Synthesis And Efficiency Evaluation of Chitosan-Alginate Hydrogel Polyelectrolyte Complex Filter for Treatment of Oil Spillage

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ABSTRACT: Crude oil spills pose considerable environmental concerns thereby demanding the development of effective, sustainable, and eco-friendly remediation solutions. In this study, we synthesized and evaluated the efficiency of a biodegradable polymer filter using sodium alginate and chitosan for the treatment of oil spillage. The sodium alginate-chitosan hydrogel polyelectrolyte complex (SACHPC) filter was synthesized via dipping method using a layer-by-layer self-assembly technique integrated with cotton wool as the filter medium. The efficiency of the filter was evaluated based on flow rate of recovered oil and reusability of the filter. Simulated oil spillage of 0.5 M was subjected to filtration using the SACHPC filter. The flow rate was determined based on the time taken for 1 L of oil to pass through the filter. The SACHPC filter exhibited underwater superoleophobic behaviour with exceptional filtration efficiency (> 98.3%) in acidic, neutral and alkaline conditions (pH 3, 7 and 11). The flow rate of the filter was 120 mL/min, while the third-use filter exhibited a decrease flow rate of 50 ml/min. Moreover, the filter achieved an impressive crude oil recovery rate of 85%. X-ray diffraction analysis confirmed crude oil adsorption in the presence of an amorphous phase while scanning electron microscopy analysis revealed the structural morphology of the SACPHC filter. Overall, the SACHPC filter maintained high filtration efficiency thereby offering a sustainable strategy for oily wastewater purification and oil spill clean-up.

KEYWORDS: Oil spillage, Polyelectrolyte, Filter, Chitosan, Hydrogel, Sodium Alginate.
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I. INTRODUCTION

Oil spills pose a significant threat to marine ecosystems and human health. It is a common occurrence in both developing and developed countries. It is usually caused by a rupture in an underwater pipeline resulting in the release of several thousands of litres of crude oil into nearby water bodies as reported in the coast of Huntington Beach (California) in October of 2021 (Naggea and Miller, 2023). Oil spillage causes significant environmental concerns with long-term impacts on marine ecosystems and human well-being. Therefore, it is crucial to develop effective treatment strategies to combat such environmental disasters. The overall goal is to provide a preliminary solution that can ultimately lead to the development of a highly reproducible and user-friendly oil/seawater filter. Although, there are advanced devices such as oil spill emergency treatment systems equipped with sensors and oil-water separating units which can aid swift and efficient clean-up operations, as well as minimize ecological damages, they are very expensive to employ (Chunjiang, 2022; Faisal *et al.,* 2023). On the other hand, the traditional oil cleanup methods are generally slow, ineffective, and may introduce harmful contaminants into water sources (Ross *et al.,* 2022). Therefore, to clean up oil spills, many techniques have been developed including bioremediation, mechanical cleaning, chemical dispersants, and *in situ* burning.

Bioremediation is a promising and eco-friendly technique that utilizes targeted microbes to efficiently break down the oil (Nidhi *et al.,* 2023). It involves breaking down of spilled oil by bacteria and microorganisms into harmless substances like fatty acids and carbon dioxide. Usually, the process is accelerated by introducing nutrients like nitrogen and phosphorus to the affected area to boost the cleaning process. Mechanical cleaning is considered one of the most effective methods because it physically removes oil from the environment. The method typically involves the use of equipment such as oil booms and skimmers to contain and collect the spilled oil, booms to surround the slick and skimmers to remove the oil from the water surface. Skimming is a technique that uses booms to encircle and collect the oil-water mixture. Skimmers then store the extracted material in a recovery tank, separating gallons of oil and water from the spill site (Ross *et al.,* 2022). Another viable approach is dispersion. Chemical dispersants are substances used to break up oil slicks, allowing the oil to mix into the water and reduce its immediate impact on wildlife and coastlines. These dispersants work by reducing the surface tension between oil and water, forming smaller oil droplets that can disperse more easily. This involves using aircraft to disperse chemical agents that break down oil

