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Influence of acid leaching on biosilica particles derived from palm oil fuel ash (POFA) for cationic dye removal

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Palm oil fuel ash (POFA) is an agricultural waste residue rich in silica, which constitutes up to 60% of its chemical composition. This study investigates the extraction of biosilica particles from POFA using a hydrochloric acid (HCl) leaching pretreatment, with a focus on the effect of a relatively low acid concentration on the product yield. Biosilica particles treated with 1 M HCl (nS-1MHCl) exhibited 11% higher yield compared to untreated POFA (nS-0MHCl). The physicochemical characteristics of the extracted biosilica particles were examined using Fourier-transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). FESEM micrographs revealed spherical silica particles with relatively uniform sizes and the presence of surface pore cavities. In batch adsorption experiments, the leached nS-1MHCl sample achieved a maximum methylene blue (MB) removal efficiency of 94% over an initial MB concentration range of 10–50 ppm. Collectively, these findings demonstrate that extracting biosilica particles from POFA for MB removal represents a viable strategy for valorizing agricultural waste ash into high-value products.

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1 Introduction

In the pursuit of sustainable green technology, biosilica particle development has attracted significant research attention across various industries. Biosilica particles refer to silica (silicon dioxide) particles synthesized from biomass or agricultural waste ash rich in silicon. Palm oil fuel ash (POFA) is a byproduct generated during the high-temperature combustion (700–1000 °C) of palm oil shells and empty fruit bunches.^{1,2} The volume of this waste has risen alongside the increase in palm oil production, particularly in Malaysia, the world's second-largest producer. The distinctive tropical climate and land availability in Malaysia have positioned the country to contribute 25.8% and 34.3% of global palm oil production and exports, respectively.^{3–5} As demand for palm oil surges, waste generation

inevitably increases;⁶ it is reported that approximately 5% of POFA is generated during production.

The increasing volume of POFA poses critical environmental risks, particularly to residents living near plantations. The fine, lightweight particles of POFA dumped in open fields can be easily dispersed by wind and may infiltrate groundwater systems, leading to air pollution and water contamination.^{2,5,7} Consequently, transforming POFA into a value-added resource has become a significance research area.⁵ POFA is recognized as a supplementary cementitious material (SCM) due to its high silica content (50–60%), which improves the cement hydration process, enhancing the durability and strength of concrete and mortar.^{5,8,9}

The high silica content in POFA makes it an ideal source of biosilica particles, offering an alternative to rice husk ash and sugarcane bagasse ash for applications such as water treatment. The chemical precipitation method (alkaline dissolution followed by sol-gel formation) is considered the most effective, simplest, and safest extraction technique, offering low energy consumption and high homogeneity.^{10–12} In this process, silica is extracted from the ash by reacting it with sodium hydroxide (NaOH) to produce a sodium silicate solution, which is then transformed into silica gel *via* pH reduction. Sol-gel approaches offer distinct advantages over other methods, such as direct calcination, including the ability to produce monodisperse silica with high yield, excellent quality, and flexibility in

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modification.¹³ However, without pretreatment, the high levels of metallic oxide impurities and carbon in agro-waste ash hinder silica extraction during alkaline dissolution, reducing both purity and yield.^{11,14,15}

Acid leaching is a pretreatment method for eliminating metallic oxides from agro-waste ash. Removing these oxides increases the available active surface area for the extraction reaction, resulting in higher-quality, higher-quantity biosilica particles.^{11,16} Acid treatment promotes the protonation of the adsorbent surface, thereby strengthening the positive surface charge density to attract and remove metal oxides.^{17,18} This hypothesis is supported by previous studies that successfully produced biosilica particles from rice husk ash with purities ranging from 95 to 99% using acid leaching and chemical precipitation.^{11,19–21} Recent studies by ref. 22 and 23 extracted biosilica particles from sugarcane bagasse ash using acid-leaching pretreatment with recorded purities of 96.8% and 98.4%, respectively. Nevertheless, the effectiveness of oxide removal depends significantly on the type of acid reagent used.

Previous studies indicate that the silica content in rice husk ash leached with hydrochloric acid (HCl) increased to 99.7%, whereas leaching with phosphoric acid (H_3PO_4) and sulphuric acid (H_2SO_4) yielded silica contents of 73.4% and 97.4%, respectively.¹⁵ Major impurities in rice husk ash, such as potassium and calcium, are easily removed by HCl,²⁴ while iron oxides are better removed by H_3PO_4 and H_2SO_4 . Oxide impurities in agro-waste ash are strongly attracted to chloride ions (Cl^-) from HCl, forming soluble salt compounds that are separated *via* filtration.^{11,25} A study conducted by ref. 24 discovered that HCl provides optimal removal of alkali and alkaline earth metals from rice husk compared to citric acid. However, current methods for extracting silica from POFA predominantly use citric acid for leaching.

Synthetic and organic dyes, particularly methylene blue (MB), are major pollutants in industrial wastewater.^{26–28} MB is a cationic dye extensively used in textiles, cosmetics, food, pharmaceuticals, and paper industries.²⁹ High exposure to MB poses toxicity risks to human health and causes anoxic conditions in plants.^{30–32} Coincidentally,³³ reported that an estimated 10–15% of synthetic dyes are discharged into water bodies. Consequently, various wastewater remediation methods have been employed.^{34–41} However, adsorption technology has emerged as a promising remediation strategy due to its high efficiency, low concentration requirements, affordability, and technological simplicity.^{31,32} Nano-sized silica has been extensively applied for the separation and removal of synthetic dyes due to its high surface area, uniform pore structure, low toxicity, high stability, and tunable functionalization.^{18,32} Previous studies have reported that the adsorption mechanisms governing the interaction between contaminant molecules and nano-silica include electrostatic interactions, hydrogen bonding, and π – π stacking.^{31,32,42}

While silica is often grafted onto other compounds to produce composite adsorbents.^{18,32,43} The utilization of extracted silica particles, particularly those derived from rice husk, holds promise.^{31,42} However, investigations into the use of bio-based silica particles extracted specifically from POFA as

a standalone adsorbent, without additional modification is underexplored. Furthermore, existing POFA silica extraction methods predominantly employ high-temperature leaching with organic acids such as citric acid.⁴⁸ The novelty of the present work lies in employing room-temperature leaching with dilute (1 M) HCl as a safer, energy-efficient alternative to concentrated organic acids. Incorporating a re-ashing pretreatment step specifically optimized for POFA and providing quantitative yield comparisons between leached and unleached samples. The study further proposed a comprehensive mechanistic framework for MB adsorption onto POFA-derived biosilica. Therefore, this study aims to synthesize biosilica particles from POFA *via* HCl leaching at room temperature combined with re-ashing pretreatment, followed by chemical precipitation, and evaluate their MB dye removal performance.

2 Experimental

2.1 Materials

Raw POFA was obtained from the Bau Palm Oil Mill (BAPOM), Sarawak, Malaysia. Before pretreatment and extraction, the raw POFA was dried in an oven for 24 h at $110 \pm 10^\circ\text{C}$, sieved to 300–200 μm to remove large particles, and subsequently ground. The chemicals used were NaOH pellets and 40% w/v HCl obtained from J. T. Baker (Phillipsburg, NJ). The MB dye was obtained from Merck KGaA (Darmstadt, Germany). All chemicals were diluted to the required concentrations using distilled water (DW).

2.2 Pretreatment of POFA

The acid leaching process was initiated by adding 40 g of POFA into a 1 M HCl solution (1:10 mass-to-volume ratio) with constant vigorous stirring at room temperature for 2 h. The beaker was covered with aluminum foil during leaching to prevent evaporation. The solution was filtered under vacuum, and the black residue was collected and washed with DW until a neutral pH (7) was achieved. The residue was subsequently oven-dried at $110 \pm 5^\circ\text{C}$ for 24 h. Both the leached POFA and the unleached POFA underwent a re-ashing process in a muffle furnace for 2 h at 600°C . The thermally treated samples were collected, weighed, and denoted as treated POFA (TPOFA).

