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Modification of Cellulose Nanocrystals with Fe_2O_3 for Linear Alkyl-benzene Sulfonate Removal from Laundry Wastewater

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ABSTRACT

This research is signifi cant to investigate the eff ect of synthesis parameters (weight loading ratio CNCs: Fe_2O_3, sonication temperature, sonication time) on cellulose nanocrystals (CNCs) modifi ed with iron oxide (Fe_2O_3) nanoparticles. The CNCs/Fe_2O_3 adsorbent was synthesized via the ultrasonic-assisted chemical co-precipitation method. All synthesized samples were analysed using linear alkyl-benzene sulfonate (LAS) removal from laundry wastewater using a batch adsorption study. The CNCs/Fe_2O_3 adsorbent was characterised using FTIR, TGA, N_2 sorption-desorption, and SEM-EDX analyses to understand its chemical and physical properties. The highest removal of LAS was found at a 1:1.5 ratio of CNCs: Fe_2O_3, 80°C of sonication temperature, and 90 min of sonication time, with ±90% removal of LAS. The FTIR analysis revealed several functional groups in the CNCs and CNCs/Fe_2O_3 adsorbent. The CNCs showed a hydroxyl group and aromatic ring in lignin around the spectrum of 3000 – 3400 cm^{-1} and 1640 cm^{-1}, respectively. The broad shoulder for the hydroxyl group in the CNCs was reduced to a small peak due to the formation of iron oxide. Thermal analysis from the TGA analysis showed a signifi cant weight loss of around 50 – 200°C due to the destruction of the cellulose structure. As for the N_2 sorption-desorption analysis, the CNCs/Fe_2O_3 adsorbent exhibits a larger surface area compared to the CNCs, in which the porous structure can be observed in the CNCs/Fe_2O_3 adsorbent from the SEM morphology. Overall, the addition of Fe_2O_3 via ultrasound-assisted co-precipitation method contributes to the development of the CNCs structure while changing the properties of the CNCs/Fe_2O_3 as a potential adsorbent for LAS in the laundry wastewater application, thereby offering a practical solution for wastewater treatment.

Keywords: Adsorption; cotton-cloth waste; cellulose-nanocrystals; Fe_2O_3 impregnation; laundry wastewater; linear alkyl-benzene sulfonate (LAS); ultrasound-assisted

INTRODUCTION

Historically, water has played a significant part in laundry activities due to the high capacity required. One coin-operated laundry typically needs 15 L of water to wash 1 kg of clothing, and each day collectively releases 400 m^3 of wastewater (Nascimento et al. 2019)(Hambali et al. 2024). Detergents and other chemicals used in washing processes are present in the wastewater from industrial laundries, which can pose significant problems for the treatment system (Braga & Varesche, 2014). One of the most active components in detergents is surfactant, given that it is persistent in the environment, particularly in water sources (Ramcharan & Bissessur, 2016). Since surfactants can change an organism's biological function, wastewater containing them can be significantly tricky for aquatic creatures. Linear alkylbenzene sulfonate (LAS) is the most common anionic surfactant used in laundry detergents because it works well in laundry operations.

Typically, anionic surfactants are found in the detergent's composition within laundry operations. Linear alkylbenzene sulfonate (LAS) is the most common anionic surfactant used in laundry detergents because it works well in laundry operations. LAS performs effectively in laundry operations due to its capacity to emulsify and suspend dirt, its resistance to hard water, compatibility with other detergent ingredients, and biodegradability. Additionally, it is cost-effective and versatile, making it suitable for a wide range of laundry formulations (Melián et al. 2023). In 2010, about 6.5 million tonnes of anionic surfactants were used around the world (Hampel et al. 2012). According to Deressa et al. (Deressa et al. 2019), anionic surfactants typically become hazardous over time at concentrations greater than 0.1 mg/L. The average surfactant concentration in domestic wastewater has been reported to be 10–20 mg/L, compared to 300 mg/L for industrial effluent (Dereszewska et al. 2015). An anionic surfactant, for example, frequently results in abnormal skin and eyes due to altered biological activity, which can have hazardous effects on both human and animal organs (Beltrán-Heredia et al. 2009a).

Laundry wastewater treatment is usually complex due to the high composition of surfactants and the intense use of detergent. Therefore, numerous technologies, including coagulation-flocculation (Mohtar et al. 2017), adsorption (Hokkanen et al. 2016), and membrane filtration (Barambu et al. 2020) have been developed to improve the quality of wastewater discharges. Due to its high efficacy in eliminating contaminants compared to other technologies, adsorption has drawn increased attention (Hokkanen et al. 2016). Economic adsorbent materials derived from abundant waste/biomass sources are the best option for the adsorption process. According to the literature survey, around 80–89% of anionic surfactants can be removed using an adsorption process with different types of adsorbents like granular activated charcoal, wood charcoal, silica gel, and rubber granules (Beltrán-Heredia et al. 2009b).

Cellulosic materials are one of the natural sources that can be used as inexpensive and environmentally beneficial adsorbents. Additionally, one of the critical factors in selecting them as promising adsorbents has been their ability to create non-hazardous products, high adsorption capacity, and minimal sludge generation (Owoyokun et al. 2021). Cotton cloth waste can be a good source for synthesising cellulose nanocrystals (CNCs) as it contains more cellulose than other raw materials (Shojaeiarani et al. 2021). A significant amount of cotton cloth waste has been produced and discarded globally (Wang et al. 2017). Since cotton waste can contribute to environmental degradation and is expensive to recycle, one option is further utilising it in CNCs. The synthesis of CNCs can be done using a variety of methods, and the most successful one is acid hydrolysis, which employs sulfuric acid (Abu-Danso et al. 2017a).