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into tiny particles (Natalia *et al.,* 2022). Although this technique benefits surface-dwelling creatures, it can negatively affect marine wildlife due to the toxic nature of dispersants used (Sühring *et al*., 2017; Onokare *et al.,* 2022). Chemical dispersants are usually employed to mitigate the spread of the oil in cases where rough seas or high winds make mechanical cleanup difficult. *In situ* burning involves controlled burning of spilled oil, which can be effective in open water or remote land areas with limited access. While it is a relatively inexpensive and rapid method, its application is constrained by weather conditions and the proximity of the spill to populated areas (Prince, 2023). Additionally, this technique releases harmful carbon emissions and leaves behind charred oil residue (Ross *et al.,* 1996). To minimize harm to humans and wildlife, favorable meteorological conditions such as gentle breezes and calm seas are necessary for a controlled burn (USEPA, 1999).

Arising from the limitations experienced with the use of traditional and conventional methods, attention is currently focused on the use of adsorbent alternative resources like polysaccharides and proteins for developing biomaterials based on their desirable properties and benefits (Sood *et al.,* 2021). Application of adsorbents offers a promising solution to address the shortcomings experienced with erstwhile cleanup methods. The approach, which involves using materials to adsorb oil from water surfaces, presents a novel and environmentally friendly alternative. The method employs natural substances like peat moss or synthetic materials like activated carbon, and it is particularly useful in sensitive ecosystems or areas with limited access. Additionally, adsorbents can be reusable, making them cost-effective and environmentally friendly (Okeke *et al*., 2022). Among the available biomaterials, hydrogels (HGs) have garnered considerable attention owing to their intrinsic properties such as biocompatibility, biodegradability, mechanical strength, and responsiveness (Pella *et al.,* 2018). HGs are soft materials that comprise three-dimensional networks of hydrophilic polymers that can swell in water and biological fluids (Trinadha *et al.,* 2021). Depending on the preparation method, HGs can be classified as physical or chemical gels. In physical gels, the polymeric chains are held together by molecular entanglements and secondary interactions, including ionic cross-links, hydrogen bonds, and hydrophobic interactions (Bashir *et al.,* 2020) On the other hand, chemical gels feature polymeric chains held together by covalent bonds.

In a recent study, sodium alginate-chitosan hydrogel polyelectrolyte complex demonstrated potential to disperse oil with zero negative environmental impact, making it a preferred polymer for experimentation (George and Shrivastav, 2023). However, a limited selection of adsorbents is currently available for treating oil spills on water bodies. Chitosan-alginate combination has numerous physical and chemical properties making it a viable option for this study. Apart from being a cationic polyamine, it has a high positive charge density at lower pH, and adheres sodium alginate to negatively charged surfaces with the ability to form hydrogels with polyanions. Additionally, chitosan is highly hydrophobic at neutral and higher pH, insoluble in water and most organic solvents, soluble in dilute acids and forms highly viscous solutions (Archana *et al.,* 2023). The compound also has a high molecular weight with reactive amino/hydroxyl groups that readily undergo chemical modification. Being a natural polymer, chitosan has several biological properties including biocompatibility and biodegradability making it relatively safe (Melo *et al.,* 2018).

The aim of the present study is to synthesize and evaluate the efficiency of a sodium alginate-chitosan hydrogel-polyelectrolyte complex (SACHPC) as a filter for oil spill cleanup. This research introduces a novel approach by leveraging the dual hydrophilic and oleophilic properties of the SACHPC. While prior studies focused on hydrophilic and oleophobic coatings for filters, the current study pushes this concept further by integrating biocompatible and eco-friendly properties of chitosan and sodium alginate into a hydrogel-polyelectrolyte matrix. It is believed that this addition would enhance oil-water separation with minimal environmental footprint.

II. THEORETICAL ANALYSIS

Layer-by-layer (LbL) techniques represent a precise and versatile method for creating functional nanomaterials by sequentially depositing nanoscale units (Woojoo *et al.,* 2023). This approach allows for exact control over coating thickness, content, and structure, making it scalable and effective for producing nanostructured thin films (Eduardo *et al.,* 2022). LbL techniques have found numerous applications in various fields, including drug delivery systems, hollow capsules, and gelatin nanostructures (Celina *et al.,* 2022). They are also capable of producing fluorescent microspheres with core-shell structures, highlighting their adaptability in creating different material designs and functionalities (Jason *et al.,* 2020). Widely used in materials science and engineering, LbL processes are cost-effective, scalable, and flexible, making them an ideal choice for generating functional materials (Luísa *et al.,* 2017). In the realm of oil spill treatment, LbL procedures employ biocompatible materials such as sodium alginate, chitosan, and cotton wool, which have exceptional oil absorption capacities. This makes them suitable for use in industrial oil spill cleanup and wastewater treatment.

