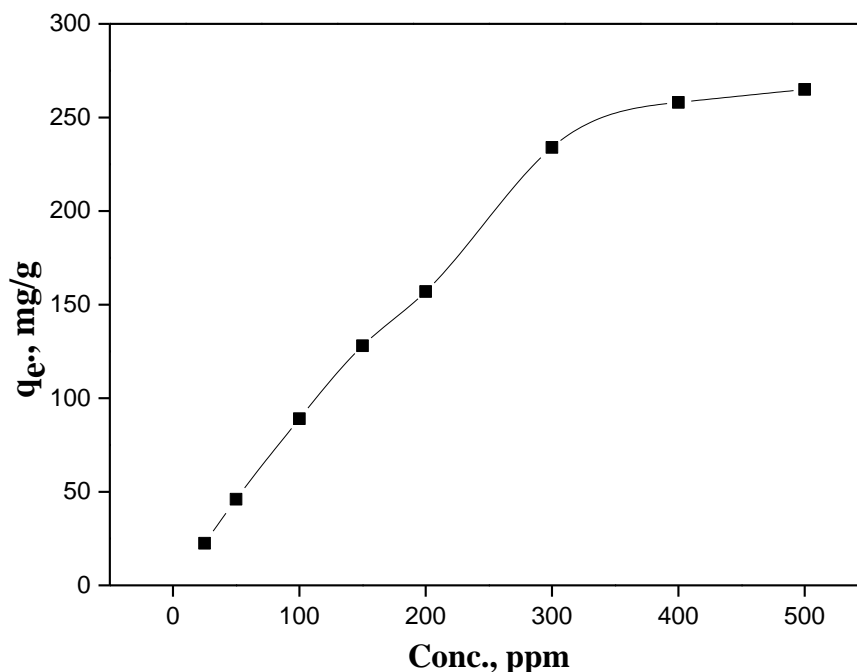


Figure 8: Influence of initial Concentrations on TEMPO-CNF/Fe₃O₄ nanocomposite adsorption capability. Experiments on adsorption: sample dose: 0.05 g/50 mL; pH: 7.0; interaction time: 24 hours.

To get more precise information on the sorption process, the Langmuir and the Freundlich isotherm models have been applied. In the case of the Langmuir model, the parameters were calculated from equation (3) [46].

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \quad (3)$$

with Q_{max} and C_e maximum adsorption capacity and equilibrium concentration respectively, and K_L is the Langmuir constant. The Freundlich model is represented in equation 4:

$$\log(q_e) = \log K_F + \left(\frac{1}{n}\right) \cdot \log C_e \quad (4)$$

The Freundlich constants K_F and $1/n$, respectively, represent the adsorption capacity and adsorption intensity.

The calculated correlation coefficients for both models are displayed in Table 2. High correlation coefficients ($R^2 > 0.992$) have been found for the Langmuir model, while the Freundlich model revealed low linear coefficient values (0.91). In addition, the values of K_F and n factors for TEMPO-CNF/Fe₃O₄ nanocomposite are 30 and 1.92. These calculations indicated that this model does not right method for MB adsorption onto the produced nanocomposite. This indicates that the Langmuir equation is consistent with the MB absorption on the TEMPO-CNF/Fe₃O₄ nanocomposite. This demonstrates that monolayer adsorption of MB happened on the nanocomposite. The findings indicated that the parameter q_{max} was 303 mg/g.

Table 2. Different equilibrium models for TEMPO-CNF/Fe₃O₄ nanocomposite MB absorption parameters.

Langmuir isotherm constants			Freundlich isotherm constants		
K_L (L mg ⁻¹)	q_m (mg g ⁻¹)	R^2	P (mg L ⁻¹)	n	R^2
0.037	303	0.992	30	1.92	0.91

In table 3, a comparison is made between TEMPO-CNF/Fe₃O₄ nanocomposites as well as other adsorbents for MB absorption. TEMPO-CNF/Fe₃O₄ nanocomposite had greater MB absorption than other cellulosic materials described in prior studies.

Table 3. The Highest MB adsorption capacities of common cellulose products.