Nevertheless, the effectiveness of CNCs' adsorbent is frequently constrained by its poor adsorption capacity due to its low surface area. As a result, modification using iron oxide (Fe_2O_3) nanoparticles is required to improve the adsorption capacity of the adsorbent (Abdalkarim et al. 2021). There is a good chance that adding Fe_2O_3 nanoparticles to CNCs will increase the adsorbent's surface area, improving the physical adsorption of target contaminants in the laundry wastewater. Additionally, due to its extraordinary qualities, including low hazardous quality, compound dormancy, biocompatibility, and super-paramagnetic, the impregnation with Fe_2O_3 demonstrated significant potential in water treatment (Oprea & Mihaela Panaitescu 2020). Metal oxide nanoparticles, such as Fe_2O_3, have high surface energy, contributing to aggregation tendency when suspended in aqueous media. Hence, a combination of both CNCs and Fe_2O_3 may develop new characteristics of adsorbent.

This research is anticipated to synthesise an adsorbent, CNCs extracted from cotton cloth wastes modified with Fe_2O_3 using an ultrasound-assisted co-precipitation method. The synthesis parameters were the weight loading ratio of CNCs/Fe_2O_3 adsorbent, sonication temperature, and sonication time. The CNCs/Fe_2O_3 adsorbent synthesised was utilised as a magnetic adsorbent in removing the LAS compound from laundry wastewater. Details of discussions related to the desirable/undesirable characteristics of the adsorbent synthesised via ultrasound-assisted co-precipitation method were enclosed in the following sections. Some limitations and future recommendations associated with this work were also included in this report.

METHODOLOGY

MATERIALS AND CHEMICALS

The raw material to synthesise the CNCs is cotton cloth wastes from unused old clothes. Several chemicals were used for the synthesis of CNC/$Fe_2O_{3,}$ which are sodium hydroxide (NaOH, Merck), hydrogen peroxide (H_2O_2, Merck 30%), glacial acetic acid (CH_3COOH, R.M Chemicals, A.R), sulfuric acid (H_2SO_4, Merk 95-97%), iron (II) chloride tetrahydrate ($Fe_2CI_3.6H_2O$, Sigma-Aldrich, 99%), ethanol (C_2H_5OH, QreC, 96%) and ammonia hydroxide (NH_4OH, ACS reagent, 25%).

EXTRACTION OF CNCS FROM COTTON CLOTH WASTE

A 5 g of cotton cloth waste was cut into small pieces (1 x 1 cm dimension) before boiling with 20 wt% of 100 mL NaOH at 70 ºC for 2 h. The treated sample was then filtered, rinsed with distilled water, and adjusted until the pH was consistently 10. The pH was adjusted to 10 by measuring NaOH. Once the pH stabilises at 10, filter the sample if needed and rinse it with distilled water to remove any excess base. Then, 1.5 wt% of H2O2 was added to the sample for decolouring treatment. Acetic acid was added dropwise to bring the pH level of the solution to 7. To obtain the cellulose, the solution had to go through three rounds of filtering and distilled water washing. The resultant cellulose was mixed with 100 mL of 60 wt% H2SO4 and heated at 50ºC for 1 h. Then, the mixed CNCs solution was sonicated using an ultrasonic bath at 55ºC for 7 h. The solution was diluted with distilled water five times before being centrifuged for 10 minutes at 6000 rpm to separate the supernatant. The suspension was retrieved and kept in a bottle (Maiti et al. 2013).

MODIFICATION OF CNCS WITH FE_2O_3 NANOPARTICLES

The CNCs/Fe_2O_3 adsorbent was synthesised using the ultrasonic-assisted co-precipitation method (Ha et al. 2021). To create a hydrophilic state, 1 g of CNCs was mixed with 10 mL of ethanol and heated in an ultrasonic bath to 80°C for 2 h. Then, the hydrophilic CNCs were impregnated into 100 mL of the aqueous solution containing Fe2CI3.6H2O and sonicated for 2 h at 80°C. Next, 50 mL of the aqueous solution containing 2M of NH4OH was utilised as the precipitation agent. To maintain a pH of 7, the NH_4OH gradually dropped. The mixture was sonicated continuously for 3 hours with 5-minute intervals at 80ºC. The sample was subsequently filtered and dried in an oven at 105 °C for 2 h. The synthesised CNCs/Fe_2O_3 were kept in a desiccator before the LAS batch adsorption experiment was used.

Three synthesis parameters were varied, which are the weight loading ratio of CNCs: Fe_2O_3 (1:0.5, 1:1, and 1:1.5), sonication temperature (50, 60, 70, and 80°C), sonication times (30, 60, 90, and 120 min). The variation of synthesis parameters followed a one-factor-at-time (OFAT) approach. The LAS removal efficiency (%R) and adsorption capacity values were calculated by using Equation (1) and (2):

$$R\,(\%) = \left[\frac{(C_o - C_t)}{C_o}\right] \times 100\% \quad (1)$$

$$Q_e = \frac{(C_o - C_t)\,V}{m} \quad (2)$$

where C_o is the initial LAS concentration, mg/L, C_t is the residual LAS concentration in solution at any time t (min), mg/L, Q_e (mg/g) was the adsorption capacity at any time t (min), V (L) is the volume of the diluted laundry wastewater, and m (g) is the mass of CNCs/Fe_2O_3 adsorbent used.