III. MATERIALS AND METHODS

A. *Chemicals and reagents*

Bonny light crude oil sample was obtained from Kaduna Refinery and Petrochemical Company (KRPC), chitosan flakes with chitolytic lot No.: 251716 and deacetylation level of ≥ 95%, sodium alginate, cotton wool and acetic acid were procured from Fluka Chemical Company (Gillingham, UK). Other chemicals and reagents used were of analytical grade.

B. *Preparation of filter*

The sodium alginate-chitosan hydrogel-polyelectrolyte complex (SACHPC) was produced using ionotropic gelation process developed by Pedroso-Santan (2020). Chitosan (25g) and sodium alginate (75g) were dissolved in 1 L of 2% acetic acid and agitated using a homogenizer for six hours to obtain a homogeneous mixture. To produce the filter, sodium alginate-chitosan (1:3) was incorporated into the SACHPC solution. The process involved using a 5 g strip of cotton wool, which was initially washed and rinsed with a NaOH solution to eliminate impurities. The cotton wool strip was treated, dried, and repeatedly dipped in the SACHPC solution to achieve the desired layers (self-assembly technique). The filter was then left to dry on a laboratory bench (Figure 1).

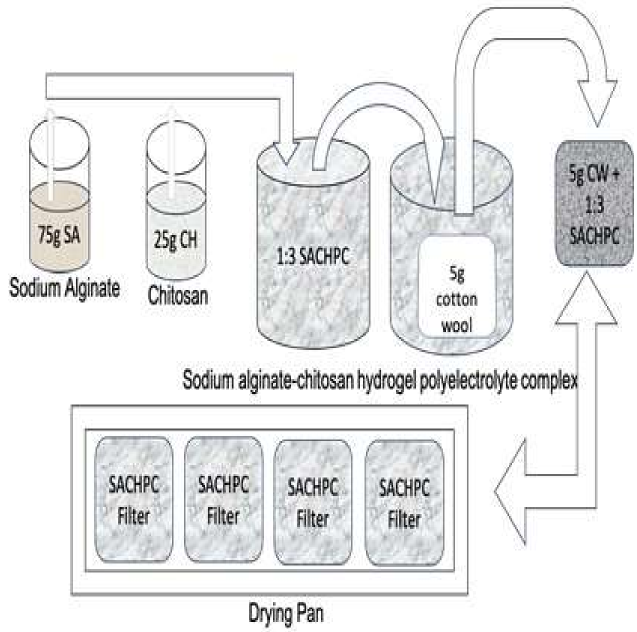

Figure 1: Schematic flow diagram procedure of SACHPC filter preparation

C. Determination of porosity

The porosity of the cotton wool strip and coated cotton strip was determined by calculating their ratio. Two strips of filters with identical dimensions were utilized for this purpose. The strips were completely immersed in hexane for 20 seconds and then taken out. The variation in the mass of hexane before and after immersion was recorded. The porosity ratio was then obtained using Eqn (1).

$$\frac{\varphi \text{ Coated filter}}{\varphi \text{ Cotton}} = \frac{\text{V pore, coated}}{\text{V pore, cotton}}\left(\frac{V\ Cotton\ sample}{V\ coated\ sample}\right) = \frac{\text{m} - \text{soaked hexane, coated}}{\text{m} - \text{soaked hexane cotton}} = \left(\frac{\delta \text{ coated}}{\delta \text{ cotton}}\right) \approx \frac{\text{m} - \text{soaked hexane, coated}}{\text{m} - \text{soaked hexane, cotton}} \quad (1)$$

Where;
φ represents porosity
m represents mass of material
v represents volume
δ represents thickness of material.