Adsorbent	Maximum adsorption of MB (mg/g)	References
TEMPO-oxidized cellulose beads	495	[47]
Graphene oxide/cellulose strands	480.8	[48]
Hybrid of cellulose-grafted SPI and hydroxyapatite	454	[2]
Our nanocomposite	303	This work
Alginate/cellulose nanocrystals	256.4	[49]
Carboxymethyl cellulose/graphene composite	222.7	[50]
Calcium phosphate and carboxymethyl cellulose-g-polymethacrylic acid	180.2	[45]
Humic acid/graphene oxide	55	[51]

3.2.4. Desorption and regeneration studies

The TEMPO-CNF/Fe₃O₄ showed good performance in recycling treatment with MB dye. The pH study showed that TEMPO-CNF/Fe₃O₄ did not significantly adsorb MB at pH < 3.0, which indicates that the adsorbed MB could be desorbed in solution with such pH values. Moreover, MB dissolved easily in organic solvents and consequently desorption of MB dye was carried out with mixture of 5% (v/v) acetic acid and methanol. The results of adsorption efficiency of the examined TEMPO-CNF/Fe₃O₄ after five cycles are shown in figure 9. The nanocomposite maintains around 67 of its original efficiency by the end of the fifth regeneration cycle.

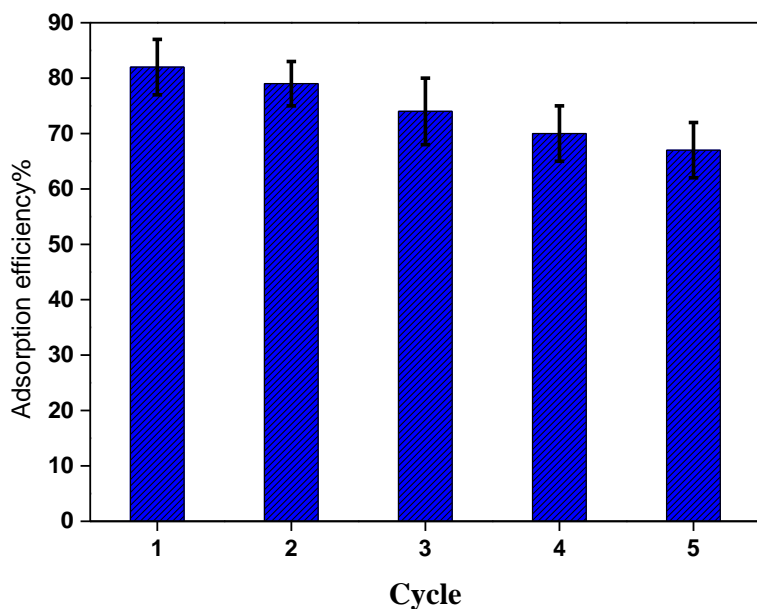


Figure 9: Adsorption–desorption cycles of MB for TEMPO-CNF/Fe₃O₄ nanocomposite.

3.2.5. Isothermal titration calorimetry

Isothermal titration calorimetry was performed to study the energy of interaction produced when MB is placed in contact with the nanocomposite. Figure 10 shows the results of the ITC experiment using a 10 mM MB solution on TEMPO-CNF/Fe₃O₄ together with a comparison of the dilution effect in the absence of powder in the cell. The shape of the heat flow is similar for the two systems. The signal is intense for the first injections, and then gradually decreases with an increasing number of injections. This indicates a regular decrease in the endothermic behavior until stabilization. The difference between adsorption and dilution is observed from the intensities of the peaks, with for example for the 1st peak, -2.8 μ W, and -4.1 μ W respectively. This indicates that the heat effect is slightly endothermic after subtraction of the dilution effect.