LAS BATCH ADSORPTION EXPERIMENT

A 1 L of laundry wastewater was collected from the selected coin laundry at UITM Cawangan Pulau Pinang and was stored in a refrigerator at 4 ºC for preservation purposes within a week for the adsorption experiment of LAS surfactant. A 10.0 mL diluted laundry wastewater sample (1:10) was alkalinised with 10 mL NaOH until pH 6.5 – 7. A 5 mL alkalinised sample was extracted into a glass test tube. A 1 g of CNCs/Fe_2O_3 adsorbent was added into the test tube, vigorously stirred for 30 s, and let the solution rest for 5 min. The concentration of LAS in the solution was analysed using a UV-VIS spectrophotometer (Lambda 35 UV-Vis Perkin Elmer). External standard calibration was established using LAS standards ranging from 0.25 to 2.5 mg/L for absorbance at 273 nm relative to air (Ramcharan & Bissessur, 2016). The batch adsorption experiment for all samples was tri-plicated for each synthesis parameter, and the standard deviation was calculated to analyse the error bar for each parameter.

CHARACTERISATIONS

The characterisation study of the CNCs and CNCs/ Fe_2O_3 was performed by analysing their physical and chemical properties. The physical analysis was performed using N_2 adsorption-desorption analysis, Thermogravimetric analysis (TGA) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX). The N_2 adsorption-desorption analysis was done to determine the surface area and porosity. The samples were analysed under an N_2 atmosphere by degassing at 383K for 12 h (Micromeritics ASAP 2020). The thermal stability of the adsorbent was investigated by TGA (Thermal Advantage Q Series - TA 1000) in the air at a heating rate of 10°C/min. The SEM was conducted to investigate the surface morphology of the adsorbent. The Fourier Transform Infrared (FTIR) analysis was analysed using Nicolet, Thermo Scientific, between 5000 cm^{-1} to 400 cm^{-1} spectrums. FTIR aims to identify the functional groups of the CNCs and CNCs/ Fe_2O_3.

RESULTS AND DISCUSSION

EFFECT OF SYNTHESIS PARAMETERS

The modified CNCs/Fe_2O_3 adsorbent was synthesised at different synthesis parameters, which are the weight loading ratio of CNCs: Fe_2O_3 from 1:0.5, 1:1, and 1:1.5 g, sonication temperature from 50, 60, 70 and 80ºC, and sonication time from 30, 60, 90 and 120 min. Figure 1 shows the %R of LAS for LAS adsorption capacity. The plotting of %R was evaluated based on the error bars of its standard deviation.

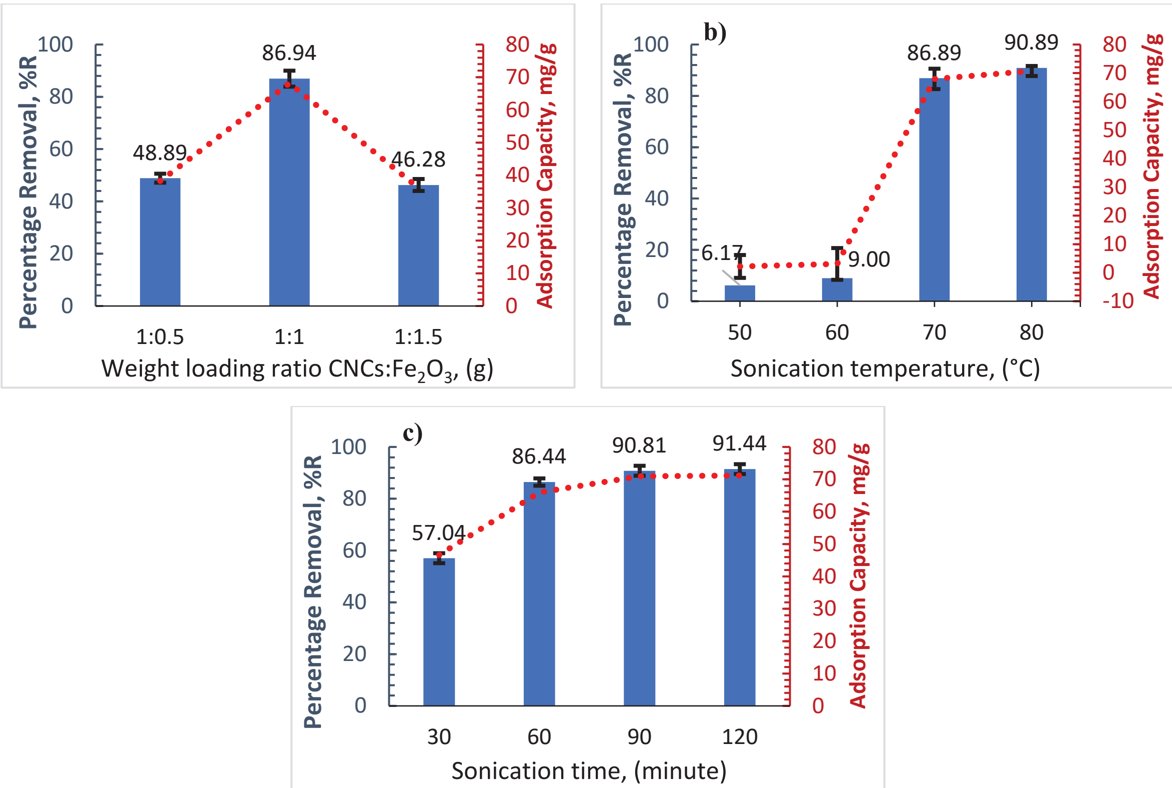


FIGURE 1. Effect of synthesis parameters of CNCs/Fe_2O_3 adsorbent towards LAS removal a) weight loading ratio CNCs: Fe_2O_3, b) sonication temperature, and c) sonication time