2.3 Synthesis of biosilica particles *via* chemical precipitation

Biosilica particles were extracted using the chemical precipitation methods *viz.* alkaline dissolution followed by sol–gel extraction. Initially 2.5 M NaOH solution was prepared and heated to $80 \pm 5^\circ\text{C}$ with constant stirring at 500 rpm. The solution was covered with aluminum foil before adding TPOFA at a 1:10 ratio (TPOFA mass to NaOH volume). The mixture was reacted for 4 h, then cooled to room temperature ($25 \pm 2^\circ\text{C}$). The solution was filtered *via* vacuum filtration; the filtrate (sodium silicate) was retained for the sol–gel process, while the ash residues were discarded. A 1 M HCl solution was added dropwise to the sodium silicate filtrate with slow, constant stirring until the pH reached 7.

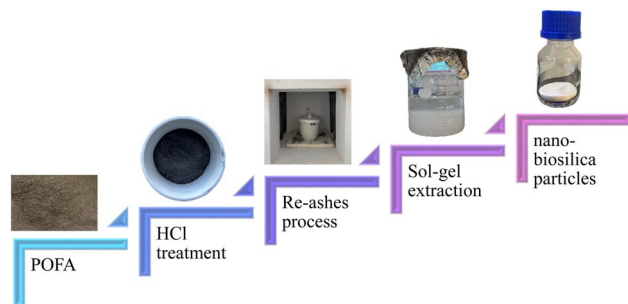


Fig. 1 Schematic flowchart illustrating the synthesis of biosilica particles from palm oil fuel ash (POFA).

The dropwise addition of HCl promotes the precipitation of fine silica particles. Silica gel formation was observed when the solution pH reached 10–11, indicated by the appearance of a cloudy white precipitate. The biosilica particles gel was aged for 24 h before being gently broken to form a slurry. The slurry was washed with DW and centrifuged. Finally, the biosilica particles gel was dried in an oven for 24 h at 100 ± 5 °C and stored in glass bottles for characterization. A flow-chart describing the synthesis procedure is shown in Fig. 1.

2.4 Characterization

The extraction yield (%) of the biosilica particles were calculated based on eqn (1), where M_{silica} is the mass of solid silica obtained and M_{TPOFA} is the mass of TPOFA. The chemical composition was analyzed using energy-dispersive X-ray (EDX) spectroscopy. EDX data for raw POFA was included to compare the silica and other chemical compounds present. Field-emission scanning electron microscopy (FESEM) coupled with EDX (JSM-IT500HR; JEOL, Tokyo, Japan) were used to investigate the morphology of biosilica particles and POFA at magnifications ranging from $250\times$ to $500\,00\times$. Samples were gold-coated before analysis. Functional groups were examined using a Fourier Transform Infrared (FTIR) analyzer (IRAffinity-1; Shimadzu Kyoto, Japan) in transmittance mode over a range of 4000 cm^{-1} . Phase structures were identified by X-ray diffraction (XRD) (MiniFlex 600; Rigaku, Tokyo, Japan) with a scan range of 2θ and a rate of 2° min^{-1} .

$$\text{Silica yield percentage (\%)} = \frac{M_{\text{silica}}}{M_{\text{TPOFA}}} \times 100 \quad (1)$$

2.5 Adsorption performance of biosilica particles

A stock solution of 100 ppm MB dye was prepared by dissolving 0.1 g of MB dye in a 1 L volumetric flask. The stock solution was diluted with DW to acquire various concentrations (10–50 ppm) using the $C_1V_1 = C_2V_2$ relation. A standard curve was generated by UV-vis spectrometry at 664 nm and used as a baseline for measuring pre- and post-adsorption concentrations.

For the adsorption experiments, 0.05 g of biosilica particles (nS-1MHCl) was added to 0.1 L of MB solution at varying concentrations (10, 20, 30, 40, and 50 ppm) at room temperature with a fixed stirring rate of 300 rpm for 50 min. The experimental design matrix is summarized in Table 1. Approximately 10 mL of the solution was withdrawn at 10 minute intervals and subsequently centrifuged at 25 000 rpm for 7 minutes. The resulting supernatant was then collected to determine the residual concentration of methylene blue (MB) via UV Vis. The equilibrium adsorption capacity, q_e (mg g^{-1}), and percentage removal, $R\%$, were calculated using eqn (2) and (3), respectively, where C_0 is the initial MB concentration (ppm), $C_{e,t}$ is the residual concentration at time t (ppm), V is the volume of the solution (L), and m is the mass of the adsorbent (g).

$$\text{Equilibrium adsorption capacity, } q_e = \frac{(C_0 - C_{e,t}) \times V}{m} \quad (2)$$

$$\text{Percentage removal, } R\% = \frac{(C_0 - C_{e,t})}{C_0} \times 100 \quad (3)$$

2.6 Adsorption isotherm and kinetics study

2.6.1 Adsorption isotherms. Adsorption isotherm describes the correlation between the adsorption capacity at equilibrium, q_e and the contaminants concentration in the surrounding medium at constant temperature and pH.^{44,45} Langmuir and Freundlich isotherm model are widely utilized for analyzing experimental adsorption data and elucidating the adsorption behavior. The Langmuir model posits monolayer adsorption on homogenous surfaces with uniform adsorption sites, where interaction between adsorbed molecules is negligible, as described in eqn (4).^{44,46}

$$\text{Langmuir model equation, } q_e = \frac{Q_{\text{max}} K_L C_e}{1 + (K_L C_e)} \quad (4)$$

where Q_{max} (mg g^{-1}) is the maximum adsorption capacity, K_L (L mg^{-1}) is a Langmuir model equilibrium constant and C_e is the solution concentration at equilibrium.

Table 1 Experimental design matrix for the adsorption of methylene blue (MB) by biosilica particles

Bio-silica, m (g)	MB initial concentration, C_0 (ppm)	Solution volume, V (L)	Stirring speed, ω (rpm)	Contact time, t (min)
0.05	10	0.1	300	50
0.05	20	0.1	300	50
0.05	30	0.1	300	50
0.05	40	0.1	300	50
0.05	50	0.1	300	50

Table 2 The type of adsorption through adsorption intensity, $1/n$

$1/n$	Adsorption
$\frac{1}{n} > 1$	Unfavorable
$0 < \frac{1}{n} < 1$	Favorable
$\frac{1}{n} = 1$	Linear

On the other hand, the Freundlich model characterizes the adsorption process on heterogeneous surfaces permitting interaction among adsorbed molecules that facilitate multilayer adsorption, as articulated in eqn (5).⁴⁴

$$\text{Freundlich model equation, } q_e = K_F C_e^{\left(\frac{1}{n}\right)} \quad (5)$$

K_F denote the Freundlich constant indicative of adsorption capacity while $1/n$ is the adsorption intensity utilized for determining the type of adsorption (Table 2). The smaller the $1/n$ value, the higher the heterogeneity of the adsorbent.^{18,44}

2.6.2 Adsorption kinetic study. Adsorption kinetics were employed to investigate the rate of adsorption process and the time required to obtain equilibrium conditions, providing information on the pathways and mechanisms during the adsorption process at solid–liquid interface.⁴⁷ The pseudo-first order kinetics, pseudo-second order kinetics and intraparticle diffusion kinetics models described from eqn (6)–(8) were utilized.

$$\text{Pseudo-first order model equation, } q_t = q_e(1 - e^{-K_1 t}) \quad (6)$$

$$\text{Pseudo-second order model equation, } \frac{d(q_t)}{dt} = K_2(q_e - q_t)^2 \quad (7)$$

