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Nanochitosan-based adsorbents for sustainable treatment of palm oil mill effluent

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Palm oil mill effluent (POME) is a highly contaminated wastewater resulting from palm oil processing, characterized by high levels of organic matter, suspended solids, oil and grease, and intense color. The improper release of untreated or inadequately treated POME leads to serious environmental issues, including water pollution, oxygen depletion in aquatic systems, and ecological harm. Traditional treatment methodologies, such as ponding systems, anaerobic digestion, and coagulation–flocculation, face numerous challenges like long treatment times, extensive land use, secondary sludge production, and inconsistent pollutant removal rates. Recently, nanotechnology has surfaced as an innovative treatment solution, with nanochitosan, a nanosized variant of the biopolymer chitosan, attracting attention for its large surface area, abundant amino groups, strong adsorption capacity, biodegradability, and environmental friendliness. This review examines synthesis techniques for nanochitosan (ionic gelation, microemulsion, precipitation), linking their structure–property relationships to pollutant removal mechanisms. A comparison between bulk and nanochitosan emphasizes how increased surface area and functional group richness enhance adsorption capability and treatment efficiency. The efficacy of nanochitosan in eliminating organic pollutants, suspended solids, oils, color compounds, and heavy metals from POME is highlighted. The integration of nanochitosan with conventional biological and physicochemical treatments is also examined to boost treatment performance and sustainability. Moreover, challenges related to large-scale applications, regeneration, economic factors, and possible environmental impacts are discussed. Overall, nanochitosan-based treatment systems show promising potential as sustainable, effective solutions for POME remediation, contributing to advancements in eco-friendly wastewater management technologies.

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1. Introduction

Palm oil mill effluent (POME) is chemically complex brownish wastewater with high organic loads, acidity (pH 3.4–5.2), suspended solids, oil residues, and trace metals[1] Its colour, odour, and turbidity pose persistent challenges for conventional treatment approaches. These characteristics not only intensify environmental risks such as water pollution and environmental toxicity[2,3] but also limit the effectiveness of standard approaches, which often rely on biologically mediated pathways that are poorly suited for the selective removal of colloidal and chemically stable pollutants.[4,5] Consequently, the management of palm oil mill effluent (POME) continues to be perceived as a regulatory requirement rather than an economic imperative, despite its evident implications for environmental sustainability.[6] The escalating regulatory pressures are thus fostering interest in material-based treatment methodologies to enhance current practices.[7,8]

Among emerging materials, chitosan and its nanoscale derivatives have attracted sustained attention due to their bio-based origin, tunable molecular structure, and high density of reactive functional groups.[9] Unlike conventional inorganic coagulants or purely biological systems, chitosan-based materials enable pollutant removal through well-defined physicochemical interactions, including electrostatic attraction, chelation, hydrogen bonding, and polymer bridging.[9,10] This review critically evaluates the structure–property performance relationships of chitosan and nanochitosan in palm oil mill effluent (POME) treatment. It systematically links synthesis methods to pollutant removal mechanisms, compares the treatment performance of nanochitosan with bulk chitosan, and examines the role of nanochitosan in integrated treatment

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systems aimed at achieving regulatory compliance and supporting circular resource recovery.

2. Characteristics and environmental implications of palm oil mill effluent

POME is the liquid waste that comes from the sterilization and clarification sections of the oil palm milling process.[11] Depending on the method of processing, it is composed of 95–96% water, 0.6–0.7% oil, and 4–5% total solids. Raw POME is a highly polluting wastewater and causes considerable deterioration of soil and water quality when discharged untreated into the environment.[12] It typically presents as an acidic solution, with pH values commonly ranging from 3.4 to 5.2,[13] although some reports indicate ranges of 4.0 to 5.0.[14,15] It is also characterized by its high temperature (80–90 °C) and a distinctive dark brownish color.[16] The bulk composition of POME is primarily water (93–95%), followed by solids (3–4%, encompassing both suspended and dissolved matter), and a minor percentage of oil (0.5–2%).[17]

The effluent contains exceptionally high levels of pollutants with Chemical Oxygen Demand (COD) values ranging from 44 000 to 100 000 mg L^{-1}, and in some instances exceeding 80 000 mg L^{-1}, Biochemical Oxygen Demand (BOD) between 25 000 and 66 000 mg L^{-1}, and Total Suspended Solids (TSS) typically within 18 000 to 46 000 mg L^{-1}.[13] Beyond these primary organic pollutants, POME also contains residual oil, heavy metals, and substantial amounts of essential plant nutrients such as phosphorus, nitrogen, and potassium.[17] Furthermore, it is rich in complex organic compounds, including carotene, pectin, tannin, phenolic compounds, and lignin.[18] It is important to distinguish that some lower reported values for parameters like TSS (30–40 mg L^{-1}), pH (7.5–8.9), BOD (20–300 mg L^{-1}), and COD (30–200 mg L^{-1}).[19] Likely pertain to treated or partially treated POME, or effluent from specific mills operating under different processing conditions, rather than raw, high-strength POME.

The direct discharge of untreated POME into the environment results in severe ecological consequences. The high concentrations of COD, BOD, and heavy metals can devastate aquatic ecosystems, leading to oxygen depletion, interfering with photosynthesis, and causing tumors or mortality in aquatic organisms.[17] On land, POME discharge increases soil acidity, negatively impacting nutrient availability for plants and facilitating the leaching of heavy metals into the soil, which in turn lead to clogging and waterlogging of soil pores, loss of agricultural land and eventual vegetation die-off.[16] Beyond ecological damage, POME exposure can pose health risks to

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humans, including irritation, poisoning, gene mutations, and even cancer.[19] Moreover, the common practice of storing POME in open lagoons contributes significantly to greenhouse gas (GHG) emissions, particularly methane (CH_4) and carbon dioxide (CO_2), which account for over 90% of GHG emissions from such systems.[1]

POME presents a complex challenge due to its dual nature: it is both a potent pollutant and a potential resource. While its high organic content and nutrient load contribute to its polluting properties, these very characteristics also represent opportunities for valorization, such as methane production for bioenergy or nutrient recovery for biofertilizers.[17] This duality suggests that effective POME management should ideally transition from merely removing pollutants to actively recovering and utilizing these valuable resources. Such a shift from a "waste management" paradigm to "resource valorization" is crucial for achieving genuine sustainability in the palm oil industry, transforming an environmental liability into an economic asset. The inherent acidity of raw POME also poses a significant challenge for many biological treatment processes, which typically operate optimally under more neutral pH conditions. This necessitates that any proposed POME treatment technology must either demonstrate robustness in acidic environments or incorporate an initial pH adjustment step, which adds to the operational complexity and cost. This


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Table 1 Typical raw POME characteristics and discharge limits

Parameter[a]	Typical raw POME range	FEPA discharge limit (1991)	NESREA discharge limit (2011)	Unit
pH	3.5–5.0	6.0–9.0		—
Temperature	80–90	<40	<40	°C
Biochemical oxygen demand (BOD_5)	25 000–35 000	50	30	mg L^{-1}
Chemical oxygen demand (COD)	50 000–100 000	90	80	mg L^{-1}
Total suspended solids (TSS)	18 000–46 000	30	30	mg L^{-1}
Total solids (TS)	40 000–50 000	—		mg L^{-1}
Total dissolved solids (TDS)	30 000–40 000	2000	2000	mg L^{-1}
Oil and grease	2000–7000	10	10	mg L^{-1}
Ammoniacal nitrogen	20–50	20	20	mg L^{-1}
Total phosphorus	100–200	5	5	mg L^{-1}

[a] Note: Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), Total Nitrogen (N), Heavy metals (HMs), Temp (Temperature).

consideration is a critical design factor for any effective treatment methodology.

Moreover, the chemical heterogeneity of POME limits the effectiveness of single-mechanism treatment processes. While biological degradation can reduce readily biodegradable fractions, residual colour, turbidity, and metal-associated species frequently persist. This highlights the need for materials capable of interacting with pollutants across multiple length scales and chemical functionalities. The variability in Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), and oil content in Palm Oil Mill Effluent (POME), constitutes the principal challenges in treatment efficacy and variability observed in reported efficiencies. This complexity underscores the need for flexible and multi-faceted treatment methodologies. Table 1 summarizes the typical physicochemical characteristics of raw palm oil mill effluent (POME) and compares them with relevant discharge limits.

3. Limitations of conventional POME treatment technologies

Conventional treatment of palm oil mill effluent (POME) has traditionally relied on biological processes, particularly anaerobic pond systems, due to their ability to their simplicity and cost-effectiveness.[17] While anaerobic digestion enables partial conversion of organic matter into biogas,[20] the treated effluent frequently retains substantial concentrations of residual chemical oxygen demand, suspended solids, and colour-causing compounds. These persistent contaminants indicate intrinsic limitations of biologically driven pathways when applied to chemically complex effluents such as POME.

