Green Transformation of River Sand into Silica Toward Wastewater Treatment: A Dual-Impact Strategy for Environmental Conservation

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Abstract:
The contamination of industrial wastewater by toxic dyes, particularly Methylene Blue (MB), urgently requires sustainable remediation strategies. Simultaneously, the abundant deposition of sand along riverbanks, a rich natural resource of silica, presents significant potential for dye removal when effectively transformed and utilized, thereby contributing to environmental sustainability and a greener future. This study explores a dual-impact strategy: transforming river sand into silica through an eco-friendly process and utilizing the extracted silica as an efficient adsorbent for dye removal from industrial wastewater. By leveraging locally available raw resources, this approach addresses regional challenges while significantly contributing to the conservation of livelihoods and ecosystems. Herein, the naturally deposited sand along a riverbank in Bangladesh was converted into SiO_2 nanoparticles (NPs) and subsequently utilized for wastewater treatment. Experimental outcomes exhibited an MB removal efficiency, *E* over 83% for 50 ppm solution with 60 mg SiO_2-NPs under UV exposure for 30 minutes. This systematic study and its substantial outcomes align with green chemistry principles and highlight a cost-effective, practical pathway to bridge natural resource utilization for environmental conservation, addressing socio-environmental issues, and promoting eco-friendly technologies for silica extraction and wastewater treatment.

Keywords: *Sand, SiO_2-NPs, methylene blue (MB), wastewater treatment, environmental remediation.*

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Received on 2025/1/7, accepted after peer reviews on 2025/7/10.

Journal of the Asia-Japan Research Institute of Ritsumeikan University, 2025.
PRINT ISSN 2435-0184 ONLINE ISSN 2435-0192, Vol.7, pp.81–100.

1. Introduction

Silica nanoparticles (SNPs) exhibit great potential for utilization in several fields, including chemical, biomedical, agriculture, environmental remediation, and even wastewater purification, due to their intrinsic properties such as high surface area, tunable pore size/diameter, mesoporous structure, biocompatibility, and polymeric hybridizability (Elizondo-Villarreal et al. 2024). Meanwhile, water pollution caused by industrial effluents, particularly those containing organic dyes and heavy metals, demonstrates a severe environmental threat, posing significant risks to ecosystems and public health. Organic dyes, commonly discharged from industries such as textiles, paper, and leather, pose a major concern due to their persistent, bioaccumulative, and toxic nature, which disrupts aquatic ecosystems and compromises human health (Afrad et al. 2020). These dyes are resistant to natural degradation processes, leading to their accumulation in water bodies, reducing light penetration and consequently inhibiting photosynthesis in aquatic ecosystems. Heavy metals further exacerbate this issue due to their toxicity and bioaccumulation, entering the food chain and threatening biodiversity and human safety. Therefore, there is an urgent need for innovations in green, cost-effective, and sustainable approaches to wastewater treatment and the remediation of environmental concerns. Conventional wastewater treatment methods, such as coagulation, flocculation, advanced oxidation processes, ozonation, membrane filtration, and biological purification, have been widely utilized to address dye contamination. Among these, adsorption stands out for its operational simplicity, cost-effectiveness, and high efficiency in removing dyes from aqueous solutions (Nasseh et al. 2020; El Nahhal et al. 2016). Adsorbents such as activated carbon, clays, and nanomaterials have been extensively studied for their effectiveness. However, challenges related to scalability, economic feasibility, and environmental impact often limit their widespread industrial application.

Numerous dyes are found in industrial wastewater, including polycyclic and solvent dyes, azoic dyes, and methylene dyes. The most observed dye is methylene blue (MB), which has a molecular formula of $C_6H_{18}N_3SC$, and a weight of 373.9 g/mol at a wavelength of 660 nm (Elizondo-Villarreal et al. 2024). Metal oxide nanoparticles, including iron oxide Fe_2O_3, copper oxide CuO, zinc oxide ZnO, and silicon oxide SiO_2, are commonly used to remove this dye from wastewater by the degradation or removal processes. To date, SiO_2 reveals a remarkable adsorption capacity and removal efficiency (E) of 71.4 mg/g for mesoporous, while it is 20.8 mg/g for banana peel, 18.6 mg/g for orange peel, 71 mg/g for Petal cells, and 13.5 mg/g for hybridized silica (ZrO_2/rice straw-derived silica) and so on (Samy et al. 2023; Elizondo-Villarreal et al. 2024). These studies reveal the strong potential of SiO_2 over other metal oxides for the removal of MB dye from wastewater.