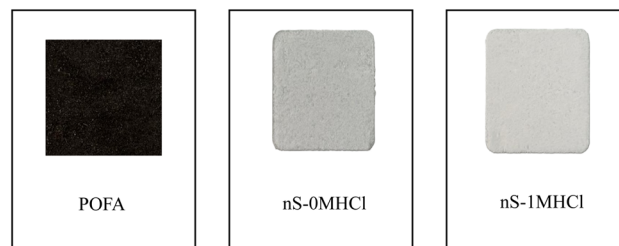
$$\text{Intraparticle-diffusion model equation, } q_t = K_p t^{0.5} + C \quad (8)$$

where; q_t (mg g^{-1}) is the amount of adsorbate adsorbed at time, t (min) while K_1 (min^{-1}), K_2 ($\text{g mg}^{-1} \text{min}^{-1}$), and K_p ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the rate of constant of pseudo-first order adsorption, rate of constant of pseudo-second order and intraparticle diffusion constant respectively. It is imperative to note that the pseudo-first order model assumes sites occupied by contaminants to be proportional to the unoccupied sites and govern by the first-rate order reaction while pseudo-second order adsorption model follow the second-order reaction rate *via* chemisorption process.^{42,47} The intraparticle diffusion model stipulates the involvement of diffusion within the pores, with the adsorption rate following the sole rate-limiting step where the linear fit passes through origin ($C = 0$).^{33,47}

3 Results and discussion

3.1 Analysis of extraction yield and physical appearances

Extraction of POFA leached with 1 M HCl (nS-1MHCl) produced a 17% yield of biosilica particles, compared to only 6% from POFA without HCl leaching (nS-0MHCl). Fig. 2 shows the

**Fig. 2** Physical appearance of POFA, unleached biosilica particles (nS-0MHCl) and acid-leached biosilica particles (nS-1MHCl).

physical appearance of POFA, unleached and leached extracted biosilica particles.

Physically, nS-1MHCl appeared as a bright white powder, while nS-0MHCl particles were greyish, as observed in Fig. 2. The leaching treatment resulted in an 11% absolute increase in yield. This improvement is attributed to the removal of metal impurities during leaching, which otherwise hinders silica dissolution during chemical precipitation. Furthermore, removing impurities enlarges the pores, thereby increasing the surface area of the POFA and enabling more effective silica extraction.⁴⁸ High impurity levels reduce the available surface area for silica dissolution in NaOH, leading to poor extraction performance even at high alkali concentrations.^{11,48} Previous studies on rice husk ash have similarly reported a 9% increase in silica content following HCl leaching due to significant reductions in oxide impurities.¹¹ Additionally, the re-ashing process, which reduces carbon and organic content, has been shown to increase the relative abundance of biosilica particles.⁴⁸ The 10% to 17% silica yield range with high whiteness indices reported by ref. 48 validates the findings of this study.

3.2 Energy-dispersive X-ray (EDX) analysis

The elemental composition of the biosilica particles and raw POFA are presented in Table 3 and Fig. 3 respectively. POFA was found to contained carbon (C) as the dominant element, followed by oxygen (O), silicon (Si), calcium (Ca), potassium (K), magnesium (Mg), and aluminum (Al). It aligns with previous studies indicating the presence of silicon dioxide (SiO_2), calcium oxide (CaO), aluminum oxide (Al_2O_3), magnesium oxide (MgO), and potassium oxide (K_2O) in POFA.⁵ The high carbon content is likely present as carbonate and char.^{48,49}

Table 3 The elemental composition (%) of POFA and extracted biosilica particles determined by EDX analysis

EDX element	POFA (%)	nS-0MHCl (%)	nS-1MHCl (%)
O	34.43	57.18	57.97
Si	6.85	30.44	35.91
Al	0.67	1.43	0.91
Mg	1.02	Not detected	Not detected
Ca	4.85	Not detected	Not detected
K	2.93	0.55	Not detected
C	49.25	6.86	4.04
Na	Not detected	2.56	1.17
Cl	Not detected	0.98	Not detected
Total	100.00	100.00	100.00

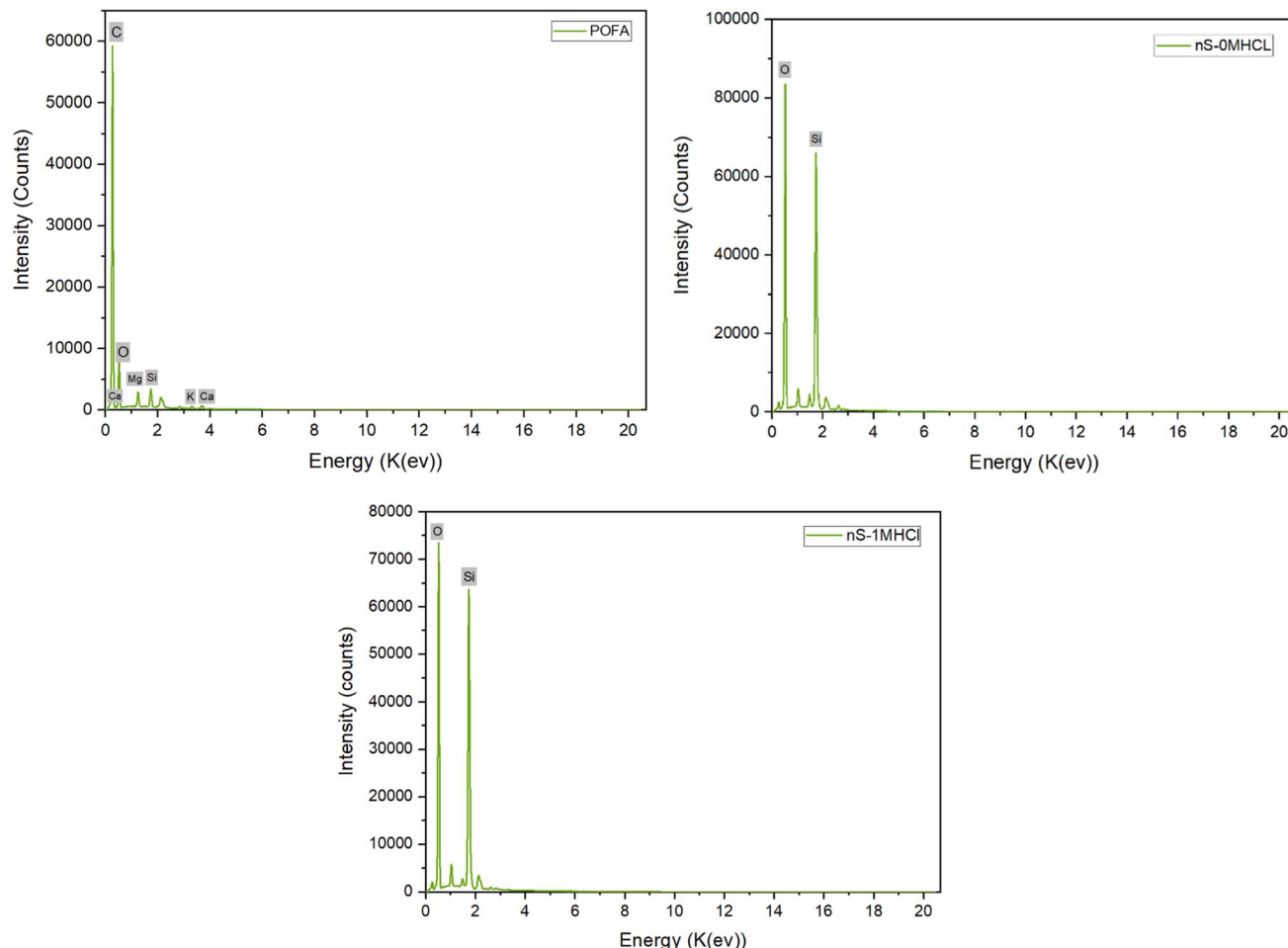


Fig. 3 Energy-dispersive X-ray (EDX) spectra of raw POFA, unleached biosilica particles (nS-0MHCl), and acid-leached biosilica particles (nS-1MHCl).