Despite these perceived benefits, conventional methods, including open lagoon systems and mesophilic digesters, are fraught with significant limitations. Open lagoons are major contributors to greenhouse gas (GHG) emissions, with methane (CH_4) and carbon dioxide (CO_2) accounting for over 90% of the GHGs released from such systems.[21] A critical failing is that the effluent discharged from these anaerobic ponds frequently does not meet the stringent government threshold limits, as observed in countries like Indonesia.[17] Even post-conventional treatment, effluents often exceed limits (COD 1400 mg L^{-1}, BOD_5 800 mg L^{-1}, turbidity 650 NTU) reported by.[13] Furthermore, the consistency of treatment outcomes across different palm oil mills remains a challenge, partly because many studies on these methods are conducted under idealized laboratory conditions that do not always translate effectively to real-world operational variability.[1]

Mechanical and chemical methods for hydrocarbon removal, while available, often prove to be economically unviable due to their restricted applicability and high costs.[17] For instance, electrocoagulation can achieve impressive removal efficiencies, such as 90% for TSS, 87% for COD, and 97% for BOD, but at an estimated operating cost of approximately 1.48 USD/m^3.[13]

The inherent conflict between economic incentives and environmental compliance is a significant hurdle in POME treatment. The perceived "cost-effectiveness" of conventional, low-tech solutions like open lagoons often comes at the direct expense of meeting environmental regulations and mitigating climate change impacts. This situation underscores the necessity for a paradigm shift towards more environmentally sound technologies, even if their initial capital investment or operational costs appear higher.

In response to these persistent limitations, a variety of emerging treatment technologies is being actively explored. These include diverse chemical approaches such as coagulation, flocculation, adsorption, and electrochemical treatment, as well as advanced biotechnological methods like enhanced anaerobic/aerobic digestion, microalgae cultivation, phytoremediation, bioremediation, and mycoremediation.[16] Membrane technologies are also gaining prominence as effective and potentially cost-efficient solutions for biogas purification and water reclamation from POME, offering a pathway to resource recovery.[18] The fact that even after conventional biological treatment, POME effluent still exceeds discharge limits.[17] Strongly indicates that a multi-stage or integrated treatment approach is often indispensable to achieve stringent discharge standards.

The limited performance of conventional biological treatments arises from their poor selectivity toward recalcitrant organic compounds, colloidal particles, and metal-associated species. Even after extended retention times, treated POME often exhibits elevated turbidity and residual organic load, necessitating additional post-treatment steps. Chemical and electrochemical polishing methods can enhance contaminant removal; however, their effectiveness is often offset by high reagent demand, secondary sludge formation, or limited compatibility with complex wastewater matrices.[13,17]

These constraints highlight a fundamental gap in conventional POME treatment: the absence of materials capable of simultaneously destabilizing colloids, binding dissolved organic species, and selectively capturing metal ions through well-defined physicochemical interactions. This limitation provides a strong rationale for exploring functional polymeric materials, such as chitosan, which offer tunable surface chemistry and multiple interaction pathways beyond those accessible through biological processes alone. Chitosan and nanochitosan, therefore, are likely to be most effective when employed as polishing steps or in conjunction with existing primary treatments, rather than as standalone solutions, to ensure full compliance and facilitate resource recovery.

The limitations of current processes for treating palm oil mill effluent (POME) reveal a disconnect between biological and chemical methods. Biological systems struggle with non-selective removal of complex components, while chemical treatments can lead to secondary pollution. This calls for research into multifunctional materials like nanochitosan that combine adsorption and coagulation. However, considerations around cost, scalability, and integration into existing systems must also be addressed.

4. Chitosan and nanochitosan

This section delves into the fundamental characteristics of chitosan and nanochitosan, outlining their molecular structure, key physicochemical properties, and the diverse methods employed for their synthesis. Understanding these factors is crucial for appreciating how they influence the applicability and performance of these biopolymers in POME treatment.

4.1 Chitosan: structure, properties, and sources

Chitosan is a linear polysaccharide composed of two randomly distributed monomer units: D-glucosamine and *N*-acetylglucosamine, linked together by a β-(1→4) glycosidic bond as shown in Fig. 1.[22,23] It is a natural biopolymer, specifically a nitrogenous polysaccharide, produced through the partial deacetylation of chitin.[24] Chitin itself is the second most abundant natural biopolymer globally, surpassed only by cellulose.[25] Its defining characteristic, distinguishing it from its precursor chitin, is its solubility in diluted acidic solutions (at pH below 7).[26] In contrast, chitin remains insoluble even in acidic conditions due to its fewer amino groups.[27]

Its physicochemical behavior is primarily governed by the degree of deacetylation, molecular weight, and functional group accessibility. The solubility of chitosan is generally enhanced with a higher degree of deacetylation (DDA) and a lower molecular weight (Mw).[26] The DDA quantifies the percentage of D-glucosamine units present within the polymer structure,[22] with high-purity chitosan potentially achieving a deacetylation degree of 99%.[28]

Under acidic conditions, protonation of amino groups confers a cationic character, enabling strong electrostatic interactions with negatively charged species.[29] Chitosan's solubility behavior is directly linked to the protonation of its amino groups ($-NH_2$) in acidic environments, converting them to positively charged $-NH_3^+$ groups.[30] The pKa of the primary amine group is approximately 6.5.[31] The abundance of these amino groups at the C2 position, along with hydroxyl (–OH) groups at the C3 and C6 positions, are critical to chitosan's powerful adsorption capacity, chemical reactivity, and its amenability to various chemical modifications.[32]

Chitosan can be obtained from various sources, predominantly from the exoskeletons of crustaceans such as crabs, shrimp, and snails.[33] Alternatively, it can be derived from bacterial and fungal fermentation.[28] Fungal sources offer distinct advantages, including independence from seasonal availability, more uniform particle size, lower molecular weight, and the absence of potential heavy metal contamination often associated with marine-derived sources.[27] Despite its numerous beneficial properties, chitosan in its natural bulk form exhibits certain limitations. These include poor solubility, specific surface area ($2–30\ m^2\ g^{-1}$), a porous structure, and suboptimal mechanical properties, such as shrinkage and deformation upon drying.[33]

The ability to tailor chitosan's properties through its degree of deacetylation (DDA) and source is a significant advantage. The DDA directly influences the solubility of chitosan,[33] with higher deacetylation and lower molecular weight generally leading to increased solubility.[26] Furthermore, the choice of source, particularly fungal *versus* crustacean, can yield chitosan with different characteristics, such as particle size uniformity and molecular weight.[27] This implies that the effectiveness of chitosan in POME treatment is not a static property but can be significantly optimized by precisely controlling its DDA and molecular weight during production, or by selecting specific sources. This capability allows for the development of highly customized chitosan variants tailored to the specific characteristics of POME or to achieve particular treatment goals, moving beyond a generic approach to wastewater remediation.

The presence of abundant amino and hydroxyl groups underpins chitosan's capacity for adsorption and coagulation–flocculation.[34] However, bulk chitosan is limited by low specific surface area and restricted accessibility of active sites, which can constrain removal efficiency for dilute or strongly bound pollutants. Fig. 1 illustrates the chemical structure of chitosan and its major natural sources, highlighting its derivation from chitin and relevance for environmental applications.

4.2 Nanochitosan: synthesis and enhanced properties

Nanochitosan, or chitosan nanoparticles, represent engineered forms of chitosan with particle sizes deliberately reduced to the nanometer range.[35] Conversion of chitosan into nanoscale

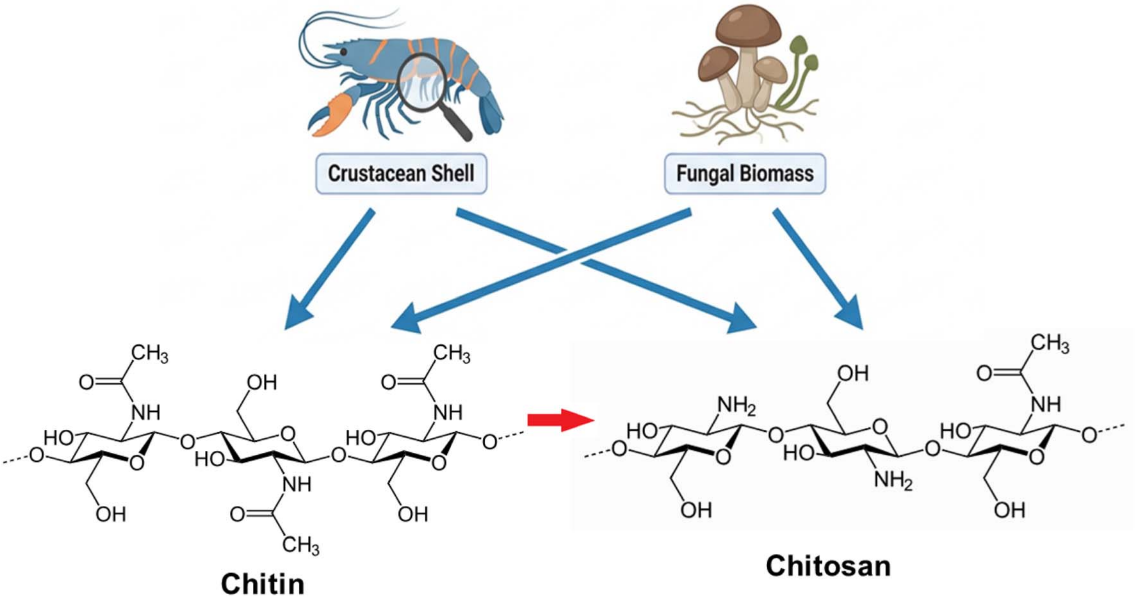

Fig. 1 Structure and sources of chitosan (created with https://www.biorender.com).

