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Synthesis and Characterization of Eggshell Membrane Functionalized with Free Fatty Acids as Potential Adsorbents for Anionic and Cationic Dyes

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In this study, eggshell membrane (ESM) was functionalized with free fatty acids (FFAs) from new and used palm cooking oil to produce ESM@FFAs-NCO and ESM@FFAs-UCO respectively for use as adsorbents for cationic and anionic dyes. The synthesis protocol was optimized, and it was found that the optimum time for the reaction of ESM with FFAs was 15 minutes and the optimum mass ratio of ESM to FFAs was 1:4. Both adsorbents were characterized using SEM and FTIR. The functionalized ESM was found to have a more extensive microporous network structure than that of non-functionalized ESM. FTIR analysis confirmed the successful attachment of FFAs onto the surface of ESM in both ESM@FFAs-NCO and ESM@FFAs-UCO. It was found that the adsorption capability of the adsorbents towards Alizarin Red from worst to best followed the order: ESM < ESM@FFAs-NCO < ESM@FFAs-UCO. Functionalized ESM produced a synergistic effect due to hydrogen bonding and hydrophobic interactions when adsorbing dyes on its active sites. A higher dye removal efficiency was obtained when using ESM@FFAs-UCO due to its greater long alkyl chain content, giving better hydrophobic behaviour. Therefore, ESM@FFAs-UCO was investigated as an adsorbent for other organic dyes such as Rhodamine B, Chicago sky blue, and Remazol dye. The removal percentages obtained were 87.83% for Alizarin Red, 84.59% for Remazol, 78.34% for Rhodamine B and 65.68% for Chicago Sky Blue.

Key words: Eggshell membrane; free fatty acid; used cooking oil; cationic and anionic dyes

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The release of toxic dyes, even in trace amounts, can alter the colour and quality of water and significantly impact the marine environment [1]. Synthetic dyes have displaced natural dyes as the dominant colourants due to lower production costs, excellent brightness, and better stability [2]. Dyes have diverse chemical structures, but the most common are azo, anthraquinone, sulphur, indigoid, triphenylmethyl, and phthalocyanine derivatives [3]. Most synthetic dyes have aromatic rings in their structures, making them highly toxic, carcinogenic, non-biodegradable, and mutagenic to human and aquatic organisms [4]. Therefore, removing these polluting dyes from wastewater before their final disposal into the environment is important. To date, a range of techniques have been employed for the removal of dyes from water/wastewater, including electrochemical methods [5], degradation [6], chemical reduction [7], membrane filtration [8], aerobic and anaerobic treatment [9,10], flocculation [11], coagulation [12], fermentation of waste activated sludge [13] and adsorption [14,15].

Adsorption is an attractive technique for dye removal due to its low cost and design flexibility, as well as the fact that it produces no harmful substances after the target compounds are removed [16]. The most common sorbent is activated carbon, but this is difficult to dispose of and expensive [17]. Therefore, in recent times, attention has shifted to the use of low-cost alternative adsorbents such as agricultural solid waste and its by-products, industrial solid waste, biomass-based cost-effective activated carbon, and various natural materials to remove dyes from water [18]. Versatile composite materials that can effectively absorb cationic and anionic dye compounds are also being developed [3–6]. Some studies have used the following adsorbents for the treatment of specific dyes: oxidized chitosan (for methylene blue and methyl orange) [19], graphene and

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graphene oxide (for methylene blue, methyl violet, Rhodamine B, Orange G) [3], activated carbon (for methylene blue, Orange II) [20], multiwall carbon nanotubes (for Auramine O, Crystal Violet 2B, Brilliant Acid Scarlet 3R) [15], Congo Red-chitosan particles (for methylene blue, Rhodamine B) [21] and ethanolamine-polyacrylonitrile-UF membrane (for methylene blue, Rhodamine B, Acid Orange, Congo Red) [22].