The extracted biosilica particles exhibited high Si and O contents with minimal carbon and metal impurities, demonstrating the efficacy of NaOH in dissolving silica. Although EDX is not an absolute confirmation of particle purity, however the reduced surface silica content and lower yield of nS-0MHCl (Si: 30.44%, O: 57.18%) relative to nS-1MHCl (Si: 35.91%, O: 57.97%) corroborate the critical role of acid leaching in the synthesis process. Without leaching, the NaOH solution becomes saturated with impurities rather than silica, inhibiting dissolution.⁴⁸ Similar research findings reported significant increase in biosilica particles purity *via* chemical leaching.⁵⁰

HCl leaching successfully eliminated K, Ca, and Mg from the nS-1MHCl sample, leaving negligible Al, similar to findings for citric acid-leached POFA.⁴⁸ During leaching, metal oxides are attracted to Cl^- ions, forming soluble salts that are removed *via* filtration. Alkali metal ions, bound in the POFA matrix as salts or covalent compounds, form weak complexes with the acidic reagent, facilitating their release into the acidic media.^{24,51} The residual carbon detected in biosilica particles is likely present as carbonates formed during alkaline dissolution or as adsorb char due to incomplete washing.⁴⁹ The minor Al presence originates from the raw POFA, while Cl detected in nS-0M HCl

(see Table 3) likely originates from the HCl used in the sol-gel precipitation step.

These findings have practical implications for POFA valorization. Current work demonstrates that 1 M HCl leaching at room temperature produces biosilica particles with yields and chemical compositions comparable to those obtained using 6% citric acid at 100 °C.⁴⁸ Vigorous stirring appears to influence the reaction between metallic and chloride ions more significantly than temperature.¹¹ The work reported that acid leaching of rice husk at 25 °C and 80 °C produced similar silica compositions (~95%). Thus, room-temperature leaching with vigorous stirring offers a more straightforward, safer, and less energy-intensive approach. Furthermore, lower pH during leaching encourages surface protonation, increasing positive surface charge density and enhancing metal ion removal.⁵² Consequently, dilute aqueous HCl is a favorable alternative to higher concentrations of organic acids.

3.3 Field emission scanning electron microscopy (FESEM) analysis

The morphological structures of POFA and the extracted biosilica particles were analyzed *via* FESEM at magnifications of

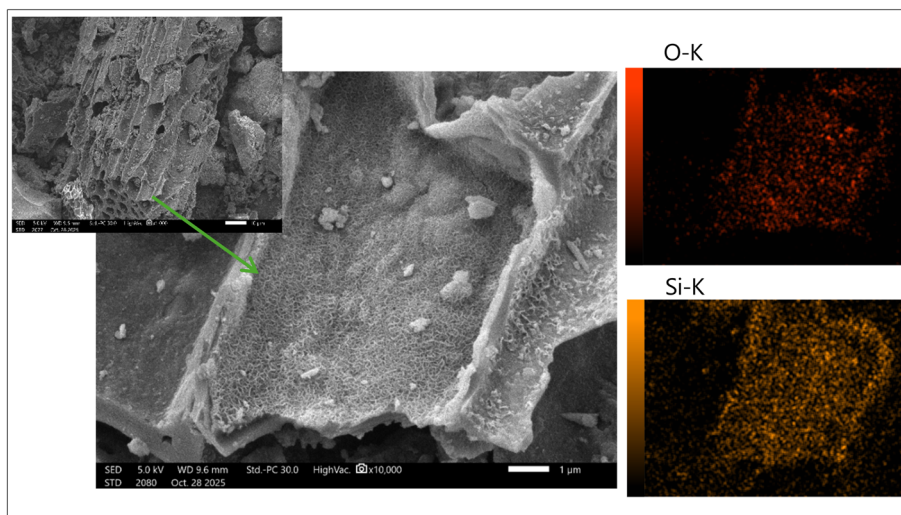
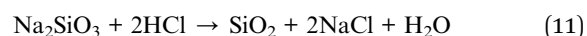
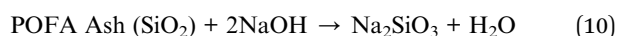


Fig. 4 The FESEM micrographs and EDX elemental mapping (Si and O) of raw POFA, revealing the silica distribution within the ash matrix.

10 000 $\times$ and 50 000 $\times$, respectively. In raw POFA (Fig. 4), silica appears as a restrained structure forming an irregular honeycomb-like framework within the fiber. EDX elemental mapping confirms that silica is predominantly concentrated on the inner walls of the POFA fiber, effectively acting as a natural structural template for the palm oil kernel shells and empty fruit bunches. This silica forms a 3D nanostructure skeleton alongside organic compounds, functioning as a structural framework and a protective outer layer absorbed by the plant roots and transported to the epidermis.^{53–55}

Through chemical precipitation (refer to eqn (10) and (11)), the silica particles potentially transformed into spherical structures (Fig. 5 and 6).¹¹ reported similar approach, where FESEM micrographs revealed spherical silica particles with an average size less than 100 nm.



The leached nS-1MHCl particles (Fig. 6) were observed to be uniformly dispersed with relatively consistent particle sizes, whereas the nS-0M HCl sample (Fig. 5) displayed an uneven particle distribution with irregular particle sizes. However, it is imperative to note that primary particles were estimated *via* FESEM as shown in Fig. 5 and 6 respectively. There is no quantitative size distribution reported in this study.

The biosilica particles in the leached sample tended to attach and overlap, forming clusters of “bio-silica stones”. Potential agglomeration (indicated by red circles) in both samples could be attributed to the dominance of strong cohesive intramolecular forces, given the potential high surface-to-volume ratio of the synthesised nanoparticles.^{11,56,57} While agglomeration is often seen as a defect, it equally promotes the

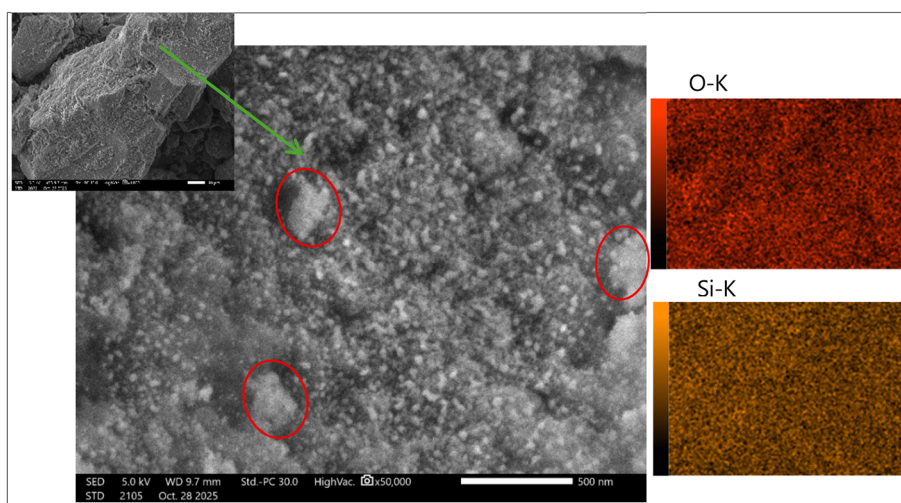


Fig. 5 The FESEM micrograph and EDX elemental mapping (Si and O) of unleached biosilica particles (nS-0M HCl).