Since the thickness is smaller than the surface area of the samples, the volume ratio of the sample can be assumed to be equal to the surface area ratio, which was controlled to be 1. Therefore, the porosity ratio between the cotton strip and coated strip filter material can be determined as the ratio of the mass difference of hexane (Ross *et al.,* 2022).

D. Determination of mass distribution

To determine the mass distribution of sodium alginate-chitosan hydrogel-polyelectrolyte complex (SACHPC) on the coated filter, the mass per unit surface area was calculated. The filter was prepared with precise dimensions (70 length x 76 width mm) and the pre-weighed sample was coated before undergoing drying process and then weighed again (Ross *et al.,* 2022). To determine mass distribution, the variance between the pre and post-coating weights was divided by the surface area of the substrate (Eqn. 2).

$$M = \frac{MD}{SA} \quad (2)$$

Where;
M represents mass distribution
MD represents mass difference
SA represents Surface area of the substrate
of the criterion C_j is calculated as:

E. Determination of flow rate

Flow rate was determined according to the method described by Ghimici et al. (2018) to evaluate the performance of the filter. A crude oil solution of 0.5 M concentration was prepared in a 1000 mL beaker and the pH was adjusted to 3. Filtration was conducted using a funnel with the coated filter set atop a graduated cylinder to evaluate its performance. The experiment recorded the time taken for 1 L of crude oil solution to pass through the filter (Figure 2). The flow rate was calculated as outlined in Equation 3 (Ross et al., 2022).

$$v = \frac{V}{Q} \quad (3)$$

Where;
v = flow rate
V = volume of oil
Q = discharge time

Figure 2: Filtration of crude oil solution using SACHPC filter.

F. Crude oil recovery and filter re-use

The filtered oil was transferred into a measuring cylinder and the amount of crude oil recovered was measured. The oil retained in the SACHPC filter was further extracted using Soxhlet extraction with toluene as the solvent (Figure 3). It was then separated using a rotatory evaporator. The SACHPC filter was cleaned and rinsed thoroughly with toluene and water to eliminate any impurities and excess oil. Finally, another batch of oil spillage was run through the used filter to evaluate its efficiency.

Figure 3: Extraction of crude oil from SACHPC Filter

G. Characterization of the filter

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to study the composition and morphology of the SACHPC filter before and after use. All traces of crude oil solution left on the SACHPC filter was dried in a desiccator before carrying out the analyses.

H. Statistical analysis

The data obtained were subjected to statistical analysis using one-way analysis of variance (ANOVA) with Tukey's post hoc test for single factor comparison and variance analysis (two-way ANOVA) with Bonferroni post hoc test for multifactorial comparisons. Statistical significance was determined at a confidence level of 95%, considering differences to be significant when $p < 0.05$. Additionally, a maximum acceptable coefficient of variation was predefined at 25%.

IV. RESULTS AND DISCUSSION

A. Porosity, mass distribution and flow rate

A cotton strip of 0.254 g and a coated strip of 0.156 g gave an overall porosity ratio of 0.612 and the mass distribution of SACHPC on the coated filter was calculated to be 0.776 g/cm^2. The flow rate of the filter was 120 mL/min, whereas the third used filter showed a decreased in flow rate of 50 mL/min giving a net flow of 70 mL/min (structural and Surface changes). The increased porosity enhanced the capacity of the filter to adsorb and retain oil, making it more effective in oil spill cleanup efforts. This finding corresponds with previous studies where biomaterials were used for oil spill cleanup (Wolok *et al.,* 2020). The consistency of the coating across the filter surface is essential for its effectiveness in oil spill cleanup. A uniform coating ensures that all areas of the filter are capable of adsorbing oil efficiently, thereby maximizing the cleanup process. The mass distribution of SACHPC on the coated filter was found to be higher than 0.70 g/cm^2, suggesting uniformity and consistency of the coating across the filter surface (Ross *et al.,* 2022). The high flow rate exhibited by SACHPC filter is an indication of its ability to efficiently filter large volumes of water contaminated with crude oil under different conditions.