Silica (SiO_2), known for its high surface area, chemical stability, and tunable structural properties, has emerged as a promising adsorbent material (Rao et al. 2005; Hazarika et al. 2016). Nevertheless, traditional silica sources such as rice husks, fly ash, and other agricultural by-products often involve energy-intensive and high-cost production processes, which conflict with the principles of green chemistry. Additionally, hybrid silica-based materials may compromise adsorption efficiency due to reduced surface area (Ngoc and Vu 2022). Sand comprises the two most abundant elements in the Earth's crust, Si and O, and is an abundant natural resource, offering a sustainable alternative for silica synthesis. Its processing into high-purity silica is both cost-effective and environmentally friendly, aligning with green chemistry principles by minimizing waste and reducing reliance on synthetically produced silica (Li et al. 2022). Advances in microwave-assisted synthesis have further enhanced the feasibility of silica extraction from sand by improving reaction kinetics that consume less power and

reduce production costs while offering sustainable adsorption characteristics. (Díaz et al. 2020; Islam et al. 2024).

The various natural and industrial by-products investigated for extracting silica and silicon nanoparticles include rice husks, fly ash, agro-waste, and river sand. Among them, river sand has emerged as a particularly promising alternative as it is predominantly composed of high-purity quartz (SiO_2 content ranging from 75% to 98%) (Samy et al. 2023; Islam et al. 2024; Sharma et al. 2022; Kuddus et al. 2022; Sarkar et al. 2021; Rovani et al. 2018). River sand offers a uniform and consistent silica source that simplifies the extraction process with enhanced reproducibility. In contrast to agricultural residues, which typically require intensive pretreatment steps such as drying, calcination, and acid leaching to remove organic and inorganic impurities, river sand requires minimal processing. This not only reduces energy consumption and chemical usage but also shortens the overall processing time, aligning closely with the principles of green chemistry and sustainable material development (Díaz de Greñu et al. 2020). Furthermore, river sand-derived silica exhibits favorable surface characteristics such as tunable porosity and high surface area, enabling strong adsorption capacity and adaptability for catalytic as well as photonic applications, particularly when subjected to post-synthesis modifications (Zaki et al. 2012; Díaz de Greñu et al. 2020; Kuddus et al. 2020; Hasanah et al. 2025). With its widespread availability and cost-effectiveness, especially in silica-rich regions such as Rajshahi, Bangladesh (Uddin and Jeong 2021), river sand represents a sustainable and scalable raw material for eco-friendly SiO_2 and Si production. These attributes underscore river sand's potential as a superior alternative to conventional silica sources for diverse applications in environmental and functional materials engineering.

Several approaches have been employed for the synthesis of silica (SiO_2), and Si from natural waste materials and sand, including sol-gel, chemical precipitation, microemulsion, electrocoagulation, pyrolysis, hydrolysis, hydrothermal, metallothermic and alkaline fusion methods (Ishmah et al. 2020). However, most conventional processes often involve multiple complex steps, prolonged reaction times, high energy consumption, and the use of strong acid purification. For instance, the sol-gel process typically requires hydrolysis and condensation of precursors like tetraethyl orthosilicate (TEOS), which not only lengthens the process but also raises environmental concerns due to the toxicity and volatility of the reagents involved. Additionally, metallothermic (thermite) reduction methods such as carbothermic, aluminothermic, magnesiothermic, and calciothermic processes are also used to extract SiO_2 and Si from various sources. However, these methods require extremely high processing temperatures (T >2000 °C), followed by acid-leaching steps, making them energy-intensive and less favorable for sustainable applications (Ishmah et al. 2020; Farirai et al. 2021; Kuddus et al. 2020). In contrast, the current study employs a microwave-assisted alkali fusion process at a low temperature of ~250 ℃ for 30 minutes, which enables a rapid and energy-efficient synthesis. In this method, microwave irradiation ensures uniform volumetric heating, significantly reduces reaction time, enhances product homogeneity and yield, and minimizes heat loss when using a microwave kiln. Furthermore, this method reduces the need for hazardous chemicals, aligning with the principles of green chemistry.

Notably, a vast deposition of high-purity sand in the Padma River near Rajshahi, Bangladesh, represents an underutilized natural resource with significant potential for sustainable energy harvesting applications. However, these massive sand sediments and shoals not only disrupt the livelihoods of riverine communities but also have far-reaching regional, national, and geographical consequences. The shifting sands lead to land erosion, geographical reshaping, and community displacement, further