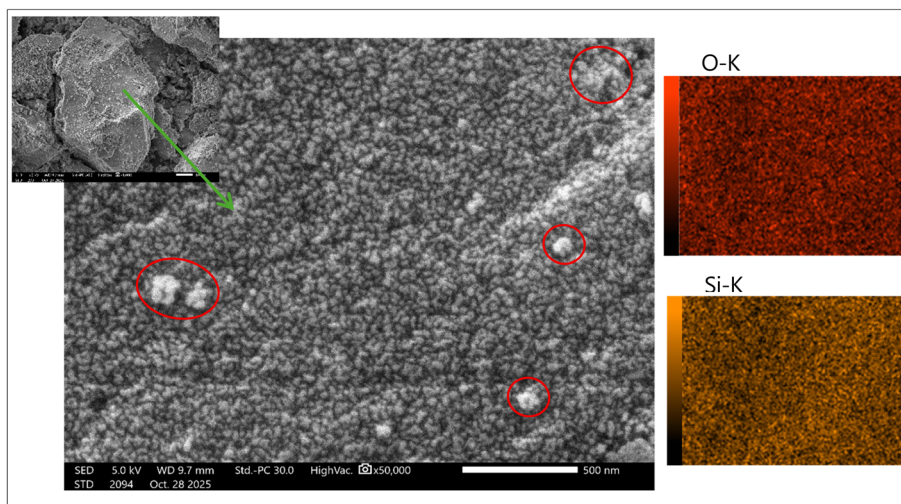


Fig. 6 FESEM micrograph and EDX elemental mapping (Si and O) of acid-leached biosilica particles (nS-1MHCl).

formation of pore cavities,⁵⁸ which increases the number of available adsorption sites. The achievement of such fine particle sizes was facilitated by the controlled gelation rate achieved through dropwise acid addition during synthesis, consistent with previous methodologies.^{11,59}

3.4 Fourier Transform Infrared (FTIR) analysis

FTIR spectra (Fig. 7) confirm the successful extraction of biosilica particles by the presence of characteristic siloxane (Si–O–Si) and silanol (Si–OH) groups. The primary silica fingerprints were observed at 400–1100 cm^{-1} and 3400 cm^{-1} , respectively. The increased intensity of the Si–O–Si and Si–OH bonding in the extracted samples compared to the raw POFA verifies the efficacy of the extraction process. Both nS-1MHCl and nS-0MHCl displayed characteristic siloxane peaks: a sharp, intense peak at 470 cm^{-1} (bending vibration) and a peak at 790 cm^{-1} (symmetric stretching). These findings align with literature reporting asymmetric stretching of siloxane groups typically between 790–801 cm^{-1} , bending vibrations at 450–470 cm^{-1} , and asymmetric stretching vibrations at 1050–1070 cm^{-1} .^{10,11,23,56,60}

The absorption peak at 1061 cm^{-1} in Fig. 7 indicates asymmetric stretching of the Si–O–Si group. The nS-0M HCl sample exhibited a sharper peak in this region compared to nS-1MHCl, likely due to the overlapping Al–O stretching caused by a higher concentration of Al_2O_3 impurities.⁶¹ The Si–OH stretching vibrations were identified by a small peak at 940 cm^{-1} .⁶⁰ Additionally, a broad peak at 3387 cm^{-1} and a smaller peak at 1635 cm^{-1} correspond to O–H and H–O–H stretching vibrations, respectively, indicating the presence of adsorbed water molecules.^{11,23,57} Spectral bands detected between 3600–3770 cm^{-1} signify the existence of isolated silanol groups; specifically, the 3600–3780 cm^{-1} band represents the tail of the low intensity O–H vibration reflecting possible overlap with residual O–H bending from absorbed moisture.^{62,63}

Notably, the nS-0M HCl spectrum showed strong intensity in the 1700–2900 cm^{-1} region, indicating the presence of organic

molecules and impurities such as alkali and alkaline earth metals.^{11,56} Specific impurity indicators included peaks at 2139 cm^{-1} (alkane C–H activation influenced by Al_2O_3 clusters).^{61,63,64} The contrast demonstrates the effectiveness of the acid-leaching pretreatment in reducing impurities. However, the continued presence of minor Al, C, and Na (Table 3) suggests that byproducts such as NaCl may have been retained due to incomplete washing.^{11,65}

3.5 X-ray diffraction (XRD) analysis

The XRD diffractograms (Fig. 8) reveal that the extracted biosilica particles is predominantly amorphous, characterized by a broad hump centered at 22.9° for nS-1MHCl and 23.43° for nS-0MHCl, with an absence of definite crystalline peaks. The broad peak structure (ranging from 15° to 35°) results from the high solubility of amorphous silica in NaOH solution and its subsequent precipitation as a gel (Easwaran *et al.*, 2022;

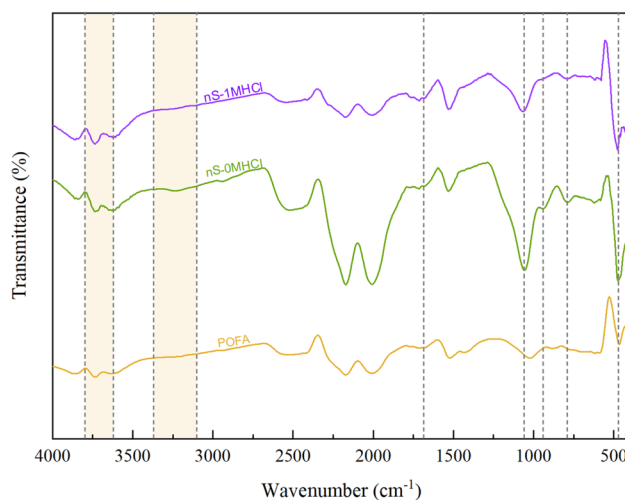


Fig. 7 The FTIR spectra of raw POFA, acid-leached biosilica particles (nS-1MHCl) and unleached biosilica particles (nS-0MHCl).

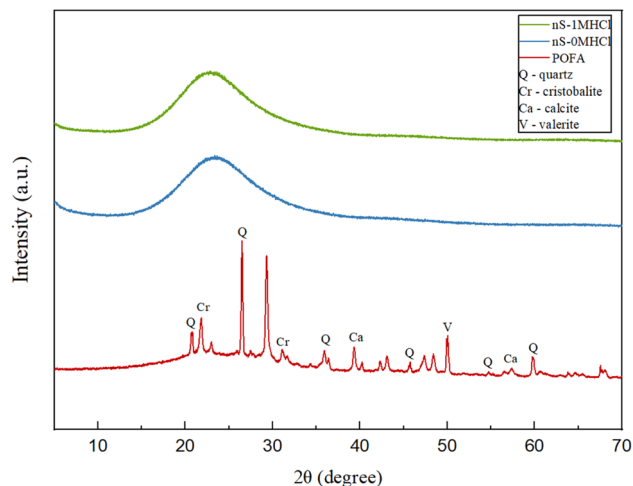


Fig. 8 The X-ray diffraction (XRD) pattern of raw POFA, acid-leached biosilica particles (nS-1MHCL), and unleached biosilica particles (nS-0MHCL).

Ebtasam *et al.*, 2025; Elanthikkal *et al.*, 2023). The amorphous nature is highly advantageous for adsorption applications due to the material's increased porosity, reactivity, and non-hazardous properties.^{11,53,66}

In contrast, the raw POFA displayed sharp peaks indicating crystalline phases, primarily quartz and cristobalite, at 2θ angles of 20.82° , 26.48° , 36.22° , 39.38° , 47.32° , and 50.04° . Previous studies have noted that POFA typically exhibits silica properties in quartz and cristobalite phases ranging from 26° to 51° , often accompanied by potassium aluminum phosphate.⁵ Furthermore, the specific cristobalite pattern in POFA is usually indicated by an intense peak at 21.9° , with less intense lines at 28° , 32° , 36° , and 47.5° .⁶⁷ Additionally, diffraction patterns indicative of calcium carbonate in its calcite and vaterite phases were observed from the raw POFA, with peaks appearing at

approximately 29.4° and 21° , respectively.^{68,69} The visible small hump between 15° and 40° in the POFA spectrum suggests the presence of some amorphous glassy material, categorizing the raw ash as a semi-crystalline material.^{5,48,70}

3.6 Adsorption performance of biosilica particles

3.6.1 Influence of acid leaching process. The removal efficacy of the leached (nS-1MHCL) and unleached (nS-0MHCL) biosilica particles was studied with an initial MB concentration fixed at 10 ppm for 50 minutes, as presented in Fig. 9(a and b). The nS-1MHCL portrays an excellent adsorption ability compared to nS-0MHCL with an approximately 18% to 24% higher. The elimination of metal impurities in the extracted biosilica particles through acid leaching process enhanced the adsorption performance of the adsorbent. This finding was consistent with previous literature, in which chemical treatment of rice husk ash with HCl significantly improved the dye removal efficiency and adsorption capacity of the extracted biosilica particles in aqueous media.⁷¹ Therefore, nS-1MHCL was selected as the primary subject for subsequent adsorption performance evaluation.