architectures markedly alters its physicochemical properties. Nanochitosan development overcomes bulk chitosan limitations (low surface area, poor solubility), markedly enhancing wastewater treatment performance. Notably its restricted surface area and poor solubility, thereby significantly enhancing its performance across various applications, including wastewater treatment. Nanochitosan exhibits increased surface area, enhanced functional group exposure, and improved mass transfer characteristics.[36] These features translate into higher adsorption capacities and faster interaction kinetics.

Various synthesis routes, including ionic gelation, ultrasonication, and covalent cross-linking, enable control over particle size and surface charge. However, nanoscale modification also introduces challenges related to aggregation, stability, and reproducibility, underscoring the importance of rational material design.

4.2.1 Ultrasonication. This technique is recognized for its simplicity and environmental friendliness, as it avoids the use of hazardous or expensive chemicals. Key parameters for producing discrete nanoparticles with a narrow particle size distribution *via* ultrasonication include increasing the ultrasonic irradiation time and wave amplitude. For instance, direct ultrasonication of a deacetylated chitosan dispersion (0.1% w/v) at specific amplitudes for a defined period, followed by centrifugation, can effectively yield CNPs.[37]

4.2.2 Ionic gelation/polyelectrolyte complexation. This is considered one of the most common and straightforward techniques, requiring neither high shear forces nor organic solvents. This method capitalizes on chitosan's intrinsic ability to form a gel and beads when exposed to polyanions, such as sodium tripolyphosphate (TPP).[38]

4.2.3 Emulsification and cross-linking. First described for CNP synthesis in 1994, this method involves the formation of an emulsion followed by cross-linking of chitosan nanoparticles, often utilizing glutaraldehyde as a covalent cross-linking agent. The final particle size can be precisely controlled by adjusting the rate of cross-linking, yielding nanoparticles that range from 30 nm to 300 nm.[39]

4.2.4 Reverse micelle method. This technique employs a surfactant (*e.g.*, sodium bis(ethylhexyl) sulfosuccinate) within a non-polar solvent like hexane. The aqueous core of these micelles encapsulates the chitosan solution, which is subsequently cross-linked, typically with glutaraldehyde.[39]

The transformation of chitosan to its nanoscale form imparts significantly enhanced properties:

Increased surface area: this is a paramount advantage, directly leading to a substantially higher adsorption capacity for pollutants due to more available binding sites.[40]

Improved solubility and chemical reactivity: nanoscale modifications facilitate better solubility and increased chemical reactivity compared to bulk chitosan, broadening its applicability.[33]

Superior pollutant removal efficiency: nanochitosan consistently demonstrates superior performance in wastewater treatment. For example, it exhibits a turbidity removal efficiency of 75.4% and dealkalization of 58.3%, significantly outperforming bulk chitosan, which achieves only 35.4% and 11.1%, respectively, for these parameters.[35]

Higher adsorption rates: for heavy metals, nanochitosan exhibits faster adsorption rates and shorter equilibrium times, making the treatment process more efficient.[40]

Enhanced stability: chemical cross-linking, a common modification technique, can substantially increase the long-term stability of nanochitosan, addressing a key limitation of the bulk polymer.[39]

The transformation to nanoscale effectively acts as a performance multiplier for chitosan. While bulk chitosan faces

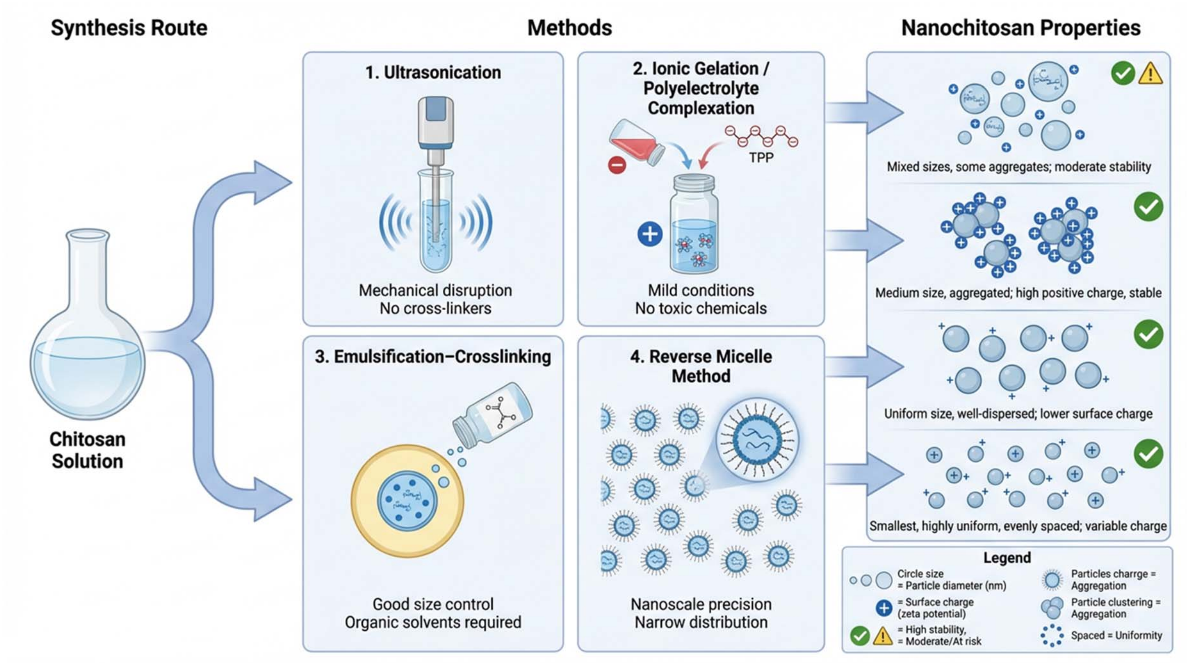

Fig. 2 Comparative synthesis routes and physicochemical properties of nanochitosan produced *via* ultrasonication, ionic gelation, emulsification–crosslinking, and reverse micelle methods (created with https://www.biorender.com).

limitations such as poor solubility, small surface area, and porous structure, nanochitosan synthesis directly addresses these shortcomings by increasing solubility and enhancing the ability to absorb metals.[33] The direct comparison of performance, showing superior turbidity removal and dealkalization by nanochitosan over bulk chitosan,[35] unequivocally establishes nanochitosan as a significantly more efficient material for POME treatment. This implies that future research and industrial applications should prioritize nanochitosan or its composites for achieving optimal pollutant removal.

A notable consideration in nanochitosan synthesis is the trade-off between simplicity and control. Techniques like ionic gelation and ultrasonication are appealing due to their straightforward nature and avoidance of harsh or expensive chemicals.[35] However, more complex methods, such as covalent cross-linking, offer finer control over critical particle properties like size and stability.[39] This control can be vital for addressing specific POME pollutant removal challenges. The selection of a synthesis method, therefore, depends on balancing factors such as cost, environmental footprint, and the precise performance characteristics required for a given POME treatment scenario. Hence, nanochitosan offers distinct functional advantages over bulk chitosan, particularly in terms of increased surface area and reactivity. Nevertheless, these advantages are mitigated by issues about synthesis variability, stability, and scalability, which are inadequately addressed in the existing literature.

Fig. 2 highlights method-dependent variations in particle size distribution, zeta potential, morphology, and stability. Ultrasonication yields polydisperse particles, ionic gelation produces highly charged but aggregation-prone nanoparticles, while emulsification and reverse micelle methods enable more uniform and stable nanostructures. Synthesis strategy governs nanochitosan performance and application suitability.

Table 2 summarizes common nanochitosan synthesis methods applied in POME treatment, including the chemicals used, particle size ranges, advantages, and associated limitations.