B. *Oil recovery and reusability*

SACHPC filter proved to be highly effective in separating 85% of crude oil from the spillage under the different conditions employed in the study. The filter also allowed extraction of adsorbed oil with great efficiency (Aranaz *et al.,* 2021). By combining both separation and extraction processes, the filter produced an impressive crude oil recovery rate of 97%. This demonstrates a significant progress in oil-water separation technologies to address adverse effects of oil spills. Cutting-edge advancements like super-hydrophilic membranes and specialized filters residue treatment mechanisms have been developed to reduce maintenance and prevent pollution and during oil extraction (Baig and Saleh, 2021; Nadeem *et al.,* 2021). The oil recovery ability and reusability demonstrated by the filter corroborate previous studies where chitosan produced an effective performance (> 99.4%) even after multiple cycles of testing (Mark *et al.,* 2023). This emphasizes the practicality and cost-effectiveness of using SACHPC filter for oil spill cleanup operations. Generally, the mass distribution, filtration efficiency, flow rate and porosity ratio recorded for SACHPC filter in this study (0.776 g/cm2, 85%, 50 mL/min, and 0.612) are better than other filter materials reported in previous research (Table 1).

Table 1: Performance of Natural Polymer-Based Filters

Filter material	Mass Distribution (g/cm^2)	Filtration Efficiency (%)	Flow Rate (mL/min)	Porosity	Ref.
Cellulose filter	0.72	70	55	0.550	Kuma and Das (2018)
Chitosan filter	0.68	70	45	0.580	Huang *et al.* (2017)
Alginate hydrogel	0.65	68	40	0.600	Zhang and Li (2014)
Bio-polymer	0.70	65	48	0.570	Wang and Zhang (2018)
SACHPC filter	0.776	85	50	0.612	This Study

C. X-ray diffraction (XRD) analysis

The X-ray diffractograms of the unused SACHPC filter and after its first use are presented in Figures 4 and 5, while Figures 6 and 7 show the diffractograms of the SACHPC filter after its second and third uses, respectively. The analyses revealed the composition of the unused SACHPC filter as well as after first, second and third use for crude oil adsorption. The diffractogram revealed that polyelectrolyte complex (PEC) and chitosan hydrogel (C_h) appeared at position 2θ degree angle of 15.20° and 22.20° in the unused filter and after first use. The diffractogram of the filter after the second and third use further revealed higher intensity that shows the PEC peak moved to 17.20° and broadened while C_h has a reduced intensive peak. The distinct peaks observed in the diffractogram confirmed the structural integrity of the unused SACHPC filter and after first use. However, the slight shift observed in the diffractogram peaks after the second and third use is an indication of change in the crystalline structure of the filter due to oil exposure (Hizkeal *et al.,* 2021).

Additionally, the reduction in intensity of the C_h peak suggests that SACHPC filter significantly adsorbed crude oil. The observed reduction C_h peak also confirmed absence of impurities in the samples (Jha *et al.,* 2022). The unused filter and the one recovered after the second use exhibited similar structures, while the filters recovered after the first and third uses also showed similar structures. The structure of the unused filter and the filter after the second use are similar because after extraction and washing of crude oil from the filter, it regained its original structure. This signifies structural integrity and filtration efficiency of the filter. These findings correspond with a similar work on adsorbent of zeolites that has ability to selectively adsorb CO_2 while maintaining structural integrity over multiple cycles is a key advantage (Hambali *et al.,* 2024).