The nS-1MHCL adsorbent demonstrated effective cationic dye removal, achieving minimum and maximum percentage removal of 91 and 94%, respectively, at initial MB concentrations ranging from 10 to 50 ppm. This quantitative performance was corroborated by physical observations, in which the dark blue aqueous solution gradually turned light, semi-transparent blue, indicating successful adsorption by the nS-1MHCL adsorbent.

3.6.2 Influence of initial MB concentration. To investigate the adsorption capacity and removal efficiency of nS-1MHCL, the initial MB concentration was varied from 10 to 50 ppm, while other parameters were kept constant (Table 1). As illustrated in Fig. 10, the dye removal percentage (R%) ranged from 91 to 94%, with the highest efficiency recorded at the lowest

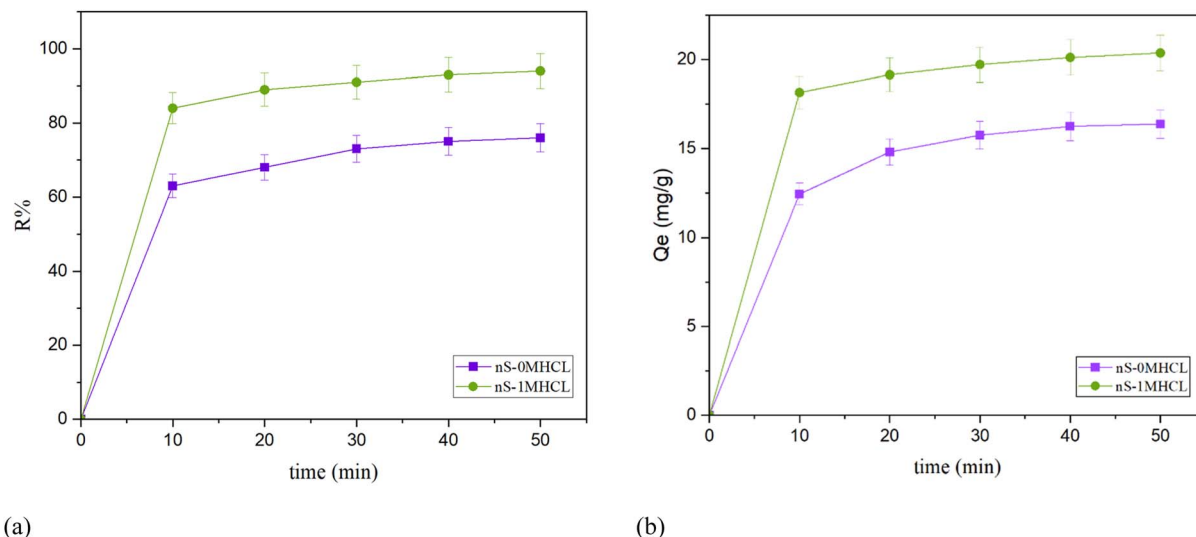


Fig. 9 Methylene blue (MB) percentage removal (R%) (a) and equilibrium adsorption capacity (q_e) (b) of biosilica particles with (nS-1MHCL) and without (nS-0MHCL) acid leaching.

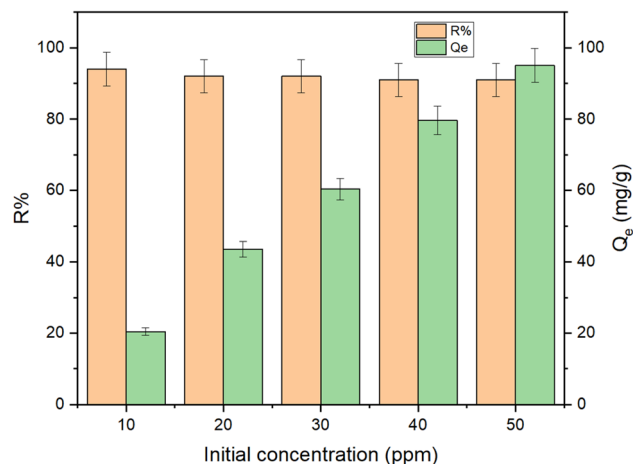


Fig. 10 Influence of initial dye concentration on methylene blue (MB) percentage removal ($R\%$) and equilibrium adsorption capacity (q_e) of nS-1MHCl adsorbent.

concentration of 10 ppm. The trend aligns with findings by,⁴³ who reported that mesoporous silica achieved removal percentages exceeding 90%, with a declining trend as MB concentration increased from 0.5 to 15 mg L⁻¹. Similarly,⁴² observed that while silica derived from coal bottom ash performed well at lower concentrations, the removal percentage dropped to 89% at an initial concentration of 50 mg L⁻¹. The removal rate, $R\%$ as the initial concentration increases is attributed to the saturation of adsorption sites; as the concentration of pollutant rises, the availability of free active sites on the biosilica particles surface decreases relative to the number of dye molecules.

In contrast, the adsorption capacity of nS-1MHCl (q_e) steadily increased with the increase in initial MB concentration (see Fig. 10). The highest q_e value of 95 mg g⁻¹ was obtained for an initial MB concentration of 50 ppm followed by 40 ppm

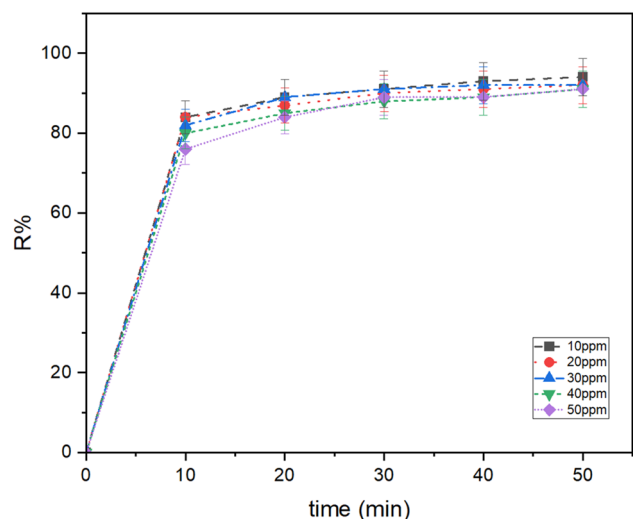


Fig. 11 Effect of contact time on MB percentage removal ($R\%$) on the nS-1MHCl adsorbent at various initial dye concentration.

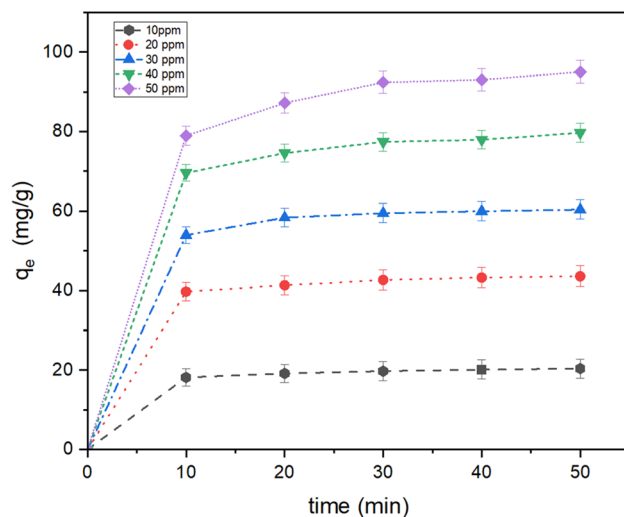


Fig. 12 Effect of contact time on the equilibrium adsorption capacity (q_e) on nS-1MHCl at various initial dye concentration.