exacerbating socio-economic challenges (Topu 2024). Addressing these issues requires sustainable mitigation strategies, including integrated river basin management, infrastructure investments, and community-centered solutions to stabilize riverine regions while safeguarding their economic and ecological significance. Harnessing this abundant natural resource for silica (SiO_2) or silicon (Si) extraction presents a promising pathway for efficiently removing toxic dyes from industrial wastewater and advancing renewable energy harvesting (Islam et al. 2019; Kuddus et al. 2017; 2020; 2022; Rafi et al. 2018; Santos Rebolledo et al. 2024). This approach not only significantly contributes to mitigating the challenges posed by sand accumulation but also provides a sustainable solution to environmental concerns, such as dye pollution. Transforming natural sand into high-performance adsorbents bridges resource utilization and environmental remediation, aligning with the principles of green chemistry and sustainable development goals. Thus, the successful application of river sand-derived SiO_2-NPs in wastewater treatment could significantly reduce industrial dye contaminants, ensure cleaner water resources, and catalyze the adoption of eco-friendly, scalable green technologies for energy-efficient water purification systems while improving livelihoods affected by the deposition of sand sediment, primarily through sediment transport and bank erosion.

In this study, river sand-derived SiO_2-NPs were found to be high-efficiency adsorbents offering sustainable and scalable growth. The experimental findings of the present research emphasize the potential and significance of local river sand-derived silica as an efficient, sustainable, and economically viable adsorbent for wastewater treatment. Leveraging an abundant natural resource not only addresses critical environmental challenges but also contributes to the development of eco-friendly technologies aligned with global sustainability goals.

2. Materials and Methods

(1) Materials

The source of silica was river sand collected from the locality of Rajshahi city, Bangladesh. Sand sediment deposits in the Rajshahi region can reach over 500 hectares per year, primarily by sediment transport and bank erosion. Reducing agents of hydrochloric acid (HCl), sodium hydroxide (NaOH), and sulfuric acid (H_2SO_4) were commercially purchased from Sigma-Aldrich and used without further purification.

(2) Silica-NPs from Sand through Alkali Fusion and Chemical Reduction

The synthesis of SiO_2-NPs involves a series of purification and chemical conversion steps in addition to an alkali fusion reaction under microwave heat treatment. **Figure 1** demonstrates the sand collection location, available sand sediment, and collection from the upper surface. A step-by-step description of the purification process, chemical reactions, and reduction is provided below.

1) Initial Purification of Collected Sand

The SiO_2-NPs extraction process begins with sourcing sand from the Padma River, specifically an abundant deposit located ~400 m from the riverbank (**Figure 1**). The collection point coordinates are latitude-24.359169 and longitude-88.625522. Padma is one of the major rivers in Bangladesh, approximately 100 km long, exhibiting a high-energy fluvial environment with a substantial sediment load (several billion tons/year), primarily derived from the weathering and erosion of the Himalayan orogenic belt (Topu 2024). Seasonal flooding and dynamic river processes naturally generate well-

sorted, silica-rich sand with minimal organic contamination. Geologically, Rajshahi lies within the Ganges Delta Basin, predominantly composed of recent alluvial deposits rich in silicate minerals. The Rajshahi area was selected due to its favorable hydrological and geological characteristics, as well as the broader objective of transforming underutilized natural resources into valuable materials. This transformation of sand into silica and silicon not only promotes scientific innovation but also addresses the economic challenges faced by thousands of people living in the region who are burdened by this underutilized green resource. Thus, the source material's location was selected based on both the scientific evidence of its high silica content and the sustainable transformation of a locally abundant, yet underexplored, resource into a valuable material (Islam et al. 2024; Kuddus et al. 2020; 2022; Rafi et al. 2018).

Initial cleaning involved washing with normal water (10 times), distilled water (3 times), and acetone (3 times) to remove organic and chemical impurities. The purified sand was then dried at 100 °C for 2 hours, followed by crushing it into tiny particles using a mortar pestle and then grinding to obtain fine powder by ball-milling, thus producing nm-size particles. To further enhance the purity and efficiency of the extracted silica, a 2 M HCl treatment was utilized to effectively remove non-silica components, such as iron, magnesium, calcium, and other mineral oxides. This approach aligns with previous reports demonstrating the role of acid leaching in improving silica quality (Ngoc and Vu 2022). This acid treatment not only purified the silica but also enhanced its structural properties, increasing the specific surface area and active sites critical for adsorption-based applications.

(a)

(b)

(c)

Figure 1. (a) Location (Google map) of the raw material (sand) collection point at the bank of Padma River, Border Guard Bangladesh (BGB) area, Rajshahi City, Bangladesh, (b) Sand sediment and shoal, and (c) collection of sand from the sediment surface

2) Microwave-assisted Alkali Fusion Reaction

The purified and finely ground sand (4.6 g) was mixed with NaOH (5.4 g) and 5 ml of water. This mixture was subjected to a microwave-assisted alkali fusion process at 250 °C for 30 minutes in a kiln, yielding sodium silicate (Na_2SiO_3) powder, commonly referred to as "water glass". Silica powder was dissolved in 50 mL of distilled water; thereafter, a repeated filtration process was performed using Na_2SiO_3. The chemical reaction between silica (SiO_2) and NaOH results in a molten intermediate, Na_2SiO_3, which can be represented by **Equation 1**.