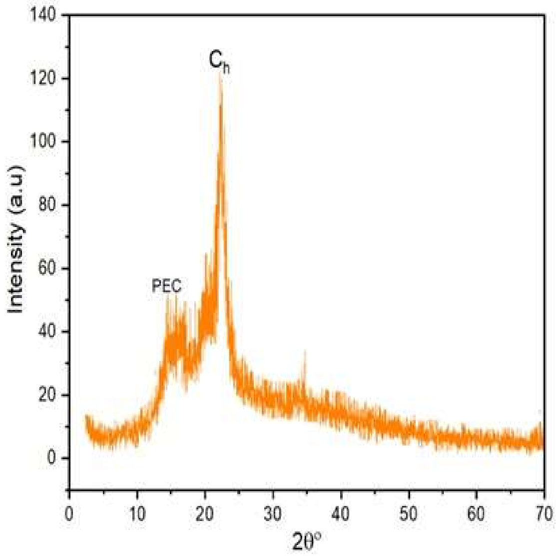

Figure 4: X-ray diffractogram of unused SACHPC filter

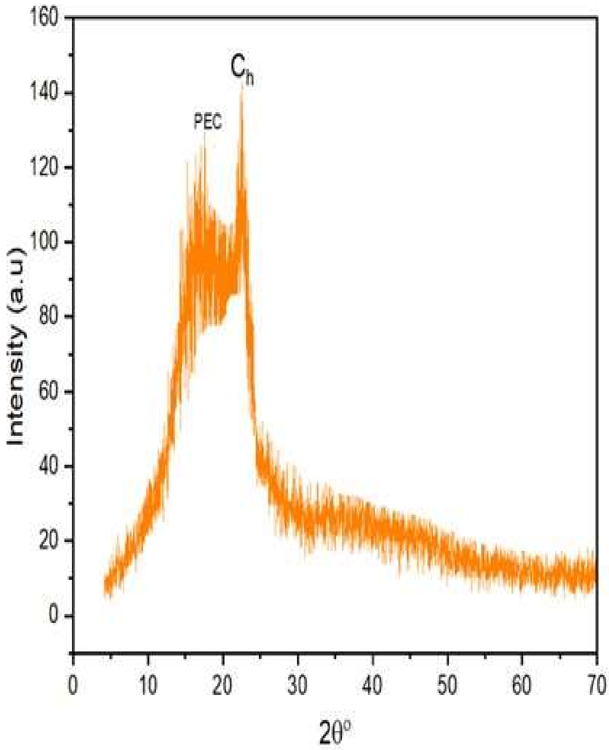

Figure 5: X-ray diffractogram of SACHPC filter after first use.