From Figure 1(a), the %R of LAS in laundry wastewater using a weight loading ratio of CNCs/Fe_2O_3 of 1:1 showed the highest removal (86.94 %R) compared to other ratios with an adsorption capacity of 68.15 mg/g. The sample with a ratio of 1:0.5 gave only 48.89 %R of LAS removal, while the sample with a ratio of 1:1.5 gave 46.28 %R. From the result obtained, enough Fe_2O_3 can enhance the adsorption capacity of CNC adsorbent and better remove LAS in laundry wastewater. In this case, cellulose acts as a coagulant that facilitates the attachment of LAS molecules from the wastewater, which indirectly attach to the cellulose polymer chain (Mohtar et al. 2017). According to Eskandari and Hasanzadeh, the reinforcing capability of the adsorbent increases with the increase of the Fe_2O_3 ratio until a certain amount is deposited onto the adsorbent (Jafari Eskandari & Hasanzadeh, 2021).The CNCs' surface area is expected to increase after the modification with Fe_2O_3, indirectly increasing their ability to trap the surfactants.

From Figure 1(b), the best sonication temperature was determined at 80ºC with 90.89 %R of LAS with an adsorption capacity of 70.72 mg/g. Samples synthesised at temperatures of 50 and 60ºC recorded small adsorption of LAS. Perhaps this is due to the incomplete synthesis reaction and insufficient energy for the interaction of CNCs and Fe_2O_3 to form new bonds if the sonication temperature was conducted at a very low temperature (Karaagac et al. 2015). Sonication temperature contributes to better synthesis of CNCs/Fe_2O_3 adsorbent by enhancing the cavitation effects, improving diffusion and reaction rates, promoting high surface area formation, optimising particle morphology, and preventing agglomeration (Sandhya et al. 2021). These improvements in adsorbent properties lead to more efficient removal of LAS from contaminated water or solutions. The reduction in the rate of adsorption with the lowest temperature may be due to the weakening of the interaction force between the active site of the adsorption surface and the metal ion (Jabbar et al. 2022).

From Figure 1 (c), the %R of LAS at 90 and 120 min indicated the highest removal of LAS, which is at 90.81 and 91.44 %R, respectively. The LAS adsorption capacity for the sample synthesised at 90 min is 70.93 mg/g, while the sample synthesised at 120 min is 71.17 mg/g. Meanwhile, the %R of LAS for samples synthesised at 30 and 60 min was 59.22 and 87.83 %R, respectively. According to the previous study, sonication time is found to be effective on the particle size since the particle size of the Fe_2O_3 nanoparticles decreases with the increase in reaction time (Karade et al. 2018). Hence, when the particle size of the adsorbent decreases, the ability to trap more LAS in the laundry wastewater also increases. Furthermore, increasing sonication time can enhance the crystallinity of the adsorbent, which improves the surface area of the active site. In contrast, if the reaction time is too long, the cellulose nanocrystal content in the adsorbent tends to lose or present only iron oxide in the synthesised adsorbent. This can decrease the effectiveness of the adsorbent in trapping the LAS.

SURFACE FUNCTIONAL GROUP OF CNCS/FE_2O_3 ADSORBENT

The surface functional groups analysis of CNCs and CNCs/Fe_2O_3 is shown in Figure 2. The FTIR spectra of the CNCs representatives' peaks at 3300-3400 cm^{-1} for the O-H stretching vibration, which can be assigned as the hydroxyl group, and a peak at 2900 cm^{-1} for the stretching vibration of CH and CH_2 groups as shown in Figure 2 (a) (Shojaeiarani et al. 2021). Next, a peak at 1640 cm^{-1} is associated with the aromatic ring, indicating the presence of lignin and absorbed water, while peaks at 1430, 1372, and 1330 cm^{-1} for bending vibration of CH_2 and OH groups and 1050 cm^{-1} for C-O stretching vibration (Abu-Danso et al. 2017a)(Qurratu et al. 2018).

In Figure 2 (b), modified CNCs/Fe_2O_3 adsorbent showed characteristic peaks of cellulose at 2300, 1319, and 994 cm^{-1} representing CH-stretching, CH_2-stretching, and C-O-C-bending, respectively. The broad shoulder peak corresponding to the free hydroxyl group of CNCs at region 3300-3400 cm^{-1} was reduced, and the peak at 1640 cm^{-1} was found to be shifted at 1652 cm^{-1} in the CNCs/Fe_2O_3. This is due to the formation of Fe_2O_3 nanoparticles on the hydroxyl surface of CNCs during the co-precipitation method, leading to the encapsulation of the hydroxyl groups in CNCs. Spectra for the modified adsorbent also show the presence of a small peak around 500-700 cm^{-1}, which represents the stretching and bending vibration of the Fe-O, confirming the formation of the Fe_2O_3. These small peaks in the CNCs/ Fe_2O_3 confirm that Fe_2O_3 nucleated mostly on the hydroxyl group of CNCs present on its surface without altering the crystalline structure of cellulose nanocrystals (Abdalkarim et al. 2021).