SiO_2 (sand powder) + NaOH (*s*) + H_2O (*l*) → Na_2SiO_3(*l*) + H_2O (*l*)……..……..(1)

The microwave-assisted approach utilized a microwave kiln, a compact and cost-effective device capable of achieving high temperatures through microwave energy. The use of microwave energy accelerates the fusion process, providing rapid, uniform heating while minimizing energy consumption compared to conventional methods.

Figure 2. Camera image of the Microwave Kiln used for the low-temperature (250 °C) alkali fusion reaction

Figure 2 shows the Micro-oven and Kiln used for the alkali fusion reaction. Importantly, the microwave heating environment ensures the purity of the silicate product by preventing contamination from external elements. The combination of microwave technology and Kiln-assisted alkali fusion not only optimizes the efficiency of sodium silicate production but also aligns with green chemistry principles, featuring reduced reaction time, low power consumption, and minimal environmental disturbance.

3) Silica Gel Extraction

The Na_2SiO_3 solution undergoes acid titration, a crucial step in converting it into silica gel. The filtered Na_2SiO_3 solution (40 ml) was titrated with 10.88 ml of 5.64 M sulfuric acid (H_2SO_4) at a pH ≈7, stirred vigorously, and kept at rest for 18 hours, resulting in the formation of Orthosilicic acid ($Si(OH)_4$) gel. Acid titration lowers the pH of the solution, promoting the removal of Na^+ ions and facilitating the formation of silica (SiO_2)-rich gel. Controlling the rate and concentration of acid during the titration process is essential for obtaining a homogeneous silica gel with desirable properties, including optimal particle size, purity, and porosity. The resulting silica gel, a colloidal suspension of silica particles, boasts a porous structure and large surface area, making it ideal for diverse applications such as catalysis and adsorption. It serves as a versatile intermediate, suitable for direct use or further refinement. The structural and morphological characteristics of the gel render it effective for wastewater dye removal, improving photo-absorption and catalytic performance. The acid titration process can be represented by **Equation 2**.

$$Na_2SiO_3\,(l) + H_2SO_4\,(l) + H_2O\,(l) \rightarrow Na_2SiO_4\,(s) + Si(OH)_4\,(aq.) \quad \text{.............................}(2)$$

The as-prepared gel was washed with DI water (3–5 times) and then filtered using the Whatman double-ring filter (paper No.102) having a nominal particle retention of 8–10 μm in open air conditions to separate the gel from the solution (DI water). After that, the drying, grinding, and finally calcination at 400 °C for 24 hours were executed, yielding silica with enhanced structural integrity and crystalline stability (**Figure 3**).

4) Synthesis of SiO_2-NPs from Silica Gel

The extracted SiO_2-gel was dried and calcinated at 400 °C for 24 hours in an oxygen-rich environment (this thermal treatment is referred to as calcination in the text). This process effectively eliminated residual moisture, organic contaminants, and other impurities, leaving highly pure SiO_2 (**Equation 3**). Then, SiO_2 was ground using a mortar pestle and a ball milling process. Thus, the silica was transformed into highly pure nanoparticles (NPs).