5. Mechanisms of pollutant removal

The primary mechanisms through which chitosan and nanochitosan effectively remove pollutants from POME focuses on the crucial roles of coagulation–flocculation and adsorption, highlighting how their unique functional groups and high surface area contribute to these processes.

5.1 Coagulation–flocculation in POME treatment

Nanochitosan's protonated amino groups ($pK_a \approx 6.5$) neutralize negatively charged POME colloids at native pH (3.4–5.2), while polymer chains bridge destabilized particles into settle able flocs.[32,41] This dual mechanism reduces sludge volume *versus* inorganic coagulants, with chitosan–magnetite composites showing synergistic agglomeration.

5.1.1 Coagulation. This initial stage involves the addition of chemical agents, known as coagulants, to wastewater. Their primary function is to destabilize finely dispersed colloidal solids, which are typically stabilized by negative surface charges that cause them to repel one another.[41] Chitosan, functioning as a cationic polyelectrolyte, introduces positive electrical charges that effectively neutralize the negative zeta potential of these colloidal particles. This charge neutralization diminishes the

Table 2 Nanochitosan synthesis methods for POME treatment

Method	Chemicals used	Particle size (nm)	Advantages	Limitations
Ultrasonication	None	Variable	Simple and green process	Broad size distribution
Ionic gelation	Tripolyphosphate (TPP)	100–500	Mild reaction conditions	Risk of nanoparticle aggregation
Emulsification–crosslinking	Glutaraldehyde	30–300	Good particle size control	Toxic cross-linking agent
Reverse micelle	Surfactant, hexane	50–200	Uniform particle formation	Use of organic solvents

repulsive forces between particles, facilitating their initial aggregation.[42] During this phase, rapid mixing is essential to ensure the uniform dispersion of the coagulant throughout the liquid, maximizing contact with the pollutants.[41]

5.1.2 Flocculation. Following coagulation, the wastewater suspension undergoes a period of gentle stirring or agitation. This slow mixing promotes further collisions among the destabilized particles and the nascent micro-flocs, encouraging them to agglomerate into larger, heavier masses known as macro-flocs. These larger flocs possess sufficient mass to settle out of the solution by gravity or to be efficiently captured and removed by subsequent filtration processes.[41]

Chitosan is recognized as a highly effective polymeric flocculant, demonstrating performance comparable to conventional inorganic coagulants like ferric salts, often achieving similar efficiencies with significantly reduced dosages.[43] Its effectiveness is rooted in the protonation of its amino groups (–NH_2) in acidic solutions, which renders chitosan positively charged (cationic). This cationic nature makes it highly attractive for binding to negatively charged surfaces through ionic or hydrogen bonding.[32] For POME treatment, the coagulation process mediated by chitosan primarily involves a synergistic combination of charge neutralization and polymer bridging mechanisms.[32,44] Furthermore, composite materials, such as chitosan-magnetite nanocomposites, exhibit enhanced performance. This is attributed to the synergistic effect of the cationic chitosan amino groups and the magnetite ions, which collectively lead to improved agglomeration, adsorption, and overall coagulation efficiency.[32]

Beyond merely achieving pollutant removal, chitosan's ability to reduce sludge generation offers a significant advantage. Optimizing chitosan-based coagulation–flocculation is noted to yield substantial environmental benefits by decreasing the reliance on toxic chemicals and minimizing the volume of sludge produced, thereby leading to less overall pollution.[43] This contrasts sharply with conventional inorganic coagulants, which are known to generate large quantities of chemical sludge requiring costly and environmentally impactful disposal. Thus, the reduced sludge volume translates directly into lower disposal costs and a diminished environmental footprint associated with sludge management, positioning chitosan as a more holistic and environmentally sound solution for POME treatment.

5.2 Adsorption

Adsorption by chitosan-based materials occurs through electrostatic attraction, chelation, and hydrogen bonding. Nanochitosan enhances these interactions by increasing the availability of surface-active sites and reducing diffusion limitations.[45] Adsorption technology stands as a highly reliable and widely favored strategy in wastewater treatment, particularly valued for its economic viability, operational simplicity, and capacity for high removal efficiency.[46] The integration of nanosized adsorbents, such as nanochitosan, significantly augments this process by providing a substantially increased surface area. This expanded surface area facilitates preferential surface adsorption of pollutants, leading to more efficient capture.[40]

Chitosan serves as an effective biomaterial for adsorption due to its abundant functional groups, predominantly hydroxyl (–OH) and amino (–NH_2) groups.[32] These groups provide numerous active sites that can interact chemically with various pollutants. Specifically, they can form complexes with metal ions through chelation, hydrogen bonding, or electrostatic attraction.[27] The inherent adsorption capacity and selectivity of chitosan can be further enhanced through targeted chemical modifications that introduce additional functionalities into its basic polymeric structure.[39]

Nanochitosan distinguishes itself among nano-adsorbents due to its exceptionally large surface area, high adsorption capacity, and inherent environmental compatibility.[39] For heavy metals, the primary adsorption mechanism involves electrostatic attraction between the positively charged amino groups on the nanochitosan surface and the negatively charged pollutant ions. Furthermore, the lone pair electrons on the nitrogen atoms within the amino and *N*-acetylamino groups can form dative bonds with transition metal ions, contributing to their effective removal from the aqueous solution with adsorption capacity for certain ions, such as lead, increases with pollutant concentration but decreases at higher pH values, where the surface charge of chitosan become more neutral, thereby reducing electrostatic attraction.[47]

At the molecular scale, the adsorption process facilitated by chitosan-derived materials is primarily influenced by the protonation-deprotonation dynamics of amino groups, where –NH_2 groups become protonated to form –NH_3^+ in acidic environments ($pK_a \approx 6.5$), thereby establishing strong electrostatic attractions with anionic species. Simultaneously, the unprotonated amino and hydroxyl groups function as electron donors, engaging in coordination bonds with metal ions *via* chelation processes. These interactions are further augmented by hydrogen bonding and van der Waals forces, which collectively contribute to the overall adsorption mechanism.[27,39] The empirical validation of these mechanisms is typically accomplished through a range of physicochemical characterization techniques. Fourier transform infrared spectroscopy (FTIR) is instrumental in identifying shifts in –NH and –OH stretching

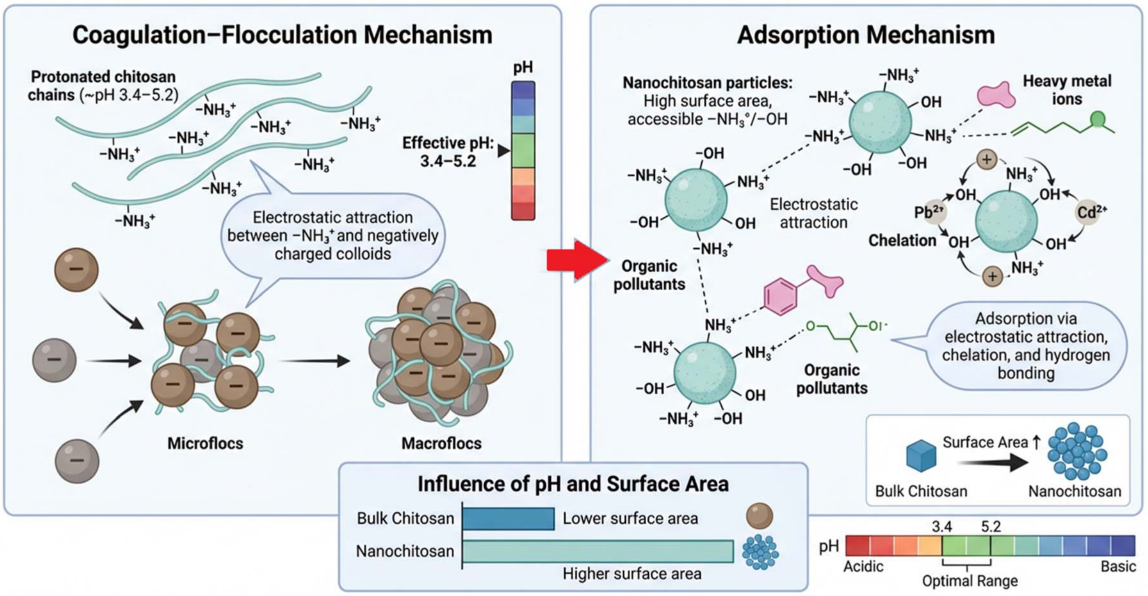

Fig. 3 Mechanisms of POME pollutant removal (created with https://www.biorender.com).

vibrations upon pollutant interaction, while zeta potential analysis elucidates alterations in surface charge in relation to pH and adsorption parameters. Furthermore, electron microscopy (SEM/TEM) offers valuable insights into morphological changes and particle dispersion, and Brunauer–Emmett–Teller (BET) analysis corroborates the significance of increased surface area in augmenting adsorption capacity.[33,36] Nevertheless, it is crucial to acknowledge that such characterizations are generally performed under controlled laboratory conditions and may not adequately reflect the intricate, multicomponent interactions and competitive adsorption phenomena that occur in actual palm oil mill effluent (POME) systems, which can significantly impact adsorption efficiency and the predominance of specific mechanisms.