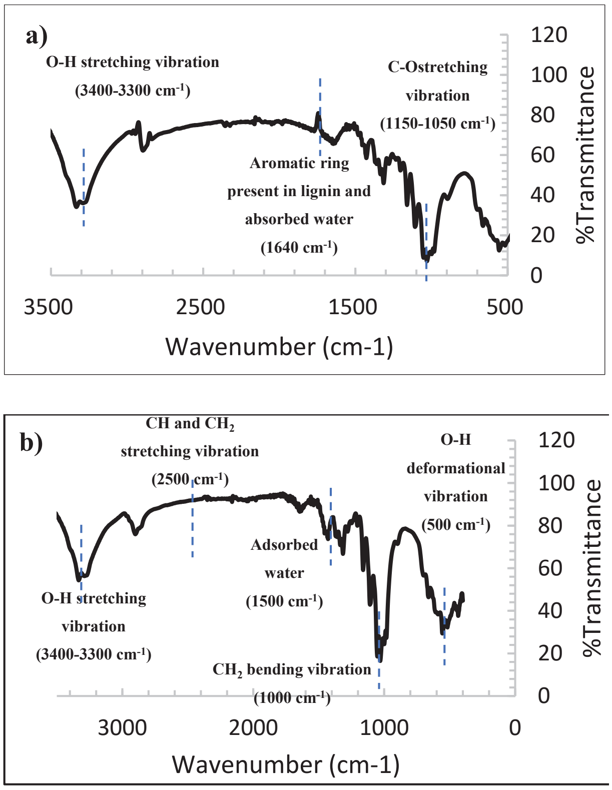
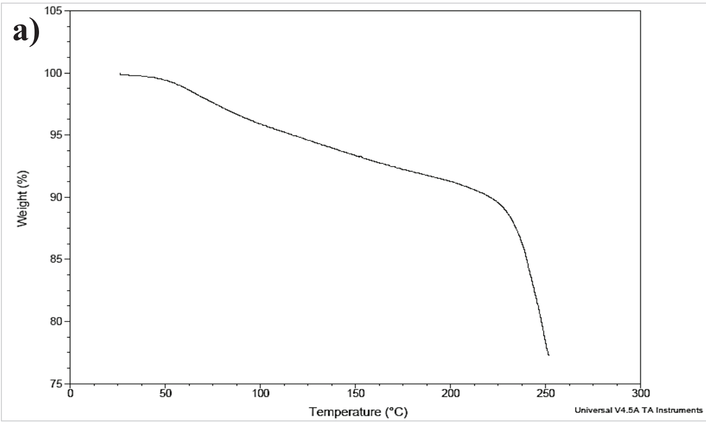


FIGURE 2. Surface functional groups of (a) CN Cs and (b) CNCs/Fe_2O_3 adsorbent

THERMAL STABILITY OF MODIFIED CNCS/FE_2O_3 ADSORBENT

The CNCs and modified CNCs/Fe_2O3 adsorbent were analysed, and thermal analysis for these samples is illustrated in Figure 3. Figure 3 (a) shows several stages of weight loss for CNCs as temperature increases. Early mass loss was found at the temperature range from 50 – 100ºC, corresponding to the evaporation of loose and physic-absorbed water on the cellulose surface. Since it is difficult to control the quantity of water throughout the synthesis of the CNCs, the amount of water released at the lower temperature stage varies. The second weight loss was found at temperatures between 100 to 150°C, and it is suggested that the weight from coordinated or crystalline water (Rashid et al. 2021). The amount of crystal water found by a thermal analysis method is similar to the broad curve of the hydroxyl group's fingerprint found at 3000–3500 cm^{-1}. The last stage of weight loss of CNCs was observed at the temperature range of 150 – 250ºC. The cellulose structure of CNCs collapses because of thermal deterioration. The complete degradation of the cellulose is observed at a higher temperature, which is around 250ºC (Kusmono et al. 2020).

Based on Figure 3 (b), the significant weight loss of CNCs has happened at the temperature range of 50 – 200ºC. The trend of weight loss gradually decreases with increasing temperature. Due to moisture and loosely bound water being physically absorbed on the surface of the modified CNCs/Fe2O3 adsorbent, weight loss was observed (Abdalkarim et al. 2021). The curve of the weight loss of the CNC/Fe_2O_3 suddenly dropped at a temperature of more than 200ºC. This sudden drop was due to the presence of CNCs started to degrade before the collapse of the structure of cellulose composite (de Paula et al. 2016). Apart from the thermal analysis of cellulose and modified CNC/Fe_2O_3 adsorbent, both figures also show that the CNC/Fe_2O_3 adsorbent was shifted to higher temperature removal than pure cellulose. Hence, this graph provides support that the composite material was successfully formed.