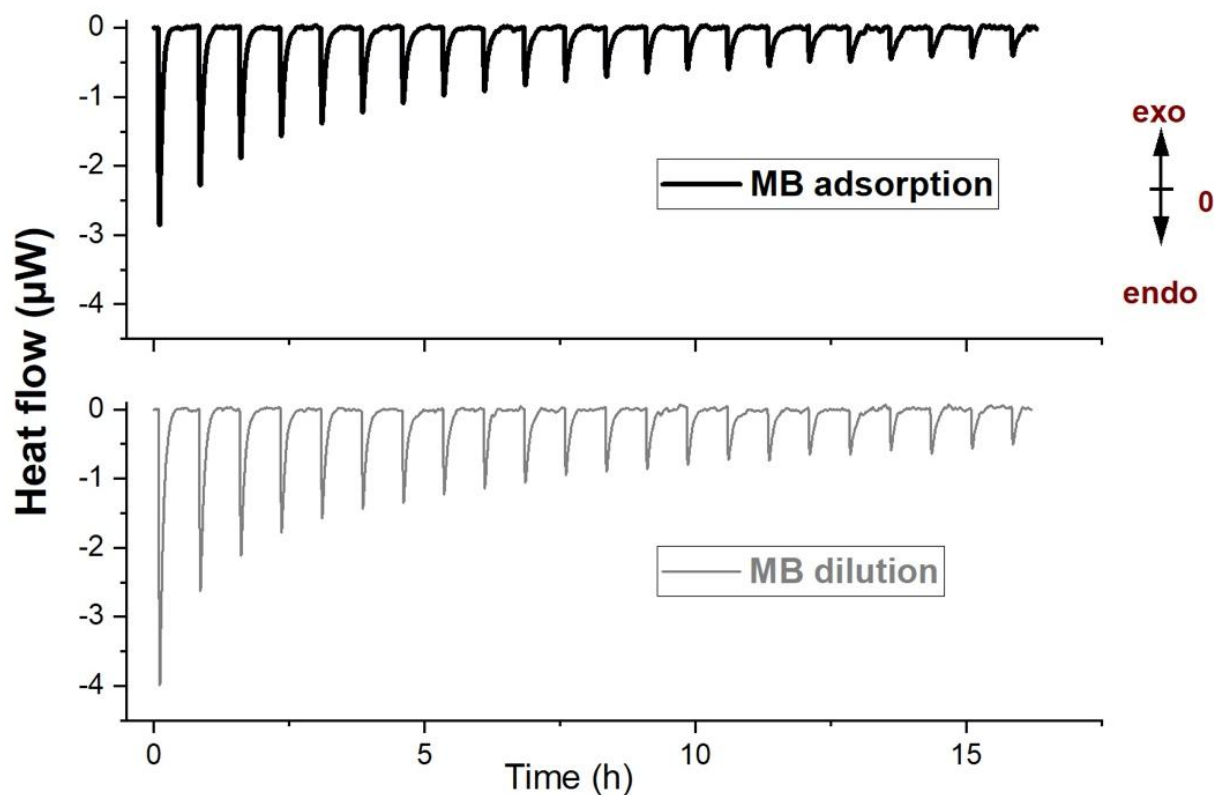


Figure 10. Thermogram of the ITC measurements of the sorption of MB on TEMPO-CNF/Fe₃O₄ nanocomposite in water performed with an initial concentration of 10 mM for the stock solution of MB (black curve measurement with nanocomposite) and the grey curve represents the dilution of MB (measurement without nanocomposite).

The enthalpic contribution has been calculated from the integration of the heat response obtained from the raw ITC data. The sorption enthalpy describes the evolution of the interactions during the loading. Cumulative displacement enthalpy ($\sum\Delta H_{dpl}$) may be plotted in function of the adsorbed amount obtained from the adsorption isotherms as displayed in Figure 11. For low coverage and before surface saturation, the ITC shows a linear evolution of the interaction process. Then, when the maximum capacity is almost reached, the enthalpy levels off. The cumulative enthalpy of displacement $\sum\Delta H_{dpl}$ or $\Delta dplH_{cum}$ was estimated on the initial portion of the adsorption isotherm. $\Delta dplH_{cum}$ is estimated at 5.2 kJ/mol and the positive value of ΔH indicated that the adsorption process was endothermic and spontaneous. The obtained value is rather small, and means that the enthalpic contribution is weak. The comparison with other studies is rather tricky. Indeed, in these studies the enthalpic contribution ΔH is classically

calculated from Van't Hoff equation with isotherm data acquired at various temperatures up to 45 °C. In studies on MB sorption thermodynamics [48,51], the enthalpy is in the range of 18-22.5 kJ/mol, higher than the present work. Nevertheless, in our case, it seems that our Langmuir constant is higher, which is in line with the pseudo second order describe before, and this could explain the observed differences, in correlation with the entropic contribution.