Eggshell membrane (ESM) is a unique biomaterial found in nature, but its utility is often overlooked due to its status as a waste material. Despite this, researchers have made important discoveries while studying this biomaterial due to its distinct properties and well-defined structure [23]. ESM effectively treats burns in mammals, provides pain relief and wound protection, and even removes heavy metals and gold from industrial waste discharge [24]. Recently, the use of ESM as an adsorbent for various pollutants in wastewater has been gaining traction [25,26]. ESM has a fibrous, porous structure with an extensive surface area that can adsorb various pollutants from water aquifers or wastewater due to its abundance of surface functional groups (i.e., hydroxyl, carbonyl, thiol, carboxyl, and amino groups). ESM has been extensively used for the removal of dyes such as Congo Red [18], sulfonated Reactive Red 120 [27], methyl orange and methylene [28], Sudan I-IV [29], anionic sulphur [30], acid orange and Toluidine Blue [31]. A mixture of ESM and eggshell (ES) has also been reported to remove anionic and cationic dyes [32]. The performance of ESM in dye removal can be improved by surface modifications of ESM. There exist several studies on the surface modification of ESM using poly-ethyleneimine-ESM [33], MXene debris-coated ESM [34], C-doped MgO-ESM [35], Cu-Ag/ESM composites [36] and polyethersulfone-ESM [35]. However, the use of fatty acids as a modifier for ESM is still uncommon.

When cooking oil is heated, it undergoes a series of irreversible complex reactions, including polymerization, oxidation, and hydrolysis [38]. The nutritional value of used cooking oil decreases and some decomposition products such as polymeric triglycerides and polar compounds are formed [39,40], turning it ino waste cooking oil (WCO). WCO, palm oil, and rapeseed oil have emerged as primary sources for biodiesel production and are becoming increasingly useful in other sectors [41]. Because of a hydrolytic process that occurs in the presence of oil and water from food, large amounts of free fatty acids are present in WCO [42]. Free fatty acids consist of long alkyl chains, making them excellent hydrophobizing agents for ESM, which can improve its capability to remove dyes from water/ wastewater. In this work, ESM functionalized with free fatty acids (FFAs) obtained from new palm cooking oil (NCO) and used palm cooking oil (UCO) were successfully synthesized, characterized, and utilized as adsorbents for Alizarin Red (AR) dye. The combination of FFAs and ESM enhances the hydrophobicity property of ESM, resulting in a stronger binding affinity towards the targeted analyte. The reaction times and mass ratio of ESM to FFAs were optimized to obtain the ideal ESM@FFAs-NCO and ESM@FFAs-UCO adsorbents. Both adsorbents were then evaluated by determining their AR dye removal efficiencies.

MATERIALS AND METHODS

Chemicals

Sulphuric acid and potassium phosphate were purchased from Sigma-Aldrich (Missouri, MO, USA). Hydrochloric acid, sodium sulphate (anhydrous), potassium hydroxide, and n-hexane were obtained from Merck (Darmstadt, Germany). Rhodamine B, Chicago Sky Blue, Remazol, and Alizarin Red S dyes were acquired from Supelco (Bellefonte, USA). All stock solutions were prepared using distilled water and stored at 4 °C before use. Eggshells were gathered from stalls at the Wang Ulu residential hostel, Perlis. UCO and NCO samples were obtained from Bangsar, Kuala Lumpur. UCO was filtered to remove any potential particulate matter. A stock solution of 100 mg L^{-1} of AR was prepared by dissolving 0.01 g of pure Alizarin Red in 100 mL deionized water. The working solutions were made daily by diluting the standard solution with deionized water to the desired concentration. Similar procedures were applied to prepare 100 mg L^{-1} solutions of Rhodamine B, Chicago Sky Blue, and Remazol dyes.

Instrumentation

FTIR spectra of ESM, ESM@FFAs-NCO, and ESM@FFAs-UCO were recorded at room temperature using a Perkin Elmer FTIR spectrophotometer equipped with a crystal diamond universal ATR sampling accessory (Massachusetts, USA). Surface morphological images were captured using a JEOL JSM-7600F Scanning Electron Microscope (SEM, Tokyo, Japan). The adsorption study on selected dyes was conducted using a UV-Visible spectrophotometer (UV-Vis) equipped with 1 cm quartz cells (Shimadzu, Kyoto, Japan).