$$Si(OH)_4\,(aq.) \rightarrow SiO_2\,(s) + 2H_2O\,(l) \quad \text{...}(3)$$

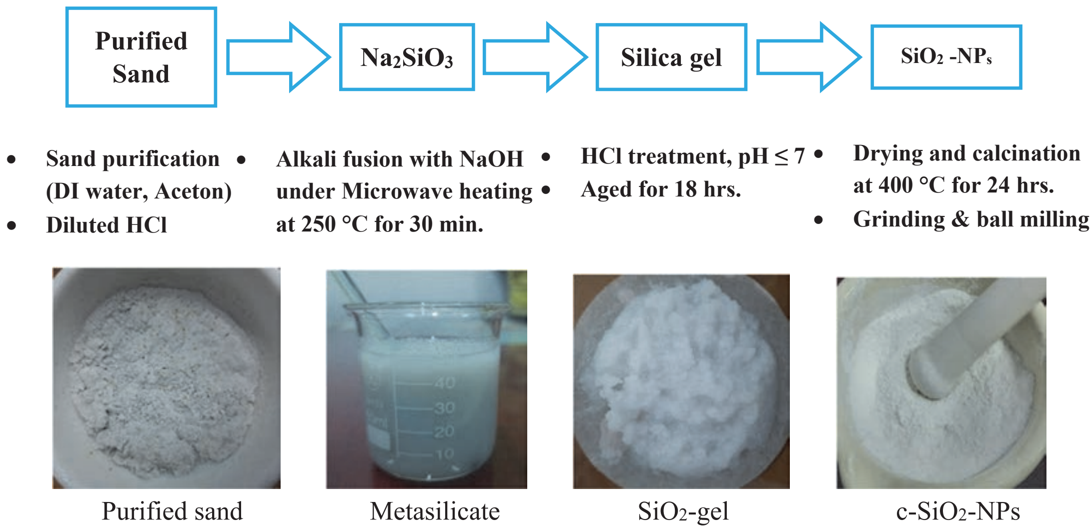

Figure 3. Block diagram and corresponding camera images of extracted SiO_2-NPs from river sand

The calcination process not only ensured the removal of these residues but also enhanced the material's crystalline structure and thermal stability. Thereafter, SiO_2-NPs were prepared by grinding with a mortar pestle. The average size distribution of SiO_2-NPs is estimated to be 71 nm, which falls within the desired range for applications with a strong potential for water treatment and energy harvesting (Luthfiah et al. 2021).

(3) Dye Removal Using SiO_2-NPs

Finally, the dye removal efficiency of the silica nanoparticles (SiO_2-NPs) was systematically evaluated using UV-visible spectroscopy by adding them to methylene blue (MB) dye solutions at varying concentrations. To achieve this, three solutions containing 0.15 g, 0.3 g, and 0.6 g of SiO_2-NPs were each added to 50 mL of MB dye solution. These mixtures were kept under three conditions, including dark, UV light, and natural sunlight, for 30 minutes; subsequently, the optical absorption of

each sample was measured. Herein, a standard artificial wastewater solution was prepared by dissolving 0.05 g of MB dye in 1.0 L of distilled water. To assess the reusability of the SiO_2-NPs, the nanoparticles were separated from the dye mixture through filtration and washed thoroughly with distilled water three times. The recovered particles were then dried at 100 °C for 24 hours. Once dried, the SiO_2-NPs were reused with 30 mL of MB solution and exposed again to dark and UV conditions for 30 minutes. The dye removal efficiency was re-evaluated following the same steps to confirm the material's reusability and effectiveness.

(4) Characterization

The synthesized SiO_2 and nanoparticles (NPs) were characterized using multiple techniques to confirm their structural, morphological, and optical properties. An SEM (Hitachi SU-8000) with an acceleration voltage of 2 kV revealed a porous and granular surface, which has a strong potential for adsorption applications. Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu FTIR-8400) confirmed the Si–O–Si functional groups at 1000–1100 cm^{-1} and minimal -OH bands, indicating chemical purity. A powder X-ray diffractometer (Rigaku RINT-2500) with Cu Kα radiation was used, employing Cu Kα radiation (λ = 0.15406 nm) with a step size of 0.033°, to demonstrate the successful synthesis of polycrystalline SiO_2-NPs through calcination. UV-visible spectrophotometry (T-60 UV-VIS spectrophotometer) was used to analyze the dye removal efficiency in the 360–1100 nm range under dark, UV, and sunlight conditions. The reusability efficiency of the amorphous structure of SiO_2-NPs was also observed through subsequent absorption studies. The results demonstrate the strong potential of local river's sand-derived SiO_2-NPs to be applied as sustainable adsorbents for wastewater treatment and absorbers in energy harvesting devices.

3. Results and Discussion

(1) Surface Morphology of Extracted SiO_2-NPs from Sand

The SEM observations of SiO_2 synthesized from river sand reveal critical structural insights that are important for their application in wastewater treatment, particularly for dye removal. **Figures 4a** and **b** present SEM images of the calcinated SiO_2 nanoparticles dispersed on a glass substrate at different magnifications: 250X with a 200 μm scale bar, and 3.5kX with a 10 μm scale bar. SEM images reveal a relatively porous morphology with layered surfaces, which enhances the effective surface interaction with dye molecules. An irregularly shaped and agglomerated structure with an average size of several hundred nm indicates the formation of larger SiO_2 clusters upon calcination (400 °C for 24 hours). Although calcination tends to reduce the surface area with densified particles, the formation of stable crystalline domains provides mechanical robustness and chemical stability, which are advantageous for repeated adsorption-desorption cycles in wastewater treatment. The porous textures and rough surfaces facilitate multiple active sites for ionic dye interaction, particularly under controlled pH conditions (Li et al. 2022; Sharma et al. 2022). This heterogeneity in particle size also promotes optimizing adsorption efficiency, as larger particles may contribute to structural stability, while smaller ones increase the surface area (Hariyanto et al. 2021). Thus, this study reveals the potential of river sand-derived SiO_2 as an effective, eco-friendly, and cost-effective resource for wastewater treatment, aligning with the principles of green chemistry and sustainable development (Luthfiah et al. 2021). Further optimization of extraction parameters, along with the development of SiO_2-based composite materials, could significantly enhance adsorption capacity and long-term

stability by tailoring particle size distribution, thereby broadening their potential for practical environmental remediation applications.