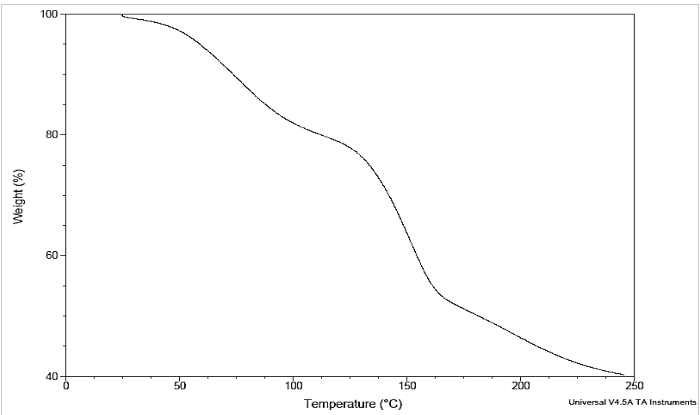


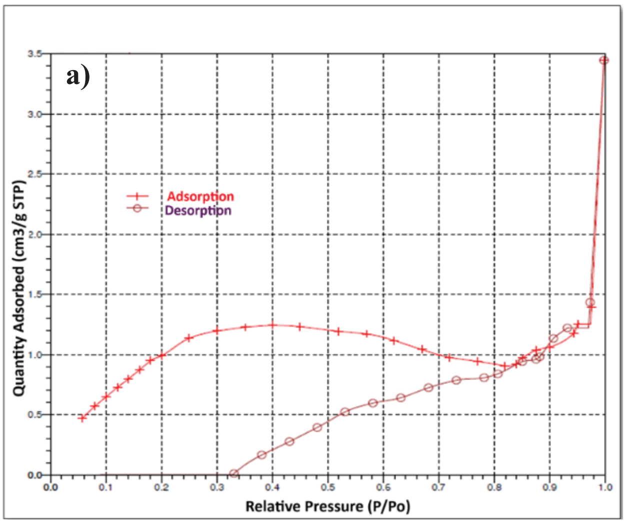
FIGURE 3. TGA analysis of (a) CNCs and (b) CNCs/Fe_2O_3

SURFACE CHARACTERISTICS OF MODIFIED CNCS/FE_2O_3 ADSORBENT

Theoretically, a large surface area significantly affects the adsorbent ability of the target adsorbate. The specific surface area of the CNCs and CNCs/Fe_2O_3 adsorbent was tabulated in Table 1. The tabulated data in Table 1 shows that the modified CNCs/Fe_2O_3 adsorbent has a higher surface area than the CNCs. The increased surface area of the modified CNCs/Fe_2O_3 adsorbent (124.15 m^2/g) is expected due to the availability of Fe_2O_3 nanoparticles bound onto the CNCs structure, which opens the cellulose strand, improving the cellulose composite structure. This is also supported by the average pore size of CNCs and CNCs/Fe_2O_3, with 22.89 and 12.67 nm, respectively. This would enhance the adsorbent's ability to capture the LAS molecules in the laundry wastewater. Instead, the modified CNCs/Fe_2O_3 adsorbent also developed more accessible active sites than the CNCs, increasing the surface area (Saghi et al. 2018).

TABLE 1. The surface area of CNCs and $CNCs/Fe_2O_3$

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore (nm)
CNCs	4.48	0.0638	22.89
$CNCs/Fe_2O_3$	124.15	0.4924	12.67



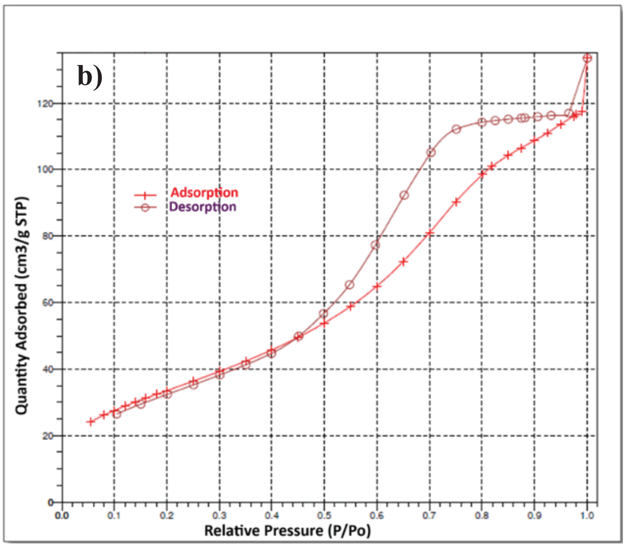


FIGURE 4. N_2 adsorption-desorption isotherm linear plot of (a) CNCs and (b) $CNCs/Fe_2O_3$

The N2 adsorption-desorption profile plots the amount of N2 gas adsorbed against the relative pressure. The analysis is based on the Brunauer-Emmett-Teller (BET) theory, where the exposed surface area of the adsorbent is determined by the amount of physical adsorption of a gas on the surface (Wu, 2016). Figure 4 shows the isotherm linear plot for CNCs and $CNCs/Fe_2O_3$ adsorbent, illustrating Type IV isotherms with mesoporous material characteristics. The linear isotherm plot clearly shows that the modified $CNCs/Fe_2O_3$ adsorbent (Figure 4(b)) has a large quantity of gas that can be absorbed against the relative pressure compared to the adsorption ability of CNCs (Figure 4(a)). There is a noticeable separation (hysteresis) between the adsorption and desorption branches at higher relative pressures (around 0.4 to 0.9) compared to low relative pressures (less than 0.4). The hysteresis indicates that the material likely contains interconnected mesopores, where the entrance to the pore is narrower than the central cavity, leading to a delayed desorption process (Abu-Danso et al. 2017b).

Thus, the isotherm for modified $CNCs/Fe_2O_3$ adsorbent indicated that the adsorbent is a mesoporous material type.

Materials with mesoporous-sized pores show strong interaction with targeted adsorbate (LAS), which resulted in increasing the amount of LAS adsorbed (Kusmono et al. 2020). The CNCs indicate a weak adsorbent-adsorbate interaction due to their low ability to adsorb LAS in their pores. This is due to the strong interaction and higher surface area of CNCs/Fe_2O_3, ensuring that the adsorbent can attract and adsorb more LAS molecules than the CNCs. Hence, it is proven that the modification of CNCs via Fe_2O_3 impregnation could enhance the surface characteristics of the adsorbent and its ability to capture more LAS in laundry wastewater.