Preparation of New Adsorbents

Preparation of ESM

ESM was carefully removed from eggshells, washed thoroughly with distilled water, and dried in an oven at 70 °C for 1 hour. The dry ESM was ground into a powder and sifted through a 300 mm sieve.

Hydrolysis of Triacylglycerol in Palm Cooking Oil

The hydrolysis of palm cooking oil triacylglycerol (Figure 1) was adapted from Rozi et al. [43]. A mixture of NCO (5 g) and ethanolic potassium

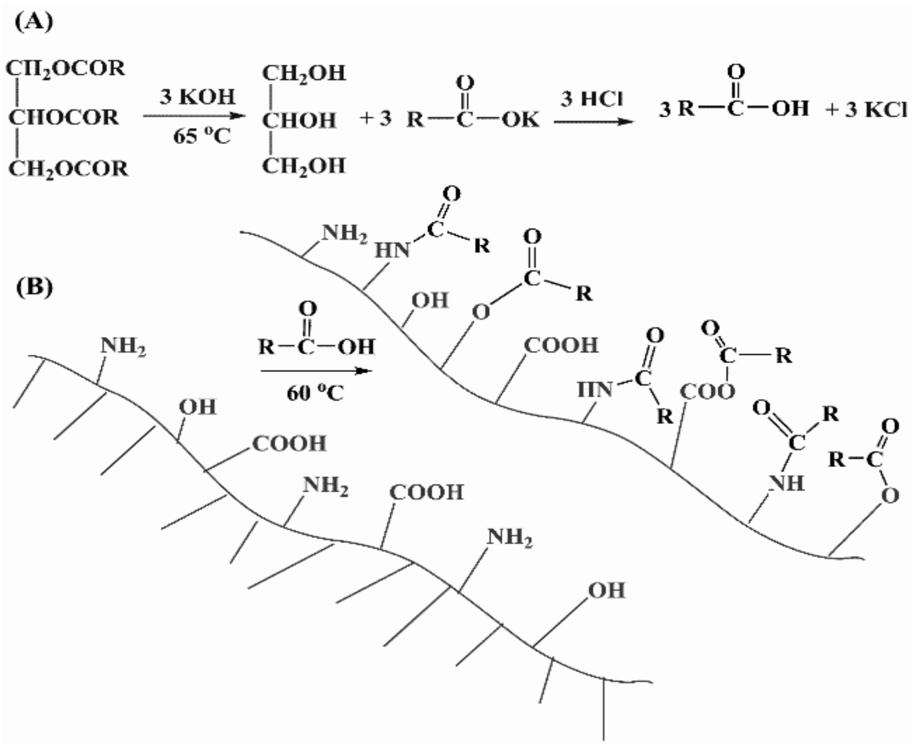

Figure 1. (A) Hydrolysis of triacylglycerol of NCO (B) Synthesis of ESM@FFAs-NCO or ESM@FFAs-UCO (R= the alkyl chain of the FFAs)

hydroxide (300 mL, 1.75 M) was heated at 65 °C for 2 hours. The unsaponifiable product formed was extracted using *n*-hexane (100 mL) and the solvent was later discarded. The solution was diluted with distilled water and adjusted to pH 1 using hydrochloric acid (6 N, 100 mL). The resulting FFAs were extracted three times with 100 mL *n*-hexane. The extraction product, a mixture of FFAs and *n*-hexane, was washed with deionized water before being dried with anhydrous sodium sulphate. The solvent was then evaporated using a rotary evaporator at 35 °C to obtain the FFAs-NCO.

Synthesis of ESM@FFAs-NCO and ESM@FFAs-UCO

The ESM@FFAs-NCO was prepared using a technique adapted from Sathasivam and Haris [44]. The synthesis procedure was as follows: 1 g ESM powder, 4 g FFAs-UCO and three drops of concentrated HCl (catalyst) were stirred into *n*-hexane for 15 minutes at 60 °C. A series of ESM@FFAs-NCO adsorbents was prepared with varying ratios of ESM to FFAs-NCO (1:1, 1:2, 1:3, 1:4, 1:5, 2:1, 3:1 and 4:1). The products were washed using *n*-hexane and dried under vacuum at 70 °C for 24 hours to obtain ESM@FFAs-NCO. ESM@FFAs-UCO adsorbents were also prepared but without the pre-treatment step. The UCO was subjected to the same protocol as FFAs-NCO to yield the final products with various ratios.