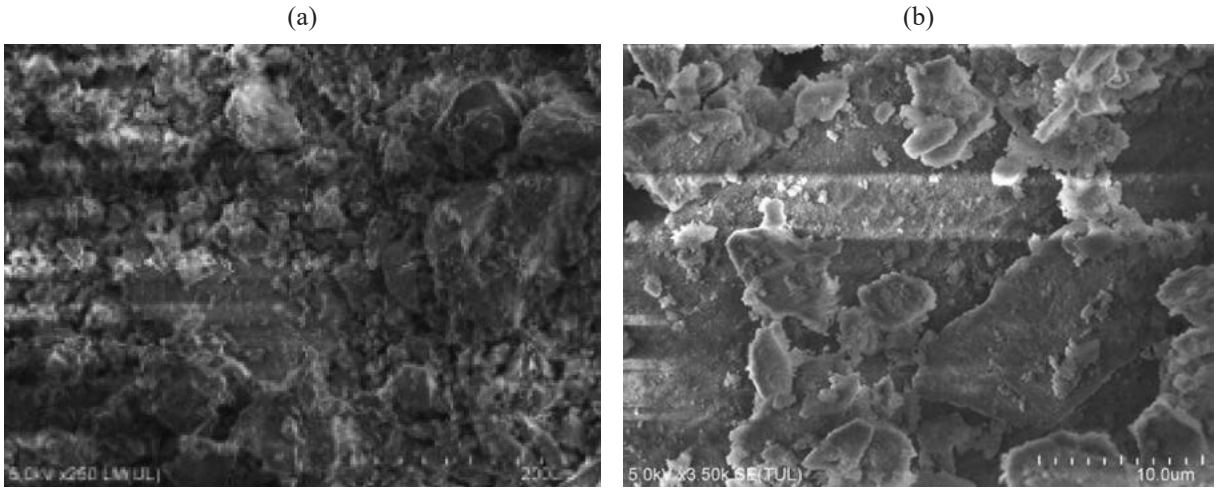

Figure 4. SEM images of extracted and calcinated SiO_2 at (a) 250X, scale bar: 200 µm and (b) 3.5kX, scale bar: 10 µm dispersed on the glass substrate

(2) Chemical Properties of Extracted SiO_2-NPs

Figure 5 presents the FTIR spectrum of the extracted SiO_2 with several absorption bands at specific wavenumbers, providing critical insights into the molecular structure of the material. Characteristics peak at 457.96 cm^{-1}, corresponding to the bending vibrations of the Si-O bond. Additionally, the absorption peak at 1238.84 cm^{-1} is attributed to the asymmetric stretching vibrations of the Si-O-Si bond confirming the presence of a tetrahedral network of silica, further validating the silicate framework. A broad absorption peak of O-H related to the bending vibrations appeared in the region of 500–1200 cm^{-1} and for the H-O-H bending mode at around 1630 cm^{-1}. The broad observed peaks in the range of 3300–3650 cm^{-1} and 3200–3550 cm^{-1} refer to the stretching vibrations of surface hydroxyl groups of O-H and adsorbed water molecules (**Table 1**).

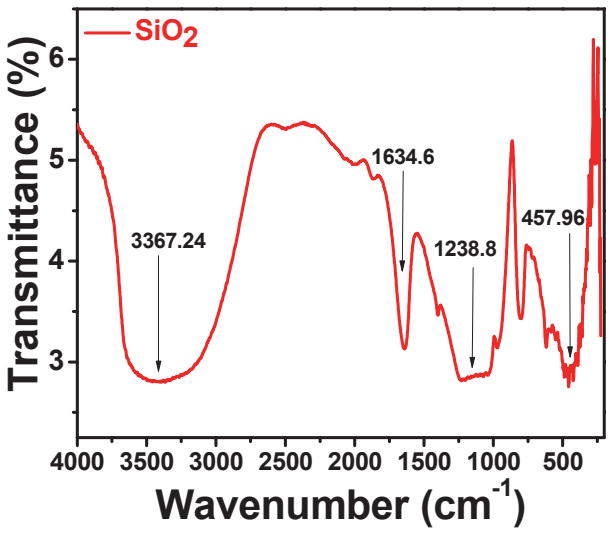

Figure 5. FTIR spectrum of extracted SiO_2 and summary of respective group vibrations