Moreover, elevated adsorption capacities observed in batch experiments may not necessarily correlate with continuous or large-scale applications due to limitations in mass transfer, particle aggregation, and fouling. These variables can considerably diminish the effective adsorption capacity in practical settings, thereby exacerbating the scalability issues addressed in this review.

The pH of POME, which is initially acidic (typically 3.4–5.2),[13] is a critical parameter influencing the performance of both coagulation–flocculation and adsorption mechanisms. Chitosan's solubility and its cationic nature, essential for effective coagulation and flocculation, are highly dependent on pH, being soluble and protonated in acidic conditions but insoluble and more neutral at higher pH values.[32] Similarly, nanochitosan's adsorption capacity for lead ions is highest at low pH due to strong electrostatic attraction, but it decreases as the pH rises and the surface charge becomes neutral.[47] For instance, optimal conditions for ammonium ion (NH_4^+) adsorption by a chitosan-based material were identified at pH 5.5.[40] This strong pH dependency implies that pH adjustment might be a necessary pre-treatment step to achieve optimal efficiency for chitosan and nanochitosan in POME treatment. Alternatively, specific chemical modifications of chitosan could be explored to enable effective performance across the wide pH range encountered in POME, adding a layer of operational complexity but also an avenue for process optimization. Fig. 3 illustrates the main mechanisms involved in the removal of pollutants from palm oil mill effluent (POME).

5.3 Role of functional groups and surface area in pollutant removal

The efficacy of chitosan and nanochitosan in pollutant removal is fundamentally rooted in their molecular structure and physical form. Chitosan's abundant hydroxyl (–OH) and amine ($-NH_2$) functional groups are paramount, providing numerous active sites for chemical interactions and enabling its powerful adsorption capacity and reactivity towards a wide range of pollutants.[32]

These functional groups facilitate pollutant removal through several mechanisms:

Electrostatic attraction: in acidic POME, the amine groups ($-NH_2$) of chitosan become protonated to $-NH_3^+$, imparting a positive charge to the polymer.[32] This cationic nature allows for strong electrostatic attraction with negatively charged pollutants, such as colloidal particles, organic acids, and certain heavy metal anions, leading to their effective removal through charge neutralization and subsequent agglomeration.[47]

Chelation and complexation: the lone pair electrons on the nitrogen atoms of the amino groups, and the oxygen atoms of the hydroxyl groups, enable chitosan to act as a ligand. This allows it to form stable complexes or chelates with various metal ions (*e.g.*, lead, cadmium, copper, chromium), effectively sequestering them from the wastewater.[27]

Hydrogen bonding: the numerous hydroxyl groups can form hydrogen bonds with polar molecules present in POME, contributing to the adsorption of organic compounds.[27]

Polymer bridging: in the coagulation–flocculation process, the long polymeric chains of chitosan can extend into the solution and adsorb onto multiple particles, effectively "bridging" them together to form larger, more easily settleable flocs.[32] While bulk chitosan possesses these functional groups, its relatively low specific surface area (2–30 $m^2\ g^{-1}$) and porous structure limit the accessibility of these active sites for pollutant interaction.[33] This inherent limitation significantly restricts its overall adsorption capacity.

The transformation of chitosan into nanochitosan dramatically enhances its performance by increasing the available surface area.[40] Nanoparticles, by definition, have a significantly higher surface-to-volume ratio compared to their bulk counterparts. This increased surface area means more functional groups are exposed and accessible for interaction with pollutants, leading to:

Higher adsorption capacity: a larger number of active sites are available for binding, resulting in a greater quantity of pollutants adsorbed per unit mass of adsorbent.[39] For example, nanochitosan-coated cotton fiber exhibited significantly higher Langmuir adsorption capacities for Cd(II), Pb(II), and Cr(VI) compared to plain cotton fiber.[41]

Faster adsorption kinetics: the shorter diffusion paths to the surface of nanoparticles allow for quicker pollutant uptake, leading to shorter equilibrium times and more rapid treatment processes.[40] Nanochitosan-coated cotton fiber demonstrated a shorter half-time of adsorption and a greater initial adsorption rate.[41]

Improved turbidity and dealkalization efficiency: as demonstrated, nanochitosan significantly outperforms bulk chitosan in removing turbidity and facilitating dealkalization, directly attributable to its enhanced surface properties.[35]

The synergistic interplay between the inherent chemical functionality of chitosan (amino and hydroxyl groups) and the vastly increased physical accessibility provided by its nanoscale form is the cornerstone of its superior performance in POME treatment. This combination allows for highly efficient pollutant capture through both charge neutralization and direct adsorption mechanisms.

The elimination of pollutants utilizing chitosan-based materials is regulated by synergistic mechanisms, including electrostatic interactions, chelation, and polymer bridging. The efficacy of these mechanisms is significantly influenced by factors such as pH, surface chemistry, and the composition of wastewater. Moreover, the inherent complexity of real-world systems frequently restricts the attainment of optimal performance.

6. Performance of chitosan and nanochitosan in POME treatment

Chitosan and nanochitosan have demonstrated significant potential in treating palm oil mill effluent (POME), primarily through coagulation–flocculation and adsorption processes. Their effectiveness in removing key pollutants like BOD, COD, TSS, and heavy metals has been highlighted in various studies.[4,32,48,49] Comparative studies consistently demonstrate superior removal efficiencies for nanochitosan relative to bulk chitosan, particularly for suspended solids and metal ions.[44,49,50] The enhanced performance is directly attributable to nanoscale structure–property relationships rather than intrinsic chemical composition alone. However, a critical examination of these studies reveals that reported efficiencies are strongly dependent on experimental conditions, initial effluent composition, and system configuration, complicating direct comparison across studies.

6.1 Performance in removing BOD, COD, and TSS

Chitosan has been extensively investigated as a primary coagulant and flocculant for POME pre-treatment, often compared with conventional agents like aluminum sulfate (alum). Studies indicate that chitosan can achieve superior pollutant reductions at significantly lower dosages compared to alum. For instance, at pH 6, an optimum chitosan dosage of 400 mg L^{-1} was capable of reducing turbidity by 99.90%, Total Suspended Solids (TSS) by 99.15%, and Chemical Oxygen Demand (COD) by 60.73%. In contrast, alum required a much higher optimum dosage of 8 g L^{-1} at pH 7 to achieve comparable reductions of 99.45% for turbidity, 98.60% for TSS, and 49.24% for COD. This suggests that the polymer bridging mechanism facilitated by chitosan is more dominant and efficient than that of alum.[44]

Nevertheless, these high efficiencies should be interpreted cautiously. Many studies, including the one above, are conducted under controlled pH and mixing conditions that may not reflect the variability of raw POME streams. In practice, fluctuations in pH, temperature, and pollutant composition can significantly influence coagulation performance, potentially reducing removal efficiency. The application of chitosan-magnetite nanocomposite particles has further enhanced treatment efficiency. These composites demonstrated superior parameter reductions at even lower dosages than chitosan alone. An optimum dosage of 250 mg L^{-1} of chitosan-magnetite particles at pH 6 resulted in turbidity, TSS, and COD reduction of 98.8%, 97.6%, and 62.5% respectively outperforming chitosan, which required 370 mg L^{-1} to achieve 97.7%, 91.7% and 42.70% reductions, with the improved performance attributed to the synergistic interactions between cationic chitosan amino groups and magnetite ions that enhances agglomeration, adsorption, and coagulation.[32]

For anaerobically digested POME (AAD-POME), coagulation solely by chitosan (2500 mg L^{-1}) achieved maximum COD and TSS removal of 70.22% and 85.59%, respectively. Combining chitosan with hydrogen peroxide (H_2O_2), significantly enhanced performance, increasing COD removal to 82.82%, and TSS removal to 89.92%. The integration of chitosan with Fenton oxidation ($FeSO_4$ and H_2O_2) resulted in 100% TSS removal and 73.08% COD removal.[51] These results indicate that while chitosan alone is effective, its performance can be further optimized through combination with advanced oxidation processes.