Preliminary Adsorption studies

The preliminary adsorption experiments were carried out at room temperature using an aqueous solution of Alizarin Red (50 mg L^{-1}). In an airtight vial, 30 mg of adsorbent and 15 mL of adsorbate (50 mg L^{-1}) were shaken for 30 min (150 rpm) at room temperature. The adsorbent was then separated by centrifugation, and the residual concentration was determined using UV-Vis spectrophotometry at a wavelength of 405 nm. The measurement of the samples was performed in triplicate. The removal percentage R (%) was calculated using equation 1,

$$R(\%) = \frac{C_0 - C_f}{C_0} \times 100 \qquad (1)$$

where C_0 and C_f are the initial and residual concentrations of AR dye (mg L^{-1}) in the solution. This procedure was applied to screen the performance of ESM@FFAs-UCO for dye removal. The R^2 value was also determined and compared.

RESULTS AND DISCUSSION

Optimization Parameters for Synthesizing Adsorbents

The parameters involved in preparing ESM@FFAs-NCO and ESM@FFAs-UCO were optimized to obtain

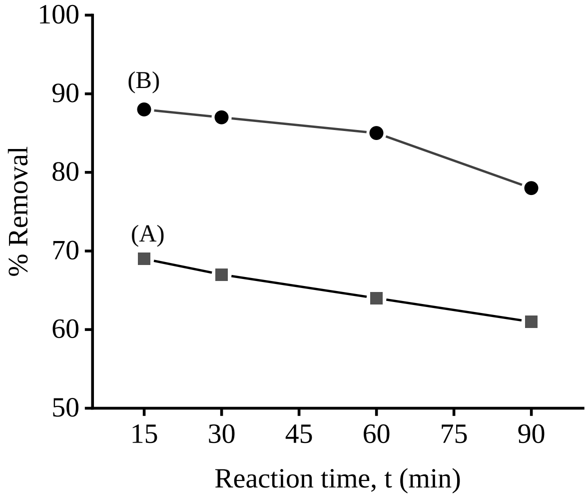

Figure 2. Removal of AR against reaction time for (A) ESM@FFAs-NCO and (B) ESM@FFAs-UCO (Adsorbent dosage: 30 mg, contact time: 30 min)

the best performing adsorbents. The reaction time and mass ratio of ESM to FFAs (derived from NCO and UCO) were major factors that affected adsorbent synthesis.

Effect of Reaction Time on AR Removal Efficiency

The effect of reaction time on the AR dye removal efficiency was studied by varying the reaction time from 15 to 90 minutes. Figure 2 shows the removal percentages of AR dye versus reaction time using (A) ESM@FFAs-NCO and (B) ESM@FFAs-UCO. According to Figure 2 (A), the concentration of the adsorbed AR dye by ESM@FFAs-NCO increased over time and reached equilibrium within 15 minutes. Further increasing the reaction time caused the AR removal percentage to decrease. In Figure 2 (B), the adsorption of AR by ESM@FFAs-UCO also showed a similar trend. The optimum percentage of AR dye removal occurred within 15 minutes for both adsorbents.

The functionalization of FFAs-NCO and FFAs-UCO on ESM was achieved through a physical coating mechanism. Upon functionalization, reaction time plays a crucial factor in ensuring the coating of FFAs occurs optimally. At optimum coating conditions, the attached FFAs on ESM provide more hydrophobic active sites for adsorption of AR, resulting in a higher removal percentage. As the reaction time increases, there is a possibility of detachment of FFAs from the ESM, causing the hydrophobicity behaviour of ESM@FFAs-NCO and ESM@FFAs-UCO to be reduced. Also, a fast reaction time is preferable for dye-containing water or wastewater treatment. Therefore, 15 min was chosen as the optimum reaction time for the ESM@FFAs-NCO and ESM@FFAs-UCO adsorbents.