Table 1. Summary of FTIR Peaks of River sand derived calcinated SiO_2 powder

Wavenumber (cm^{-1})	Bonds
457.96	Si-O bending
500–1200	O-H bending
1238.84	Si-O-Si
1634.6	H-O-H bending
3200–3650	O-H stretching

The respective functional groups and prominent vibrational peaks corresponding to various bonds are summarized in **Table 1**. These observed peaks were found to be similar to standard SiO_2 spectra as observed in previous literature on silica derived from natural sources (Gan et al. 2016; Homaunmir et al. 2013; ; El Nahhal et al. 2016; Ramasamy et al. 2014). Thus, the extracted silica, characterized by a sharp peak with prominent structural purity and minimal impurities, was found to have strong potential for applications in dye adsorption and energy harvesting.

(3) Structural Properties SiO_2-NPs

Figure 6 illustrates X-ray powder diffraction (XRD) patterns of calcination SiO_2 powder at 400 °C for 4 hours. An amorphous characteristic of as-prepared SiO_2 (without high-*T* heat treatment) was reported in earlier studies (Islam et al. 2024; Kuddus et al. 2022; Nzereogu et al. 2023). The SiO_2 characteristics peaks at 2θ angles of ~20.8°, 26.96°, 32°, 36°, 38.42°, 44.58° and 65.2 correspond to the (100), (101), (100), (110), (102), (200) and (300) crystallographic planes, respectively. By referring to the polycrystal phase, which combines the crystal phases of Quartz, Tridymite, and Cristobalite polymorphs, these peaks are found to be consistent with reported literature (Hariyanto et al. 2021; Kumar et al. 2018; Oufakir et al. 2012; Samy et al. 2023). The XRD pattern showed one characteristic of the Quartz phase forming a peak at 26.68°, while the tridymite phase formed peaks at 21.53° and 35.71°, and the cristobalite phase formed peaks at 22.05°, 28.49°, 31.43°, and 35.99° (Munasir et al. 2018). The parameter of an average crystal size of 71.375 nm of calcinated polycrystalline SiO_2 powder was determined by Debye-Scherrer's equation (**Equation 4**).

$$D=k\frac{\lambda}{\beta}\cos\theta \quad \text{.....(4)}$$

Where D = Crystal size, k = Scherrer constant with the value from 0.9 to 1, λ = Wavelength of X-ray, β = In radians, full width at half maximum (FWHM) of the peak, θ = Bragg angle in radians. Thus, activated sites with polycrystalline behavior reveal the potential for diverse applications.

The size distribution of amorphous SiO_2 NPs was 50–150 nm before the calcination process (Islam et al. 2024). In contrast, calcinated c-SiO_2 NPs had porous morphology and irregular shapes, with agglomerated structures exhibiting an average size of several hundred nm (**Figure 4**, SEM images), indicating the formation of larger SiO_2 clusters upon calcination (400 °C for 24 hours). Although calcination tends to reduce the surface area with densified particles, the formation of stable crystalline domains provides mechanical robustness and chemical stability, which are advantageous for repeated adsorption-desorption cycles in wastewater treatment.

Herein, the study focused on achieving a crystalline SiO_2 NPs (c-SiO_2 NPs) phase through post-synthesis thermal treatment at 400 °C for 24 hours, due to the distinct advantages of c-SiO_2 NPs.

Crystalline silica with a highly ordered framework, which provides consistent and stable adsorption characteristics across a wide pH range, along with remarkable resistance to degradation during reuse cycles, even after simple washing or mild thermal treatments (Rovani et al. 2018). Although a reduction in specific surface area and adsorption capacity is typically observed when compared to amorphous silica, the improved chemical and structural stability of crystalline SiO_2 NPs is a significant benefit for ionic dye removal applications. Furthermore, the surface of crystalline SiO_2 exhibits pH-dependent, well-controllable charge behavior: below the point of zero charge (pHpzc), the surface tends to be positively charged, and above it, negatively charged. This surface charge modulation influences the adsorption of different dye species, depending on their ionic nature (cationic, anionic, or neutral). Since most dyes present in wastewater, including Methyl Blue (cationic) and Methyl Orange (anionic), exhibit charged characteristics, crystalline SiO_2 NPs, under carefully controlled pH conditions, emerge as a potential candidate for efficient and stable adsorption of a wide variety of ionic dyes (Marć et al. 2024; Rastegari et al. 2024).