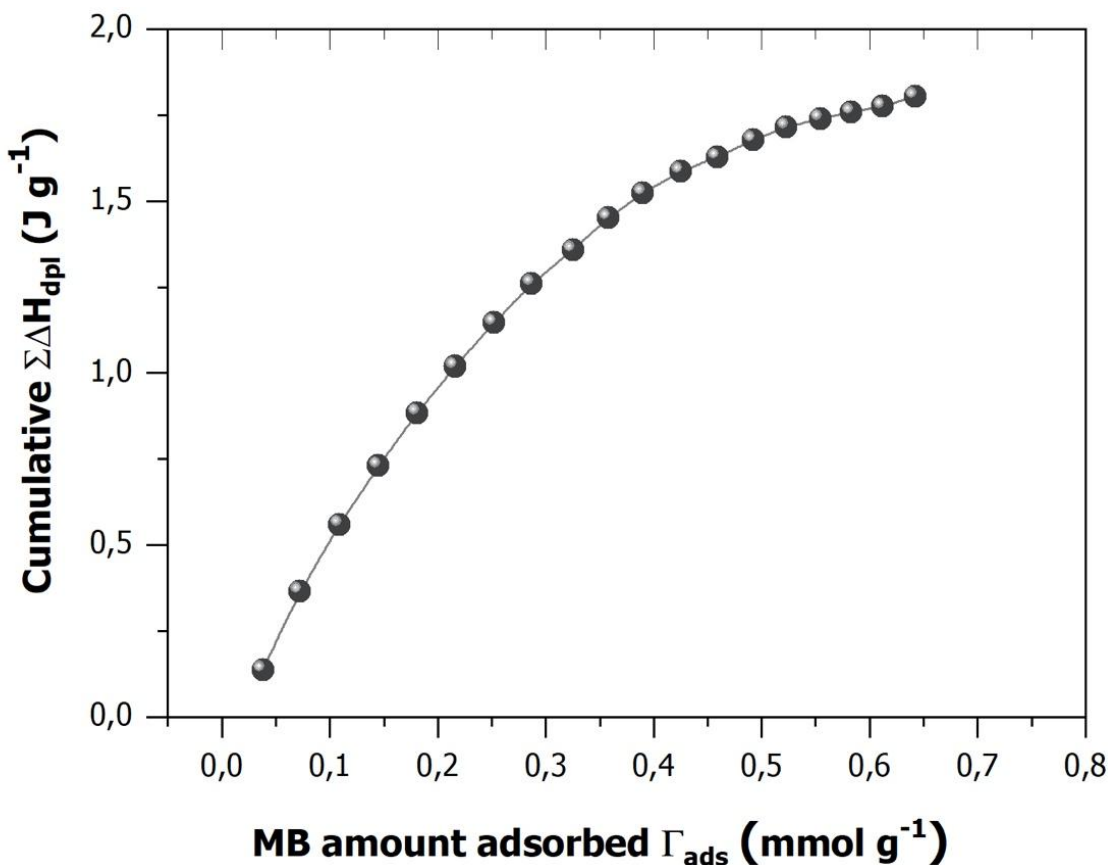


Figure 11: Cumulative displacement enthalpy versus the adsorbed amount for adsorption in the water of MB on TEMPO-CNF/Fe₃O₄ nanocomposite.

4. Conclusion

Tempo-oxidized cellulose nanofiber/magnetite composite (TEMPO-CNF/Fe₃O₄) was prepared through the co-precipitation technique as a versatile adsorbent for the removal of MB from wastewater. TEM observation exhibited the successfully preparation of cellulose nanofiber with a diameter ranged from 10-15 nm and homogenous spherical magnetic nanoparticles (Fe₃O₄) were immobilized. A pseudo-second order and Langmuir isotherm with an adsorption capacity of 303 mg/g and a weak interaction enthalpy define MB adsorption onto TEMPO-CNF/Fe₃O₄.

This study provides an alternative bio-nanocomposite adsorbent, TEMPO-CNF/Fe₃O₄, with effective organic pollutant adsorption capacity.

Availability of data and materials

The research data associated with a paper is available.

Conflict of interest:

The authors declare no conflict of interest.

Ethical statement

In the manuscript, the authors stated that no informed consent was obtained for animal or human experiments.

Author Contributions:

Ahmed Salama and Benedicte Prelot shared equally in funding acquisition and project administration. A.S., B.P., R. A., M. D., M. A. investigation, methodology, validation, and writing—original draft. P. H. methodology, writing—review and editing. All authors have read and agreed to the submitted version of the manuscript.

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