Effect of Adsorbent Mass Ratio on AR Removal Efficiency

The amount of coating also influences the adsorption capabilities of adsorbents. Figure 3 shows the influence of different ratios of ESM to FFA (i.e., 1:1, 1:2, 1:3, 1:4; 2:1, 3:1, 4:1) in NCO and UCO on AR dye removal. In Figure 3(A), the percentage removal increased from 61 % to 70 % when the ESM to FFAs-NCO ratio increased from 1:1 to 1:4. At other ESM: FFAs-NCO ratios (2:1, 3:1, and 4:1), the percentage removal dropped, even to as low as 52 % for 4:1. A similar observation was obtained using ESM:FFAs-UCO (Figure 3 (B)). Increasing amounts of FFAs-UCO in ESM@FFAs-UCO improved the percentage removal of AR dye from 84 to 90 % (ESM:FFAs-UCO; 1:1, 1:2, 1:3, and 1:4). However, the percentage removal fell from 84 % to 74 % when the ESM: FFAs-UCO ratio was changed from 2:1 to 4:1. The ESM:FFAs-NCO and ESM:FFAs-UCO ratios were optimal at 1:4 (ESM: FFAs). An increase in the FFA content increased the hydrophobic behaviour of the ESM:FFAs, which in turn improved the interaction of the dye's aromatic core with the alkyl chains of FFA on the ESM surface. Therefore, the optimum ESM: FFAs mass ratio for synthesizing ESM@FFAs-NCO and ESM@FFAs-UCO was 1:4.

Characterization of Adsorbents

The FTIR spectra of ESM, ESM@FFAs-NCO, and ESM@FFAs-UCO are shown in Figure 4. Curve A represents the unmodified ESM's FTIR spectrum. The significant peaks for ESM were assigned as follows: 3299.45 cm^{-1} (N-H and O-H stretching), 1536.04 cm^{-1} (N-H bending), 1400.90 cm^{-1} (C-H bending) and 1237.40 cm^{-1} (C-O stretching). The characteristic peaks of the synthesized ESM@FFAs-NCO were observed at 2924.48 cm^{-1} and 2852.30 cm^{-1} (Figure 4 (B)) which correspond to the asymmetric and symmetric stretching of a methylene group ($=CH_2$). For curve C, sharper CH_2 stretching bands appeared at 2924.52 cm^{-1} and 2953.85 cm^{-1} for ESM@FFAs-UCO. The new peaks present in the spectra of the modified ESMs confirmed the functionalization of FFAs on the surface of the ESMs.

The morphologies of ESM, ESM@FFAs-NCO and ESM@FFAs-UCO are shown in Figure 5. The ESM image reveals a macroporous network of interconnected and coalescing shell membrane fibres (Figure 5 (A)). The ESM is capable of trapping and adsorbing FFAs because of its porous and fibrous surface. In comparison to the unmodified ESM, functionalization of FFAs from NCO (Figure 5 (B)) and UCO (Figure 5 (C)) resulted in a more extensive and improved network. The micrographs show that FFAs were successfully doped in the macroporous network of ESM protein fibres.

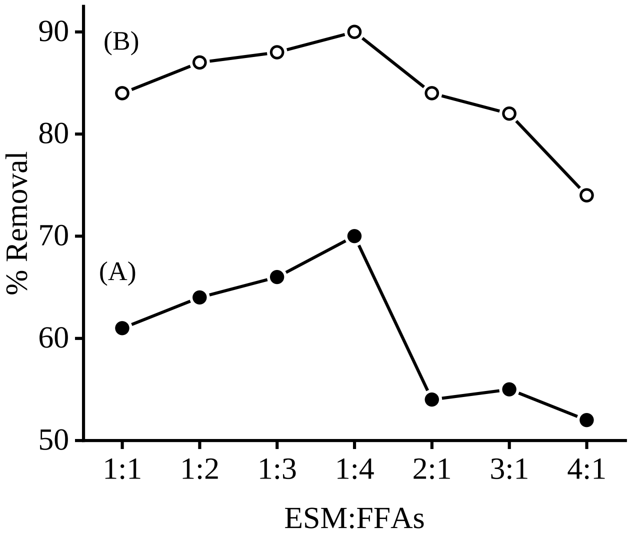

Figure 3. Effect of mass ratio of ESM to FFAs from (A) NCO and (B) UCO on AR dye removal percentage (Adsorbent dosage: 30 mg, contact time: 30 min)