Notwithstanding these benefits, the performance of raw palm oil mill effluent (POME) systems frequently exhibits greater inconsistency compared to pretreated wastewater. The existence of emulsified oils and greases can obstruct flocculation processes, while elevated ionic strength and the presence of competing ions diminish adsorption efficacy by occupying the binding sites available.[52] Furthermore, the variability in the composition of raw POME from various processing mills generates unpredictability in treatment results and constrains the reproducibility of documented efficiencies.[53] It is essential to acknowledge that the majority of existing research on the treatment of raw palm oil mill effluent (POME) predominantly relies on batch experimental methodologies, which may not adequately represent the continuous flow conditions typical of industrial settings. Key elements such as sludge management, material recovery, and regeneration especially concerning nanochitosan are infrequently explored within real effluent systems, yet they are vital for enhancing process scalability and ensuring economic feasibility. The inherent acidity of POME (pH 4.5) is particularly conducive to the coagulation action of chitosan and chitosan–magnetite composites. At this pH, chitosan–magnetite nanocomposite demonstrated excellent destabilization of POME, achieving over 99% turbidity reduction.[32] Chitosan-based systems exhibit significant efficacy in reducing suspended solids and turbidity; however, the removal of chemical oxygen demand (COD) is characterized by greater variability and is frequently incomplete. This limitation is indicative of the existence of recalcitrant organic compounds within palm oil mill effluent (POME) that are not effectively eliminated through coagulation methods alone. Consequently, this underscores the necessity for the implementation of integrated treatment approaches.

6.2 Efficiency in heavy metal removal

Chitosan and nanochitosan are highly effective in removing heavy metals from industrial wastewater due to the presence of abundant hydroxyl and amino functional groups that serve as active sites for binding metal ions. These functional groups can form complexes with metal ions *via* chelation, hydrogen bonding, or electrostatic attraction.[27]

Nanochitosan, in particular, demonstrates superior efficacy in heavy metal adsorption. Its small size and high surface area contribute to a high adsorption capacity and faster adsorption rates compared to bulk chitosan.[40] The adsorption mechanism is primarily based on the electrostatic attraction between the positively charged amino groups on the nanochitosan surface and the negatively charged pollutant ions.[39] The nitrogen lone pair electrons in the amino and *N*-acetylamino groups can also establish dative bonds with transition metal ions.[47]

Specific studies highlight the high removal efficiencies for various heavy metals:

Lead (Pb): nanochitosan nanoparticles have shown promising results for lead removal. Their positively charged surface at low pH facilitates adsorption through electrostatic attraction.[36] An adsorption capacity of 192.3 mg g^{-1} for lead ions was reported at pH 6.1 with a contact time of 59.9 minutes.[47] Nanochitosan-coated cotton fiber (NCCF) achieved a maximum Langmuir adsorption capacity of 6.40 mmol g^{-1} for Pb(II).[41]

Chromium (Cr): NCCF exhibited a maximum Langmuir adsorption capacity of 12.50 mmol g^{-1} for Cr(VI).[41] Chitosan crosslinked with diethylenetriaminepentacetic acid or trimesic acid showed adsorption coefficients of 192.3 mg g^{-1} and 129.53 mg g^{-1} for Cr(VI) ions at optimal pH values.[47]

Cadmium (Cd): NCCF demonstrated a maximum Langmuir adsorption capacity of 4.76 mmol g^{-1} for Cd(II).[41]

Iron (Fe) and manganese (Mn): chitosan nanoparticles have been employed to eliminate Fe(II) and Mn(II) *via* adsorption, achieving capacities of 116.2 mg g^{-1} and 74.1 mg g^{-1}, respectively.[54] Another study documented remarkable efficiencies of 99.94% for Fe(II) and 80.85% for Mn(II) removal using nanochitosan.[41]

The enhanced performance of nanochitosan in heavy metal removal is a direct consequence of its nanoscale properties, which overcome the limitations of bulk chitosan's lower surface area and porosity. This makes nanochitosan a highly effective and environmentally friendly adsorbent for heavy metal pollution in POME. Despite these promising results, several limitations warrant consideration. Firstly, the efficacy of adsorption is significantly influenced by pH, with optimal removal generally achieved in acidic environments where chitosan becomes protonated as stated in Section 5.2. This pH dependency may require adjustments in actual palm oil mill effluent (POME) treatment processes, thereby complicating operations and elevating costs. Secondly, the majority of adsorption investigations are performed using single-metal systems or simplified matrices, which fail to incorporate the competitive adsorption phenomena prevalent in multicomponent wastewater like POME. Moreover, elevated adsorption capacities observed in batch experiments may not necessarily correlate with continuous or large-scale applications due to limitations in mass transfer, particle aggregation, and fouling. These variables can considerably diminish the effective adsorption capacity in practical settings, thereby exacerbating the scalability issues addressed in this review.

Chitosan and nanochitosan exhibit notable removal efficiencies when subjected to optimized conditions; however, their performance displays significant variability across different studies and tends to be less reliable within actual Palm Oil Mill Effluent (POME) systems, especially concerning Chemical Oxygen Demand (COD) removal. This variability highlights the disparity between laboratory findings and their practical implementation in real-world scenarios.

7. Comparative analysis: chitosan *vs.* nanochitosan

The transition from bulk chitosan to its nanoscale form represents a significant advancement in POME treatment, offering enhanced performance and broader applicability. A

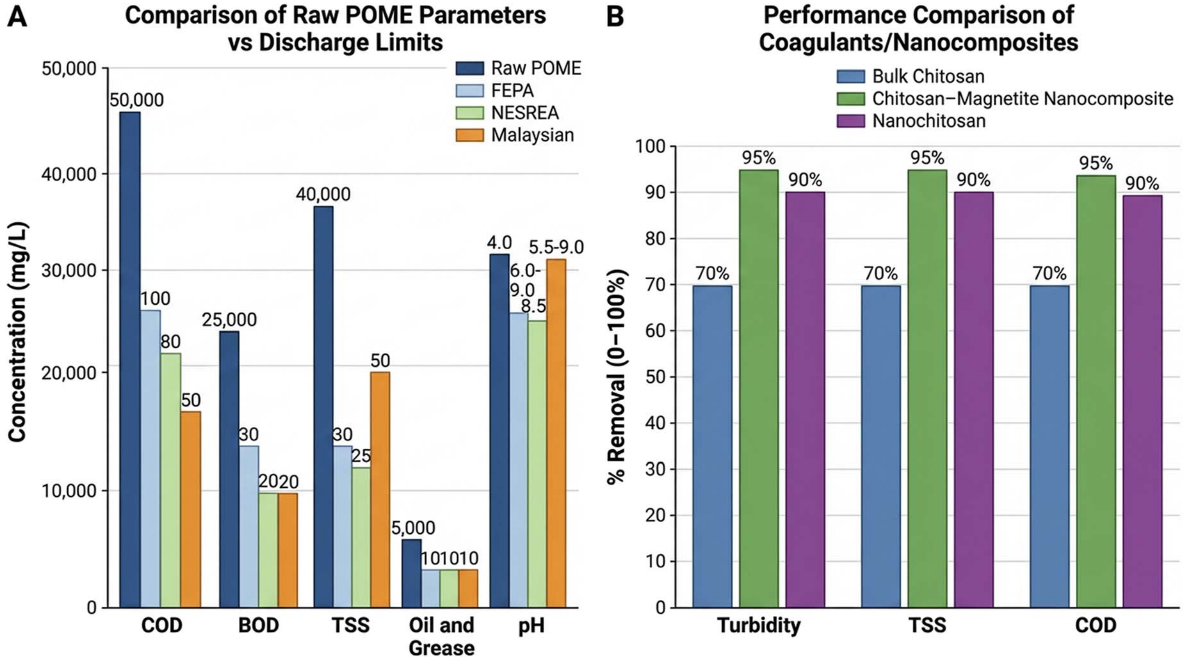

Fig. 4 (A) Comparison of raw POME parameters with FEPA, NESREA, and Malaysian discharge limits. (B) Performance comparison of bulk chitosan and chitosan–magnetite nanocomposites for COD, TSS, and turbidity removal efficiency (created with https://www.biorender.com).

comparative analysis reveals distinct advantages of nanochitosan, particularly concerning efficiency, although considerations of cost, reusability, and scalability remain critical.

7.1 Performance comparison

Few studies have documented the use of nanochitosan in the remediation of palm oil mill effluent (POME). A study by[35] revealed that nanochitosan greatly improves wastewater treatment, attaining a turbidity removal efficiency of 75.4% and a dealkalization efficiency of 58.3%. The values were significantly greater than those achieved with bulk chitosan, which demonstrated turbidity reduction and dealkalization efficiencies of merely 35.4% and 11.1%, respectively. This enhanced efficacy is primarily attributed to the increased surface area of nanoparticles, which provides more active sites for pollutant interaction and adsorption.[40]

The pre-treatment of POME, chitosan-magnetite nanocomposite particles demonstrated better reductions in turbidity, TSS, and COD at a lower dosage (250 mg L^{-1}) compared to chitosan alone (370 mg L^{-1}). The nanocomposite achieved 98.8% turbidity, 97.6% TSS, and 62.5% COD reductions, whereas chitosan yielded 97.7% turbidity, 91.7% TSS, and 42.70% COD reductions.[32] This indicates that the synergistic effect of the nanoscale modification, particularly with magnetic properties, significantly improves the efficiency of pollutant agglomeration, adsorption, and coagulation.