SURFACE CHARACTERISTICS OF MODIFIED CNCS/FE_2O_3 ADSORBENT

SEM is an instrument that displays the morphology of a solid substance through three-dimensional imaging (3D). Figure 5 shows the surface morphology of CNCs and CNCs/Fe_2O_3 adsorbents at different magnifications. From the observation, it can be seen that the CNCs' surface structure is clumpy with a smooth and flat surface. The morphology verified the isotherm linear plot's finding of a low porosity surface area. The obtained surface area and low porosity are consistent with the acquired SEM images.

In opposition to the CNCs structure, the observation for the CNCs/Fe_2O_3 structure clearly showed a clumpy with fibrous cellulose, where some deposited solid on the surface. This caused an uneven and rough structure with the development of pores observed at low magnification. The fibrous structure is evenly scattered, displaying a variety of solid particle sizes deposited on the surface. Even though some particles are well-separated, others are agglomerated and aggregated into cluster particles. The agglomeration of the particles demonstrates that Van der Waals forces attract the Fe_2O_3 because of intermolecular hydrogen bonds and a strong hydrophilic hydroxyl group on the surface of the CNCs (de Paula et al. 2016). In addition, this suggested that the sonication energy provided via ultrasonic-assisted co-precipitation was not enough to well-dispersed or break the agglomeration of the CNCs structure and the distributions of Fe_2O_3 nanoparticles. Due to the adsorbent's clumpy and agglomeration structure, the CNCs/Fe_2O_3 nanostructure cannot be seen clearly. However, in Figure 5b), at a magnification of 7k, tiny fibrous pores were observed with diameters less than 10 µm. Even though no clarity was found in the SEM images, from Table 1, the average pore values suggested that the composite was in nano sizes for CNCs and CNCs/Fe_2O_3 adsorbents.

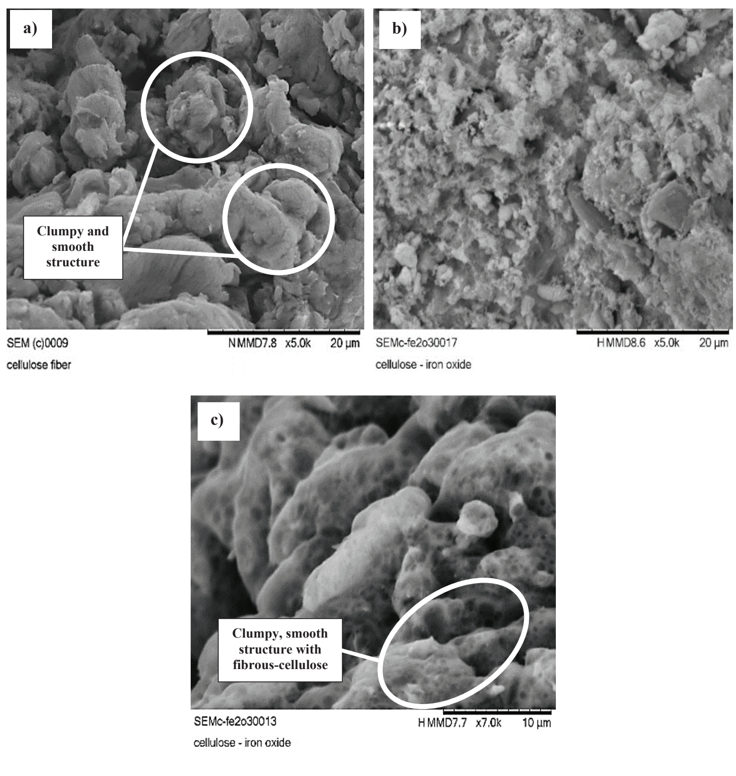


FIGURE 5. SEM images of a) CNCs at 5.0k magnification, b) CNCs/Fe_2O_3 at 5.0k magnification, and c) CNCs/Fe_2O_3 at 7.0k magnification

EDX analysis was also employed to observe the elemental composition of the CNCs and CNCs/Fe_2O_3 adsorbents. Figure 6 displays the EDX spectra of CNCs and CNCs/Fe_2O_3 adsorbents, and Table 2 tabulates the weight % of the elements found. The EDX spectrum of CNCs indicated the existence of C, O, and S elements. The composition of C and O elements gives the highest percentage of weight composition, representing cellulose characteristics with the chemical formula of $(C_6H10O_5)_n$. The only present exchangeable element in the adsorbent was the S element. This element may be due to the acid hydrolysis process using sulfuric acid during CNCs extraction from cotton cloth waste. On the other hand, the EDX spectrum of the modified CNCs/Fe_2O_3 adsorbents shows the presence of C, O, and Fe elements. Fe gives the highest percentage of weight composition compared to C and O, which dominates the surface structure of the CNCs. This indicates that the Fe distribution onto the CNCs structure is relatively dispersed via an ultrasonic-assisted co-precipitation approach (Abdalkarim et al. 2021).