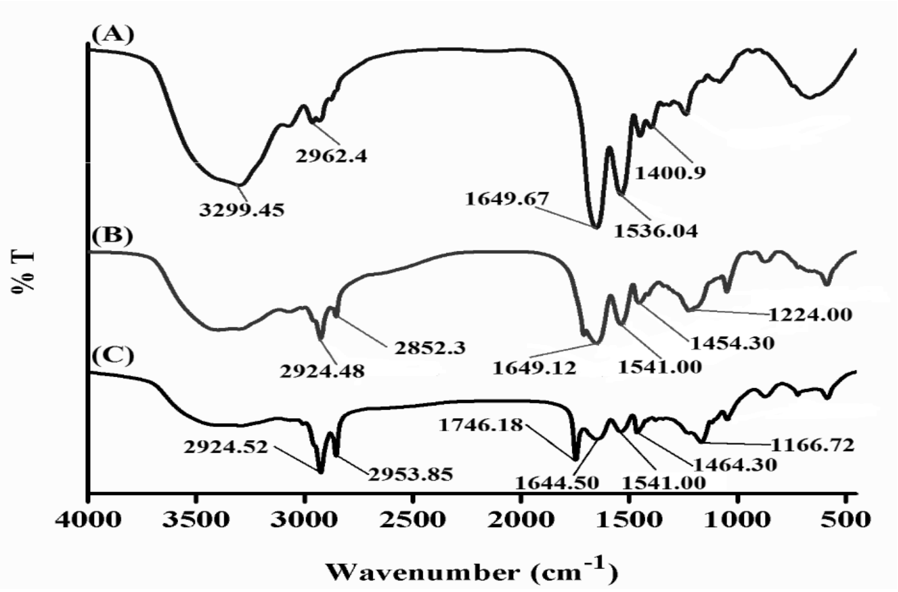

Figure 4. FTIR spectra of (A) ESM, (B) ESM@FFAs-NCO, and (C) ESM@FFAs-UCO

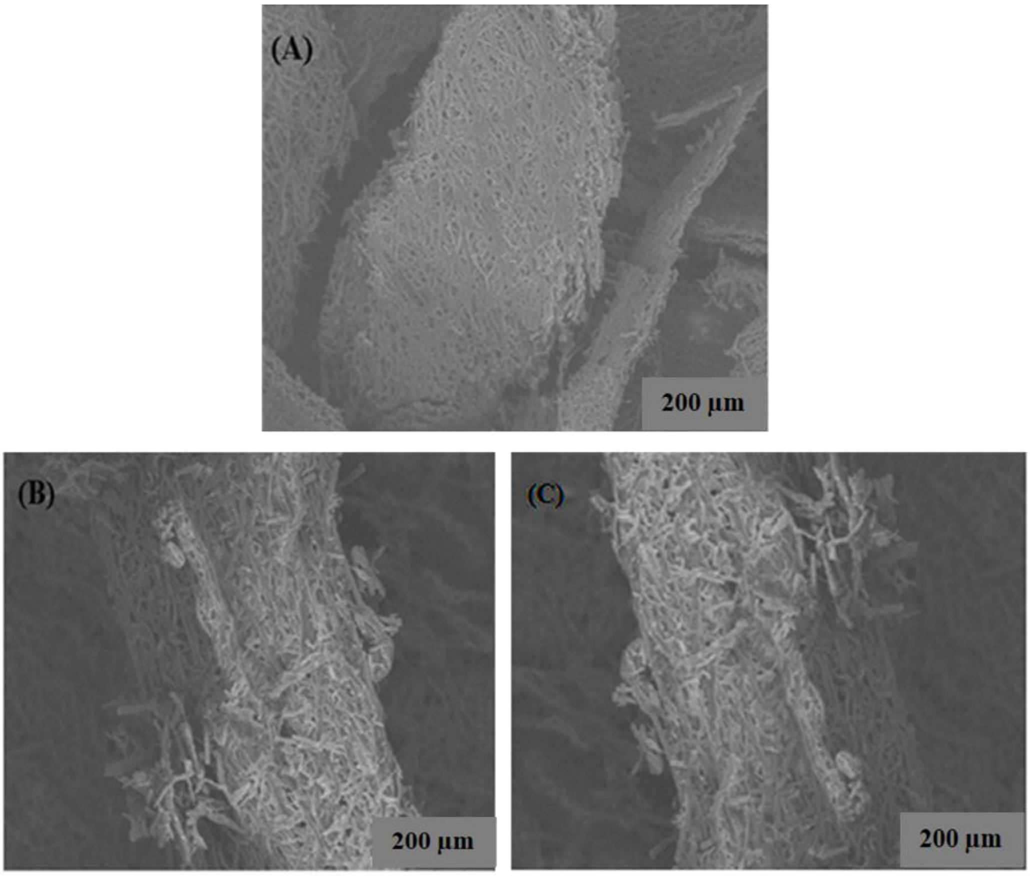

Figure 5. SEM images of (A) ESM, (B) ESM@FFAs-NCO and (C) ESM@FFAs-UCO

Alizarin Red Removal Performance of Adsorbents

A comparative screening study was conducted to evaluate the dye removal performance of the newly synthesized ESM@FFAs-NCO and ESM@FFAs-UCO using Alizarin Red (AR) dye (Figure 6). The AR removal percentage (R %) of the adsorbents followed the order: ESM (33 %) < ESM@FFAs-NCO (63 %) < ESM@FFAs-UCO (80 %). The good performance of ESM@FFAs-NCO and ESM@FFAs-UCO was due to the higher amount of accessible active sites contributed by hydrophobic interactions and hydrogen bonding. On the other hand, unmodified ESM can only interact with the dye by hydrogen bonding (Figure 7). ESM@FFAs-UCO performed better than ESM@FFAs-NCO because of the greater content of long alkyl chains in its FFAs [45,46].

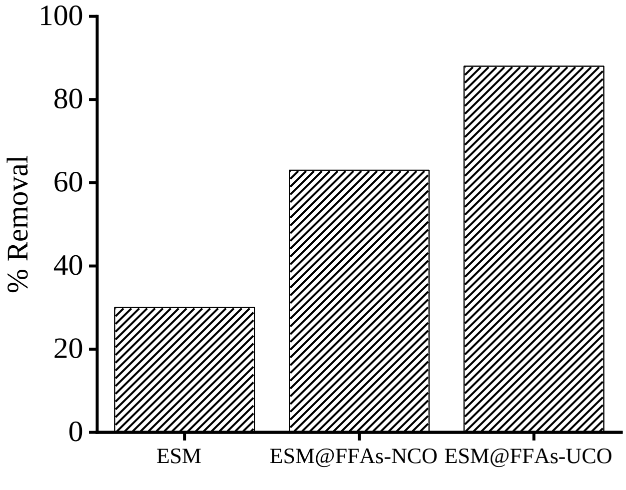

Figure 6. Comparison of percentage removal of AR dye for ESM, ESM@FFAs-NCO and ESM@FFAs-UCO (Contact time = 30 min, adsorbent dosage = 30 mg)