The nanoscale transformation of chitosan effectively acts as a performance multiplier,[24] while bulk chitosan is limited by its poor solubility, small surface area, and porous structure. Nanochitosan synthesis directly addresses these shortcomings by increasing solubility and enhancing the ability to absorb pollutants.[33,36] The direct comparative data on turbidity removal and dealkalization[35] unequivocally establish nanochitosan as a more efficient material for POME treatment. This suggests that for optimal pollutant removal, future research and industrial applications should prioritize nanochitosan or its composite forms. Nonetheless, the benefits of nanochitosan's performance need to be weighed against the greater complexity of its synthesis, potential instability, and the difficulties associated with its recovery. As mentioned in Section 9, these aspects could restrict its practical use, even with enhanced removal efficiencies. Fig. 4 compares raw POME characteristics with regulatory discharge limits and illustrates the removal performance of bulk chitosan, chitosan–magnetite composites, and nanochitosan. It highlights both the severity of untreated POME and the improved treatment efficiency achieved with nanochitosan-based systems.

7.2 Cost, reusability, and scalability considerations

While nanochitosan exhibits superior pollutant removal compared to bulk chitosan, its broader application is constrained primarily by materials-related factors rather than removal efficiency alone.[39] The synthesis of nanochitosan introduces additional variables, including particle size distribution, surface charge stability, and functional group accessibility, all of which influence reproducibility and long-term performance. Variations in synthesis conditions can result in inconsistencies in adsorption capacity and coagulation behaviour, underscoring the need for improved control over material design.[36]

Reusability and regeneration are central to the practical viability of chitosan-based materials. Several studies have demonstrated that chitosan and nanochitosan can retain appreciable adsorption capacity over multiple regeneration cycles;[36,39,55] however, progressive loss of activity is commonly observed due to surface fouling, partial deprotonation of amino groups, or structural degradation.[36,56] These effects are particularly pronounced under complex wastewater conditions, where competitive adsorption and irreversible binding of organic matter can limit regeneration efficiency.

Scalability considerations are therefore closely linked to the stability and robustness of chitosan-based materials under repeated use rather than to production volume alone.[57] Approaches such as chemical cross-linking, incorporation into composite matrices, and magnetic modification have shown promise in improving structural integrity and facilitating material recovery.[58] Nevertheless, further optimization is required to balance enhanced stability with preservation of functional group accessibility, which remains critical for effective coagulation and adsorption.

Nanochitosan consistently demonstrates superior efficiency and kinetics compared to bulk chitosan, its practical benefits are mitigated by increased production complexity, difficulties in recovery, and ambiguous cost-effectiveness when produced at scale.

8. Nanochitosan in integrated POME treatment systems

Conventional palm oil mill effluent (POME) treatment systems, typically consisting of anaerobic ponds followed by facultative and aerobic polishing stages often struggle to achieve regulatory discharge standards due to persistent chemical oxygen demand (COD), colour, and trace metal contaminants. Nanochitosan offers a complementary solution when strategically integrated into treatment trains, owing to its broad pH compatibility, multifunctional removal mechanisms, and relatively low sludge production. Integration enhances the overall efficacy of treatment methodologies; however, it simultaneously introduces increased complexity in processes, augmented operational expenditures, and challenges related to material handling. The viability of such systems hinges on the equilibrium between performance enhancements and the economic as well as operational limitations, which are inadequately explored in the existing academic discourse.

8.1 Primary coagulation–flocculation

Nanochitosan can function effectively as a primary coagulant, significantly improving solid and turbidity removal. Studies report reductions of total suspended solids (TSS) of up to 87%, while turbidity removal reaches 75.4%, compared with 35.4% for bulk chitosan. Nanochitosan also enhances dealkalisation efficiency (58.3% *versus* 11.1%) and forms denser flocs with lower sludge volume than conventional coagulants such as alum.[13,35] These properties improve effluent clarification prior to biological treatment and reduce organic loading to downstream pond systems.

8.2 Post-biological polishing

Following anaerobic treatment, nanochitosan adsorption can be applied as a polishing step to remove residual contaminants that are resistant to biological degradation. Additional COD removal exceeding 80% has been reported, along with effective

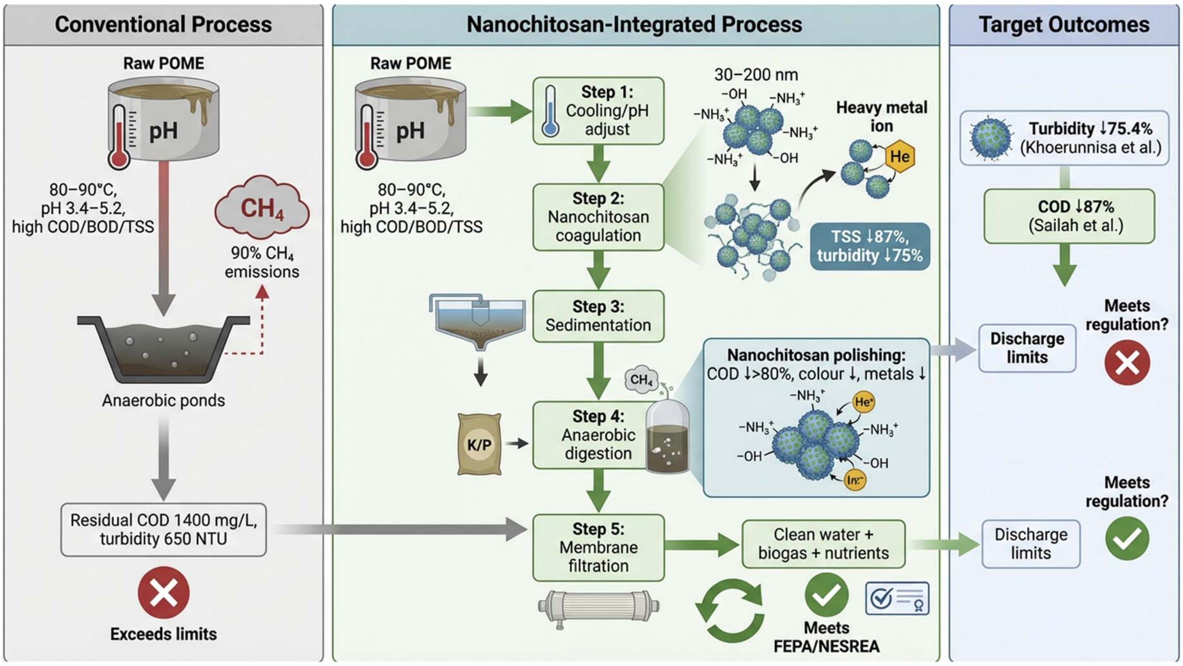

Fig. 5 Nanochitosan-integrated POME treatment enhances coagulation, polishing, and membrane filtration to reduce COD, turbidity, oil, colour, and heavy metals while improving clean water, biogas, and nutrient recovery (created with https://www.biorender.com).

Table 3 Nanochitosan integration benefits compared with conventional POME treatment

Parameter	Conventional ponds	Nanochitosan-enhanced system	Improvement
Footprint	Large (months retention time)	Compact treatment units	70–80% reduction
Sludge volume	High (inorganic coagulants)	Low sludge generation	50–70% reduction
Regulatory compliance	Often fails discharge limits	Meets FEPA/NESREA standards	Improved compliance
Resource recovery	Limited	Biogas and nutrient recovery	Enhanced circular outputs

elimination of phenolic compounds and heavy metals such as Pb^{2+} and Cd^{2+} through chelation interactions.[40] The use of nanochitosan–magnetite composites further enable magnetic separation and recovery of the adsorbent, facilitating regeneration and reuse.[32]

8.3 Hybrid membrane integration

Nanochitosan pretreatment can also enhance the performance of advanced membrane systems. By reducing suspended solids and organic fouling precursors, nanochitosan improves membrane stability and extends the operational lifespan of ultrafiltration and reverse osmosis units. This integration supports additional resource recovery processes, including biogas purification and nutrient recovery (*e.g.*, potassium and phosphorus for fertilizer applications).[18] Fig. 5 illustrates the optimized treatment configuration incorporating nanochitosan within conventional POME management systems.