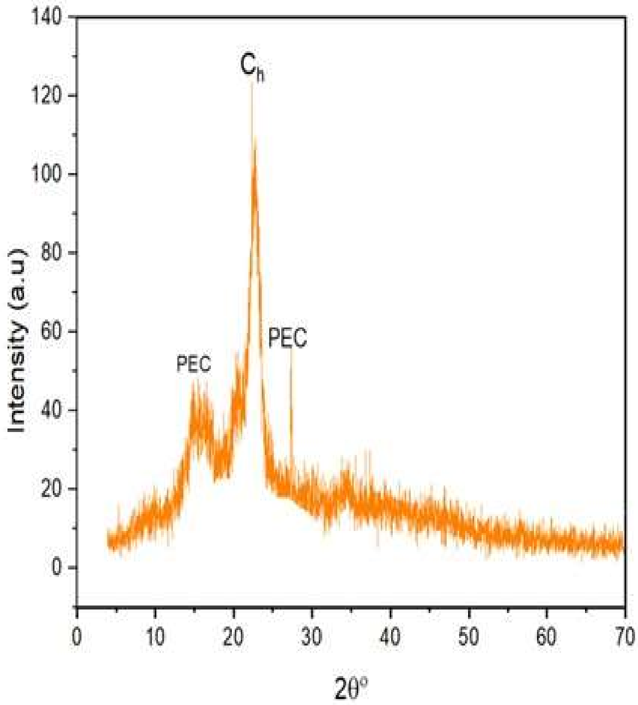

Figure 6: X- ray diffractogram of SACHPC filter after second use

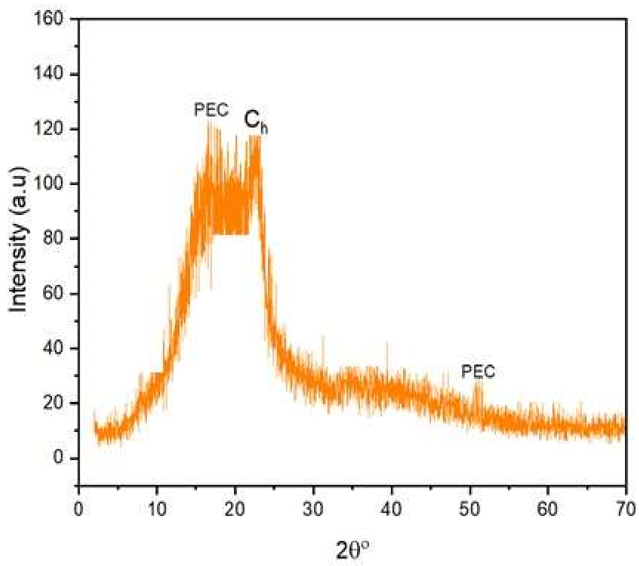

Figure 7: X-ray diffractogram of SACHPC filter after third use

D. Scanning electron microscopy (SEM) result

Third use with a cellulose diameter 13.2 microns. The increase in pore size may be attributed to random dispersion of nano-cellulose in the filter following contact with crude oil (Mautner and Bismarck, 2021). This may be responsible for the enhanced crude oil adsorption capacity demonstrated by the used filter by virtue of their ability to retain more oil in the pores (Ross *et al*., 2022). The image of the unused filter revealed a surface morphology with strip-like patterns and no visible particles, attributed to the incorporation of nanocellulose and cotton wool. However, after contact with crude oil, the cellulose particles became freely aligned, maintaining the regular strip pattern observed in the unused filter (Abu *et al.,* 2024).

The observed changes in the pore size and cellulose diameter of unused SACHPC filter and after crude oil adsorption suggest significant morphological alterations due to the interaction of oil with SACHPC filter. The increase in pore size from 50.6 microns to 60.1 microns after oil adsorption indicates that the filter material underwent expansion or swelling, possibly Figures 8 and 9 depict the morphological features of unused SACHPC filter and after first used for crude oil absorption. The unused filter had a relatively smaller pore size with a cellulose diameter of 50.6 microns when compared to the pore size of the filter after first use with a cellulose diameter of 60.1 microns. Figures 10 and 11 depict the morphological features of SACHPC filter after second and third use respectively. The filter after the second used had a smaller pore size with a cellulose diameter of 16.1 microns when compared to the pore size of the filter after the due to adsorption of oil into the cellulose structure. This expansion could be attributed to oil molecules penetrating and spreading within the filter matrix, thereby causing the cellulose fibers to loosen and the overall pore size to enlarge. However, after the first and subsequent use, the pore size decreased, with the cellulose diameter shrinking from 16.1 microns to 13.2 microns. This reduction suggests that the filter material might have undergone some form of structural compression or densification during repeated cycles of oil adsorption and desorption. The shrinkage is a result of the SACHPC filter becoming more compact as the adsorbed oil is expelled during reuse, leading to a tighter fiber network and smaller pore size. These observations are consistent with previous studies further supporting the applicability of PEC filters in crude oil spillage cleanup (Escudero-Oñate *et al.,* 2018; Guarnizo-Herrero *et al.,* 2021; Alexandre *et al.,* 2024).

Additionally, studies on hydrogel-based adsorbents have reported similar trends, where initial swelling occurs upon exposure to the adsorbate, followed by a gradual densification or collapse of the polymer network after multiple cycles (Boyuan, 2024). The observed decrease in pore size after reuse also impacted adsorption efficiency of SACHPC filter. As the pores become smaller, the SACHPC filter exhibited increase selectivity for smaller oil molecules, but its overall capacity for oil adsorption reduced. This highlights the importance of optimizing SACHPC filter properties for specific applications, ensuring that they maintain their structural integrity and adsorption efficiency at least after three uses (Massimo *et al.,* 2024).

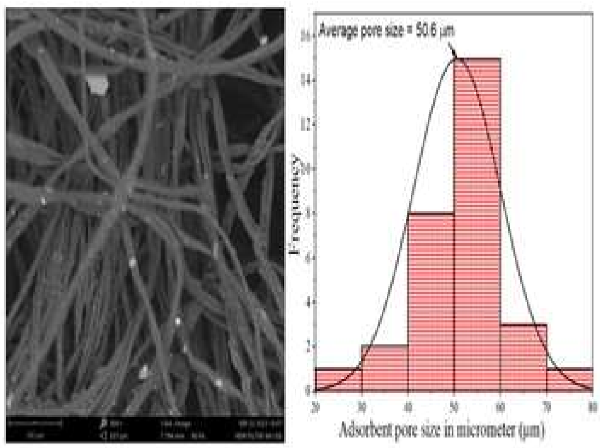

Figure 8: SEM Image of the SACHPC unused filter and the histogram of pore size (magnification 100 µm)