(79.70 mg g⁻¹), 30 ppm (60.39 mg g⁻¹), 20 ppm (43.58 mg g⁻¹) and 10 ppm (20.37 mg g⁻¹). Consequently, higher initial dye concentrations were observed to create a steeper concentration gradient, which could acts as a driving force for the mass transfer of dye molecules from the bulk solution to the adsorbent surface.^{32,33} While the percentage removal may decline as a result of possible active site saturation, the equilibrium adsorption capacity (q_e), expressed as the total mass of dye adsorbed per gram of silica, was observed to increase. This trend can be attributed to the enhanced driving force, which effectively overcomes the resistance to mass transfer.

3.6.3 Influence of contact time. The effect of contact time on MB adsorption was examined over 0–50 min at room temperature. As shown in Fig. 11 and 12, the uptake of MB dye rose sharply during the first 10 min, then gradually slowed until it reached equilibrium at approximately 30 min. Such behavior is typical of silica adsorbents, where the abundance of free adsorption sites drives the rapid initial rate. As the process continues, these sites become occupied, leading to surface saturation and steric hindrance that restricts the access of dye molecules to the internal pore channels.^{31,33}

The nS-1MHCl adsorbent displayed extraordinary affinity for the cationic dye, reaching stable adsorption relatively quickly. However, the stabilization time varied slightly with concentration. Specifically, the q_e values for initial concentrations of 40 and 50 ppm continued to increase steadily until the 50 min mark. In contrast, for lower concentrations (10–30 ppm), the q_e values plateaued and remained constant after 30 min. The

Table 4 Adsorption of isotherm parameters via Langmuir model

Langmuir model		Freundlich model	
$Q_{\max}$ (mg g ⁻¹)	198.0198	n	1.0484
K_L (L mg ⁻¹)	0.1226	K_F ((mg g ⁻¹) L ^{1/n} mg ^{-1/n})	2.3505
R^2	0.9640	R^2	0.9957

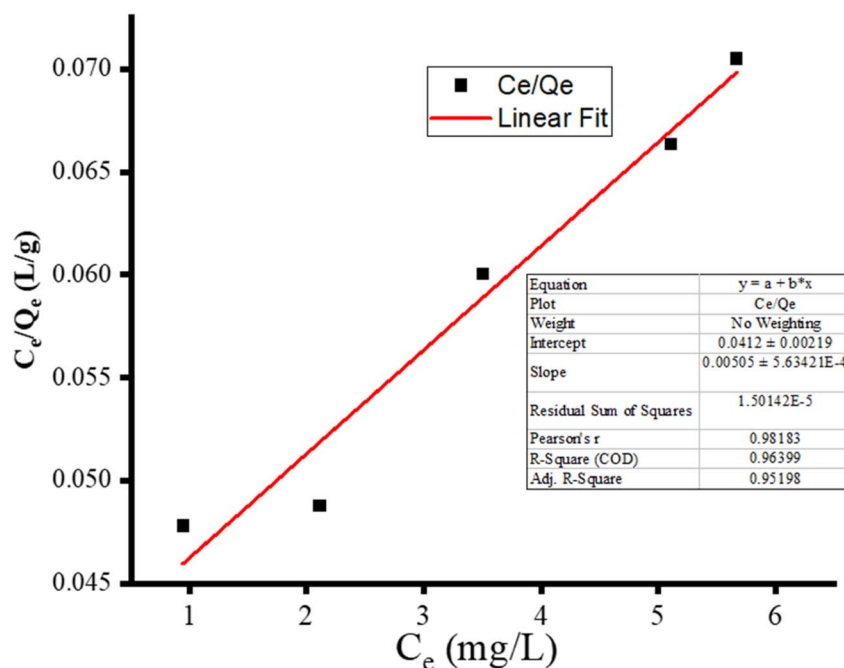


Fig. 13 The linear adsorption isotherm of Langmuir model.

discrepancy further substantiates that the diffusion process and the mass transfer of dye molecules over time are substantially dependent on the initial dye concentration gradient.

3.6.4 Adsorption isotherm and kinetics study. The experimental equilibrium adsorption capacity data for nS-1MHCL were analyzed using the linear Langmuir and Freundlich adsorption model to evaluate which model best represents the adsorption behavior of the nanosilica toward MB.³¹ The plot of adsorption capacity at equilibrium (q_e/C_e) against equilibrium concentration (C_e) was constructed, and the fitting parameters are provided in Fig. 13 and Table 4 respectively. The correlation coefficients ($R^2 = 0.9640$ and $R^2 = 0.9957$ for the Langmuir and Freundlich models respectively) indicated agreement between the experimental data for MB removal and the respective model predictions. However, Langmuir model predicted a higher

maximum adsorption capacity ($Q_{\max}$) than the experimental value, implying its limited suitability in representing the adsorption system. Conversely, the Freundlich model (refer to S1) exhibits a better correlation with the experimental data, with its adsorption intensity ($1/n$) value situated between 1 and 0, indicating a favorable adsorption mechanism. These results suggest that the adsorption of MB molecules on nS-1MHCL surfaces is likely governed by heterogeneous surface interaction which allows multilayer adsorption.^{18,42}

The adsorption kinetics were evaluated to estimate the adsorption rates and possible reaction mechanism involved through non-linear pseudo-first order, pseudo-second order, and intraparticle-diffusion models. The calculated parameters for pseudo-first order, pseudo-second order, and intraparticle-diffusion models obtained through the plotting of q_e against

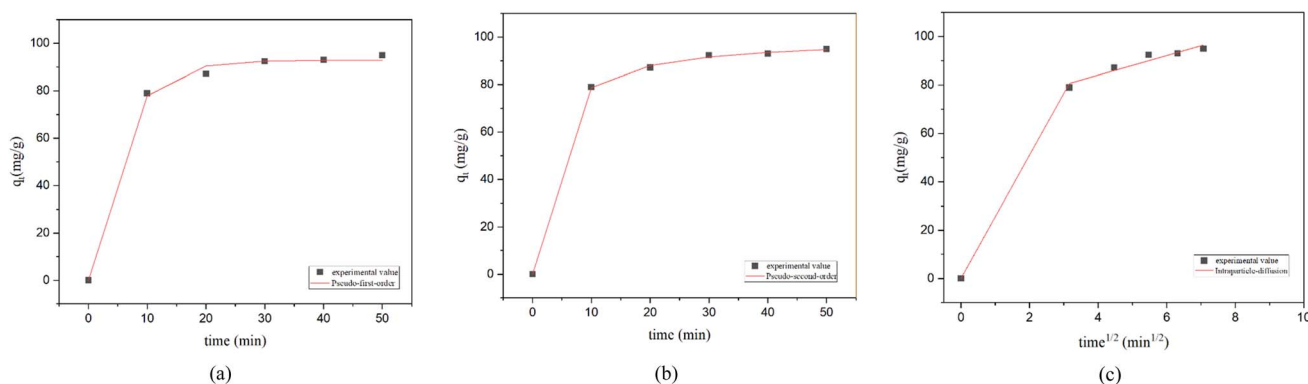


Fig. 14 Non-linear adsorption kinetic models of nS-1MHCL for pseudo-first order (a), pseudo-second order (b), and intraparticle-diffusion models (c) of nS-1MHCL.