Integrated nanochitosan-based treatment systems offer several operational advantages, including reduced land requirements compared with large pond systems, lower greenhouse gas emissions associated with open lagoons, and improved opportunities for circular resource recovery, such as biogas, treated water, and nutrients. Additionally, sludge production can be 50–70% lower than that generated by conventional inorganic coagulants. These benefits position nanochitosan not merely as an auxiliary additive but as a key enabling technology for achieving regulatory compliance and resource-efficient POME management. The integration of nanochitosan with biological and advanced treatment methodologies presents the most promising avenue for the efficient remediation of palm oil mill effluent (POME), as it facilitates synergistic removal mechanisms. Nonetheless, the intricacy of the system and considerations of economic viability continue to pose significant challenges. Table 3 compares the operational benefits of nanochitosan-enhanced systems with conventional POME pond treatment, highlighting improvements in footprint, sludge generation, regulatory compliance, and resource recovery.

9. Challenges, limitations, and future outlook

Despite the significant promise of chitosan and nanochitosan in POME treatment, their widespread industrial application faces several challenges and limitations. Addressing these aspects is crucial for realizing their full potential and shaping future research directions.

9.1 Challenges and limitations

The use of chitosan and nanochitosan for Palm Oil Mill Effluent (POME) treatment faces several challenges.

9.1.1 Solubility and stability. Chitosan's solubility is limited in neutral and alkaline conditions,[26] and its stability is compromised by environmental factors such as high temperatures and humidity, which can lead to structural degradation, reduced mechanical integrity, and loss of active functional groups.[57,59] These effects compromise reproducibility and limit long-term storage and reuse. Despite their demonstrated effectiveness, the performance of chitosan and nanochitosan in POME treatment is constrained by several intrinsic material limitations.[48,49] Chitosan exhibits strong pH-dependent behaviour, with solubility and surface charge governed by protonation of amino groups.[60] While acidic conditions favour coagulation and adsorption, variations in effluent chemistry can alter surface charge density and reduce interaction efficiency with target pollutants.[26,61] This inadequate long-term stability and the challenge of determining an adequate shelf life pose significant obstacles for industrial implementation.[59]

9.1.2 Low adsorption capacity of bulk chitosan. In bulk form, chitosan has a low adsorption capacity due to its small surface area,[33] which nanochitosan can mitigate, but the high cost of synthesis remains a barrier. Additionally, a standardization of chitosan derivatives is needed to ensure consistent treatment results, and separating and regenerating fine particles post-treatment poses operational difficulties. POME's complex composition complicates the efficiency of pollutant removal.

9.1.3 Standardization and consistency. There is a recognized need to standardize the description of chitosan derivatives, especially concerning molecular weight and degree of deacetylation.[62] Inconsistencies in commercial production can affect the reliability and reproducibility of treatment outcomes.[59]

9.1.4 Separation and regeneration. After treatment, separating the chitosan or nanochitosan from the treated effluent can be a challenge, particularly for very fine particles. While magnetic modifications can aid separation,[32] efficient and cost-effective regeneration for multiple reuse cycles remains an area for improvement.

9.1.5 Complex POME composition. Another key limitation may lie in the heterogeneity of POME itself. The coexistence of high organic load, suspended solids, oil residues, and metal ions introduces competitive interactions that can suppress selective adsorption and reduce overall removal efficiency.[17] While chitosan and nanochitosan are versatile, optimizing their performance for the simultaneous removal of all these diverse pollutants can be challenging. Addressing this complexity requires materials that maintain functional performance under non-ideal, multicomponent conditions.

9.1.6 Economic viability at scale. While chitosan production can be economically viable,[63] the overall cost-effectiveness of implementing chitosan or nanochitosan treatment systems at the large industrial scale required for palm oil mills needs further validation. This includes capital expenditure, operational costs, and the cost of raw materials.

These challenges underscore the importance of rational material design strategies, including controlled deacetylation, surface functionalization, and composite formation, to enhance stability, selectivity, and durability without compromising adsorption efficiency.

9.2 Future research directions and outlook

The unique characteristics of chitosan and nanochitosan position them at the forefront of technological innovation for environmental sustainability. Future research and development efforts should focus on overcoming current limitations to unlock their full potential in POME treatment:

Advanced functionalization and derivatization: designing novel chitosan derivatives for specific applications is a priority.[62] This includes modifying chitosan to improve its solubility across a wider pH range, enhancing its mechanical strength and stability, and increasing its selectivity for particular pollutants (*e.g.*, specific heavy metals or recalcitrant organic compounds).[33] Research into covalent cross-linking and graft copolymerization can create more robust and efficient materials.[39]

Sustainable production and green processing: continued focus on green extraction methods and eco-friendly processing techniques for both chitin and chitosan is essential.[62] Exploring alternative, sustainable sources like fungal fermentation, which offer advantages such as seasonal independence and freedom from heavy metal contamination, should be prioritized.[27]

Mechanistic insights: deeper elucidation of the biological and chemical interactions between chitosan/nanochitosan and various POME pollutants will allow for more targeted and efficient material design.[62] Understanding the precise mechanisms of degradation and stability will also inform storage and application strategies.[59]

Integration into smart biomaterials and hybrid systems: developing multifunctional systems by integrating chitosan/nanochitosan with other materials (*e.g.*, magnetic nanoparticles, other polymers, or advanced oxidation processes) can create hybrid adsorbents with enhanced performance and easier separation capabilities.[32] Combining chitosan coagulation with advanced oxidation processes (AOPs), for instance, has shown improved COD and TSS removal.[51]

Pilot-scale and industrial implementation studies: moving beyond laboratory conditions to conduct more pilot-scale and full-scale studies is crucial to validate performance, optimize operational parameters, and assess the long-term economic viability and scalability of chitosan-based POME treatment systems under real-world conditions.[1]

Standardization and regulation: the development of international quality standards for chitosan derivatives is imperative to ensure consistency, facilitate commercialization, and build confidence in their application in environmental remediation.[62]

The ongoing development and application of chitosan in both scientific and industrial sectors depend heavily on these further explorations. Chitosan-based materials hold immense potential to contribute significantly to environmental sustainability and improved wastewater management, particularly in industries like palm oil production. The advancements highlighted in current research underscore the dynamic and evolving landscape of chitosan science, promising more effective and sustainable solutions for complex industrial wastewater challenges.

Significant obstacles to widespread implementation encompass scalability, regeneration efficiency, economic feasibility, and environmental safety. This underscores the necessity for future research to emphasize system-level optimization, standardization, and empirical validation in practical contexts.

10. Conclusions

Nanochitosan has emerged as a promising bio-derived adsorbent capable of overcoming the limitations of bulk chitosan through its higher surface area, greater accessibility of functional groups, and multiple pollutant-removal mechanisms in palm oil mill effluent (POME) treatment. Evidence reviewed indicates that nanochitosan enhances treatment efficiency across different stages of the process. As a primary coagulant, it significantly improves turbidity removal and dealkalization compared to bulk chitosan. When applied as a polishing step after biological treatment, nanochitosan effectively removes residual COD, colour, and heavy metals through mechanisms including electrostatic interactions, chelation, and hydrogen bonding. Nanochitosan can help meet regulatory discharge standards when used in multi-stage treatment systems. It also makes less sludge than traditional inorganic coagulants.

Beyond treatment efficiency, nanochitosan supports a more sustainable and circular approach to POME management. By improving effluent quality prior to downstream processing, it can enhance anaerobic digestion and biogas recovery while enabling nutrient recovery for potential reuse in agriculture. The use of chitosan derived from crustacean or fungal sources further contributes to waste valorisation and resource efficiency, as it allows for the conversion of waste materials into valuable products, thereby reducing environmental impact and promoting sustainability. These advantages point to the power of nanochitosan to transform POME management from a pollution-control challenge into an opportunity for resource recovery within a circular bioeconomy framework.

Despite these advances, large-scale industrial implementation still faces several challenges. Future research should focus on scalable and environmentally benign synthesis approaches, improved regeneration and reuse of nanochitosan materials, techno-economic comparisons with established treatment technologies, and comprehensive ecotoxicological assessments of potential nanoparticle release. Addressing these priorities will be essential for translating laboratory-scale success into practical, sustainable solutions for POME treatment and broader wastewater management applications. Hence, nanochitosan constitutes a promising, albeit not fully realized, approach for the treatment of palm oil mill effluent (POME), with its optimal efficacy likely residing in integrated systems rather than isolated applications. The successful implementation of this biopolymer is contingent upon addressing significant technical, economic, and environmental hurdles.

Author contributions

Ramat Onyeneoyiza Raji: conceptualization, writing – original draft, investigation. Helen Shnada Auta: writing – review & editing, supervision. Oluwafemi Adebayo Oyewole: writing – review & editing, supervision. Olabisi Peter Abioye: writing – review & editing, supervision. Abdulrazaq Izuafa: investigation, visualization, software.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

No new data were generated or analyzed in this study. All information presented in this article is derived from previously published literature, and the sources are cited within the manuscript.

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