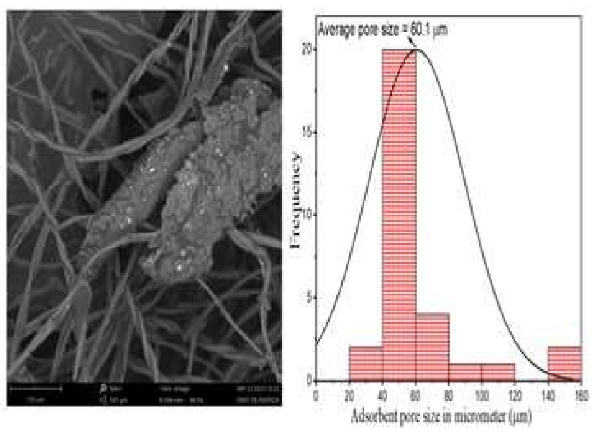

Figure 9: SEM image of SACHPC filter after first use and the histogram of pore size

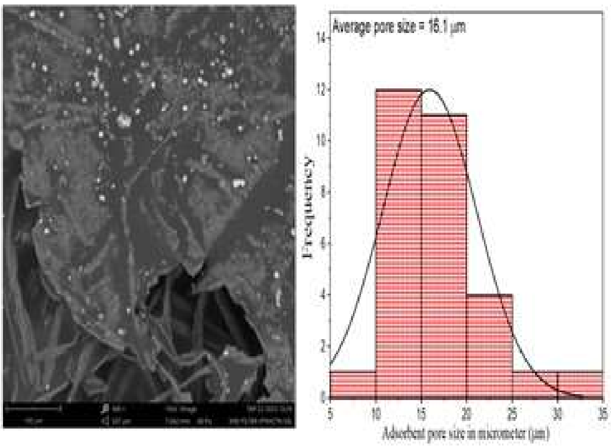

Figure 10: SEM image of SACHPC filter after second use and the histogram of pore size

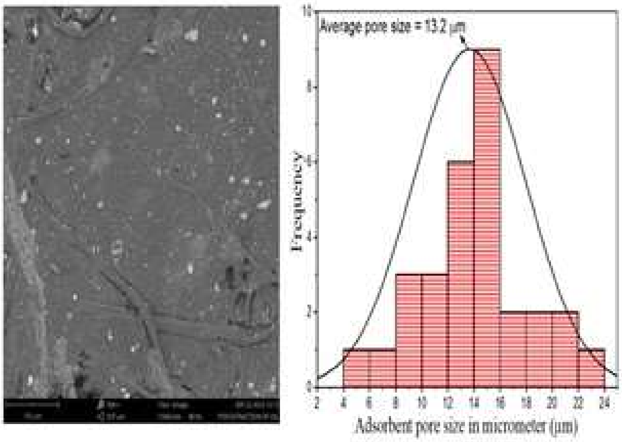

Figure 11: SEM image of SACHPC filter after third use and the histogram of pore size

V. CONCLUSION

The study underscores the efficiency and adaptability of SACHPC filter as a promising solution for oil spill cleanup. The utilization of biocompatible materials and innovative filtration techniques represents a significant step towards development of sustainable strategies for oil spill management. Structural analysis using XRD and SEM techniques revealed the integrity of the filter even after exposure to crude oil, indicating its robustness and reliability in oil spill treatment. Overall, the eco-friendly nature, reusability and stability of the SACHPC filter, coupled with its high oil recovery efficiency, positioned it as a preferred solution for addressing oil spills with minimal environmental impact. Further research and development are crucial to optimize the performance and scalability of SACHPC filtration systems for practical deployment in real-world scenarios.

AUTHOR CONTRIBUTIONS

M. Baba Saje: Conceptualization, Methodology, Formal analysis, Investigation, Project administration, Validation, Writing - original draft, Writing - review & editing. **T. O. Uthman**: Resources, Supervision, curation, Visualization, Formal analysis, Validation, Writing - review and editing. **S. Surgun:** Resources, Methodology, Software, Writing - review and editing.

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