Table 5 Kinetic parameters from kinetic models

Pseudo-first order		Pseudo-second order		Intraparticle-diffusion	
q_e (mg g ⁻¹)	92.8949	q_e (mg g ⁻¹)	99.8216	C (mg g ⁻¹)	67.8763
K_1 (min ⁻¹)	0.1825	K_2 (g mg ⁻¹ min ⁻¹)	0.0037	K_p (mg g ⁻¹ min ^{-0.5})	4.0478
R^2	0.9873	R^2	0.9987	R^2	0.9902

time (Fig. 14a–c) are given in Table 5. The pseudo second-order model was found to be the best model fit in terms of the maximum R^2 value (close to unity) and agreement with the calculation and experimental adsorption capacities at equilibrium, in comparison to other models with its rate constant of 0.0037 g mg⁻¹ min⁻¹. This indicated that the adsorption process is primarily governed by chemisorption mechanisms involving the removal of MB molecules *via* chemical interactions, such as electrons sharing or exchange between MB molecules and nS-1MHCL surfaces (silanol and siloxane functional groups). The chemical nature of binding mechanism highlights the features of an efficient and functionalized adsorbent.⁷² Similar outcomes have been reported in previous findings.^{32,42}

3.6.5 Proposed mechanism for MB removal. Three primary interactions are proposed for the adsorption of MB onto nS-1MHCL based on the Freundlich isotherm and pseudo second-order kinetic model, as illustrated in Fig. 15. Initially, MB molecules occupy the available adsorption sites (pores) on the nS-1MHCL surface, forming a monolayer through ionic binding between the Si-OH groups of the silica and the nitrogen atoms of the MB molecules. Electrostatic attraction typically dominates in basic conditions (pH > 4.5), where the deprotonation of silanol groups ((SiO)₃-SiOH) to form negative silicate ions (-Si-O⁻) is enhanced.^{18,31} However, the high removal efficiency observed in this study indicates that neutral conditions were sufficient to generate the necessary negative surface charge on the nS-1MHCL to attract cationic MB molecules. The observations align with,⁴² who reported similar electrostatic

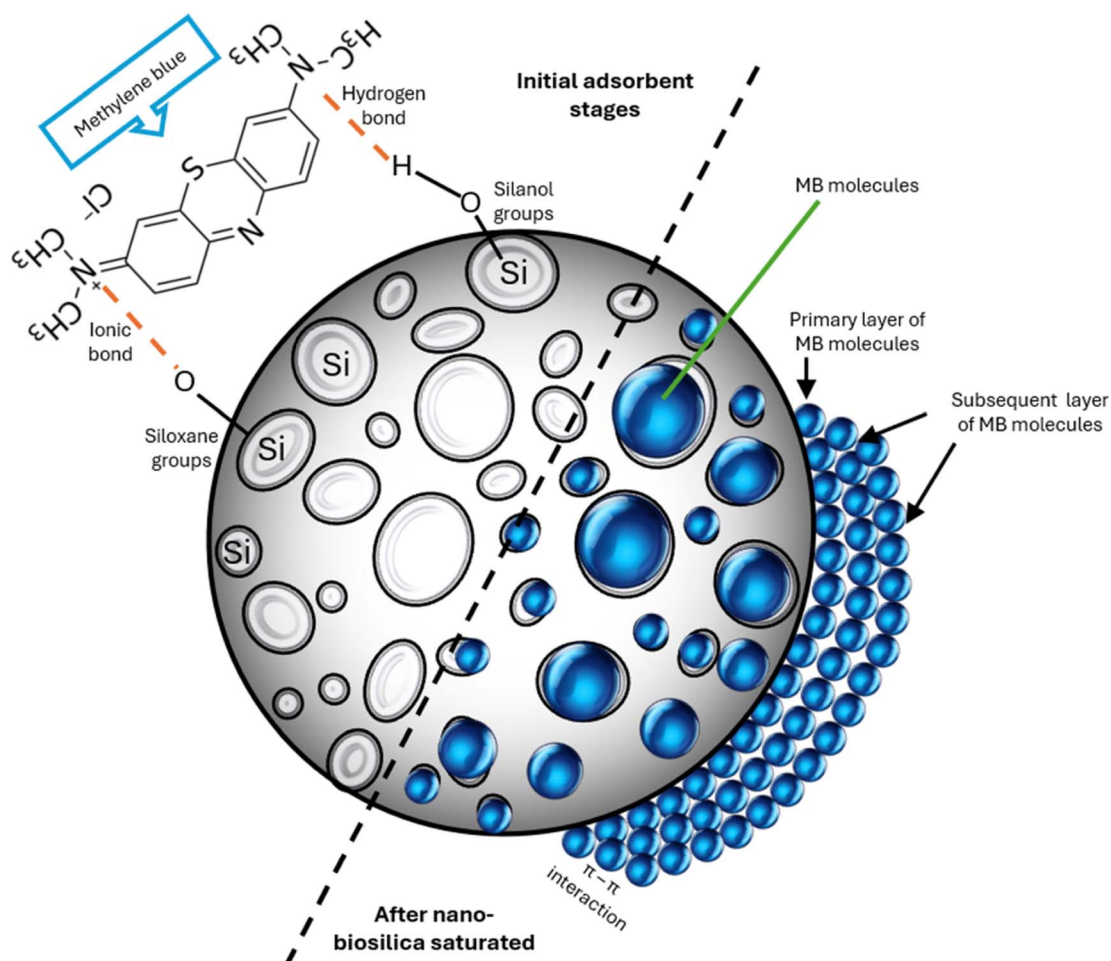


Fig. 15 The proposed adsorbent mechanism of biosilica particles (nS-1MHCL).

interactions at neutral pH for coal bottom ash silica. The high surface area, presence of oxygen-rich zones (such as peroxy radicals), and the abundance of silanol groups within amorphous biosilica particles are key factors that contribute to this effective adsorption without pH adjustment.⁷¹

Simultaneously, a strong hydrogen interaction likely occurs between the silanol (Si–OH) groups on the adsorbent surface and the nitrogen atoms in the MB molecules. Such interaction stabilizes the adsorbed MB molecules on the silica surface.⁴² The presence of hydrogen bonding is supported by the broad FTIR peaks observed in the 3300–3500 cm^{−1} region.³¹ Furthermore,³³ noted that such interactions often involve the hydroxyl groups of silica and the sulphonate or amine groups of the dye pollutants, which significantly enhance contaminant uptake. As the adsorption process progresses and the active pore sites become saturated, a multilayer adsorption phenomenon occurs. This subsequent layer of MB molecules is likely formed *via* weaker van der Waals forces or π – π stacking interactions. These interactions involve polar electrostatic forces, charge transfer, and van der Waals interactions between the aromatic rings of the MB molecules.^{31,42}

4 Conclusion

Biosilica particles were successfully extracted from POFA with high yield and amorphous character using an acid leaching and chemical precipitation approach. Acid leaching with 1 M HCl at room temperature proved effective in reducing impurities, resulting in an 11% increase in yield (nS-1MHCl vs. nS-0MHCl) and the production of bright white, spherical nanoparticles. The nS-1MHCl exhibited excellent methylene blue removal (91–94%) and a maximum adsorption capacity of 95 mg g^{−1}. The adsorption mechanism involves electrostatic attraction, hydrogen bonding, and π – π interactions and governs by adsorption models. While effective, complete elimination of aluminum and other impurities was not achieved. Future studies should explore higher HCl concentrations (*e.g.*, up to 3 M).

While the present study demonstrates the efficacy of nS-1MHCl for MB removal, it should be noted that BET surface area and pore size distribution analyses were not performed due to instrumentation constraints. Future investigations should include these measurements to establish quantitative structure property relationships between textural characteristics and adsorption performance. Furthermore, adsorption experiments were conducted using synthetic MB solutions rather than real industrial wastewater and adsorbent regeneration and reusability were not investigated in this work.

Author contributions

A. N. B. Mohd Sufian: writing–original, conceptualization, methodology, formal analysis, investigation, validation; M. R. Rahman, K. A. B. M. Said, E. B. Junaidi, M. Namakka, F. K. Liew, J. Uddin, I. Rahman: writing–review & editing, visualization, validation, supervision, fund acquisition, project management.

Conflicts of interest

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

Data availability

Data available within the article or its supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6ra01489e>.

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