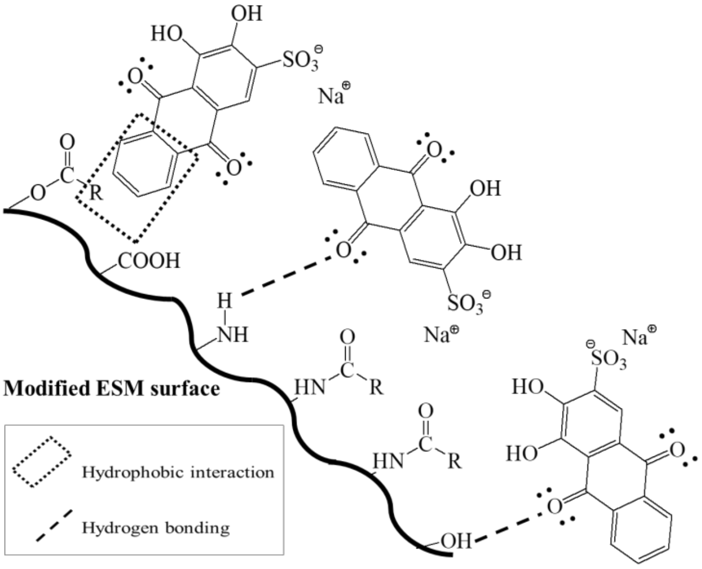

Figure 7. The interactions between the adsorbent (ESM@FFAs-NCO and ESM@FFAs-UCO) surfaces and AR dye substrate

Evaluation of the AR Dye Removal Performance of ESM@FFAs-NCO and ESM@FFAs-UCO

Adsorption performance is an essential indicator in assessing the selected adsorbent's application. The AR removal percentages of ESM@FFAs-NCO and ESM@FFAs-UCO were compared to determine the feasibility of these adsorbents. Using the optimum adsorbent dosage and treatment time, ESM@FFAs-NCO and ESM@FFAs-UCO were tested for their ability to remove AR dyes in aqueous solution. The AR removal percentages of ESM@FFAs-NCO and ESM@FFAs-UCO were found to be 70 % and 89 %, respectively. The ESM@FFAs-UCO was found to have a better performance compared to ESM@FFAs-NCO for the adsorption of AR. This result can be explained by the composition of FFAs in NCO and UCO. UCO contained 41.67 % of long alkyl chains of oleic acid followed by 40.56% palmitic acid, while NCO comprised only 28.55 % oleic acid and 59.64 % palmitic acid [43]. The greater content of long chain fatty acids caused a higher hydrophobicity in ESM@FFAs-NCO, increasing the interactions between the adsorbent and the hydrophobic fused ring of AR. Therefore, ESM@FFAs-UCO was used in subsequent studies.

Screening for Anionic and Cationic Dyes using ESM@FFAs-UCO

The screening for anionic and cationic dyes was conducted using ESM@FFAs-UCO. Besides AR, the removal of Rhodamine B (RB), Chicago Sky Blue (CSB), and Remazol (Re) dyes were also investigated. results showed that the removal percentages of RB, CSB, Re and AR were 78.34 %, 65.68 %, 84.59 % and 87.83 %, respectively. The results proved the successful adsorption of anionic and cationic dyes using ESM@FFAs-UCO. Interestingly, ESM@FFAs-UCO was preferable for anionic dye removal (Re and AR). Overall, this newly developed ESM@FFAs-UCO can be regarded as a versatile adsorbent with high potential since it was able to efficiently remove both anionic and cationic dye molecules. This finding is significant because there are many different cationic and anionic pollutants in actual wastewater samples. The new adsorbent developed in this study, ESM@FFAs-UCO, has been found suitable for future use in decontaminating and treating organic dye pollutants in the environment.

CONCLUSION

ESM@FFAs-NCO and ESM@FFAs-UCO were successfully synthesized, characterized, and used to remove AR dye molecules from aqueous solutions. The optimum synthesis reaction time and ESM: FFAs mass ratio were 15 min and 1:4, respectively, for both adsorbents. FTIR and SEM analyses confirmed the attachment of FFAs onto the ESM surface. The adsorption mechanism of AR dye by the modified ESMs can be attributed to hydrogen bonding and hydrophobic interactions. The hydrophobicity of ESM was improved in the following order: ESM <ESM@FFAs-NCO <ESM@FFAs-UCO. The greater content of long alkyl chain FFAs led to the better performance of ESM@FFAs-UCO compared to ESM@FFAs-NCO for the removal of AR. This study proved that ESM@FFAs-UCO was a versatile adsorbent with high removal efficiencies for organic dyes in the following order: AR>Re>RB >CSB.

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CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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