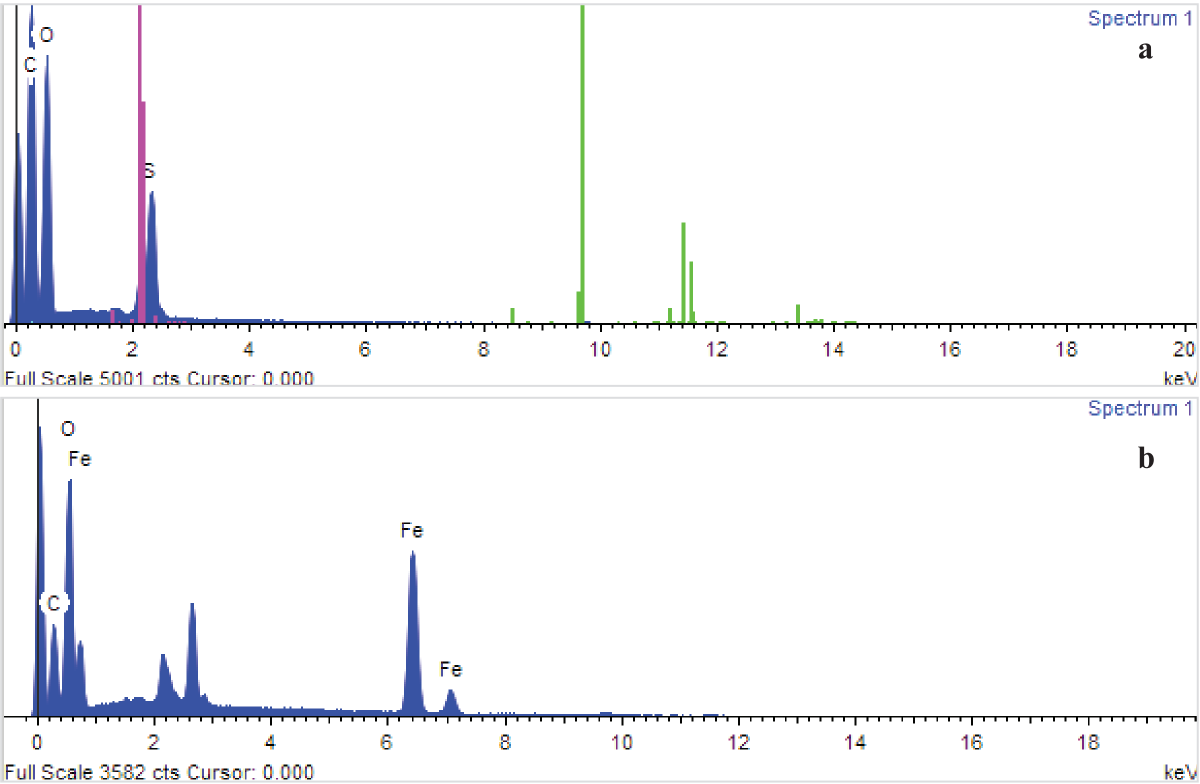


FIGURE 6. EDX spectrum of elements identification for (a) CNCs and (b) CNCs/Fe_2O_3

TABLE 2. wt% of elements identified in CNCs and CNCs/Fe_2O_3

Element	CNCs	CNCs/Fe_2O_3
	wt%	wt%
C	48.13	22.38
O	47.57	31.72
S	4.30	-
Fe	-	45.90

LIMITATIONS OF THE CURRENT WORK AND FUTURE RECOMMENDATIONS

The current research is to synthesise CNCs from cotton cloth wastes and further modify them with Fe_2O_3 using the ultrasonic-assisted co-precipitation method. The modified adsorbent was aimed at reducing the LAS concentration in laundry wastewater. The discussed LAS adsorption results showed that the synthesised CNCs/Fe_2O_3 adsorbent successfully removed LAS up to ±90 %R. Nevertheless, the morphology analysis describes that the adsorbent structure was clumpy and agglomerates, which suggested unfavourable nano-size formation for the CNCs. For this reason, further characterisation, such as transmission electron microscopy (TEM), was not conducted.

A few factors were identified to troubleshoot the problem that arose. It was presumed that the synthesised clumpy CNCs/Fe_2O_3 adsorbent is a result of the treatment of cellulose with sulfuric acid (H_2SO_4), which produces negatively charged cellulose crystals due to the esterification of hydroxyl (-OH) groups by sulfate ions, which is unsuitable for cotton-based material (Wang et al. 2017). This will also contribute to the modification step, where using the ultrasonic-assisted co-precipitation approach of Fe_2O_3 was inefficient. High surface energy in the Fe_2O_3 nanoparticles made the combination of the clumpy CNCs with Fe_2O_3 nanoparticles as an agglomeration composite due to less sonication energy provided during co-precipitation synthesis at 80ºC (Oprea & Mihaela Panaitescu 2020).

Hence, some recommendations are suggested for future improvement. To improve the CNCs' size, Abu-Danso et al. suggested including an alkali cotton dissolution agent, such as a combination of NaOH-thiourea-urea-H_2O solution during the CNCs synthesis method, which resulted in the disappearance of fibre structure upon the dissolution process (Abu-Danso et al. 2017a). The dissolution of CNCs-derived cotton is expected to improve the dispersion surface energy of the Fe_2O_3 nanoparticles later.

CONCLUSIONS

The modified CNCs/Fe_2O_3 adsorbent could remove Linear alkyl benzene sulfonate (LAS) from the laundry wastewater. The adsorption capacity of the modified CNCs/Fe_2O_3 adsorbent highly depends on the best synthesis parameters. From this work, the best synthesis parameters in the modification of CNCs/Fe_2O_3 adsorbent are CNCs: metal loading of 1:1, sonication temperature of 80ºC, and sonication time of 90 min, which give the %R of 90.81%R of LAS removed. The characterisation studies suggest that the physical and chemical characteristics of the modified CNCs/Fe_2O_3 adsorbent contribute to the development of adsorbent compared to the CNCs. The outcomes from this research work can be a benchmark for developing CNCs/Fe_2O_3 adsorbents in removing LAS surfactant in the laundry wastewater source.

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DECLARATION OF COMPETING INTEREST

None.

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