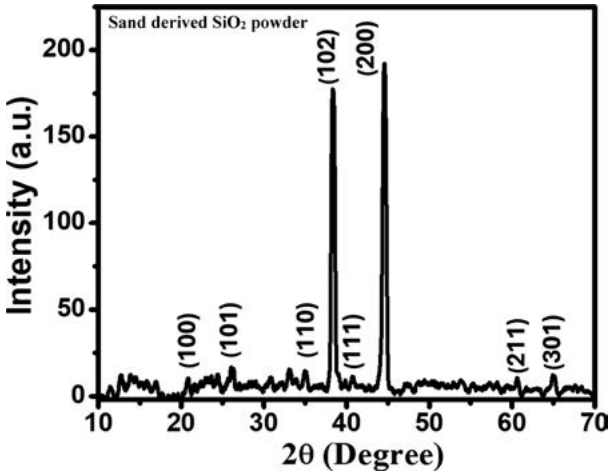

Figure 6. XRD spectrum of extracted SiO_2 powder calcinated at 400 °C for 24 hours

Table 2 demonstrates the X-ray fluorescence (XRF) analysis (wt%) of raw silica sands, physically separated sands, and alkali fusion-derived silica. The XRF analysis of the raw river sand revealed a silica (SiO_2) content of approximately 76% with notable additives of Al_2O_3, 10.62%, K_2O 3.19%, CaO 2.55%, and Fe_2O_3 3.39%, and trace elements of MnO, Y_2O_3, Cr_2O_3, NiO, ZrO_2, BaO, and Rb_2O. Interestingly, the physical separation of sand particles with a size of approximately 125 μm resulted in an approximately 86% (10% higher) yield, accompanied by a significant reduction in iron oxide, alumina, phosphorus pentoxide, manganese oxide, and chromium oxide (Rafi et al. 2018). Notably, the XRF analysis of the microwave-assisted c-SiO_2 NPs content was approximately 92% (Islam et al. 2024). However, a careful multi-step washing procedure, including acid leaching with HCl, is essential during extraction to achieve a silica purity exceeding 98 wt%, as was required for Si-NPs (≥97 wt%) extraction from the same raw material sand (Kuddus et al. 2020).

Table 2. XRF analysis (wt%) of the raw silica sands, physically separated 125 µm sands, and alkali fusion-derived c-SiO_2 NPs (Islam et al. 2024; Rafi et al. 2018). Other trace elements with value <0.3 wt% include MgO, P_2O_5, Cl, TiO_2, MnO, NiO, ZnO, Rb_2O, SrO, Y_2O_3, ZrO_2, BaO.

Name of the material	Raw sand (wt%) (without treatment) (Rafi et al. 2018)	Physically separated 125–500 µm size sand particles (wt%) (Rafi et al. 2018)	Alkali fusion-derived silica (SiO_2) NPs from raw sand (wt%) (no repetitive purification)
SiO_2	76.3709	85.8465	91.400
Al_2O_3	10.6174	6.8625	2.0305
Fe_2O_3	3.3980	1.6167	1.5300
Na_2O	1.7107	1.8261	2.0833
SO_3	0.0081	0.0105	1.4872
K_2O	3.1859	2.1010	0.1447
CaO	2.5473	0.9145	0.0683
Cr_2O_3	0.3603	0.5566	0.5636
*Others	~1.8014	~0.2656	~0.6924

*Others includes MgO, P_2O_5, Cl, TiO_2, MnO, NiO, ZnO, Rb_2O, SrO, Y_2O_3, ZrO_2, and BaO.

(4) Dye Removal Efficiency of SiO_2-NPs

Figure 7 shows the photodegradation performance of SiO_2 nanoparticles (SiO_2-NPs) for methylene blue (MB) dye. The absorbance spectra of MB solution without and with SiO_2-NPs under dark and UV light conditions for 30 minutes reveal distinct trends at a 300–800 nm region. Pure MB solution exhibits a broad prominent peak at 450–750 nm region with a bump at 644 nm possessing a peak intensity of 3.8 (a. u.). No significant change was observed under dark or UV exposure for pure MB, even after 30 minutes. However, an addition of SiO_2-NPs drastically alters the spectral features, revealing effective dye degradation. Under dark conditions, the inclusion of 0.15 g SiO_2-NPs in MB (50 ppm solution) reduces peak intensity down to 2.8 from 3.4 (a. u.) and reshapes the spectrum by shrinking at 550–700 nm, leaving two new peaks at 664 nm and 611 nm (**Figure 7a**). The trend of reduction in peak intensity continued from 2.8 to 1.7 to 0.4 with a significantly reduced shape when 0.3g and 0.6g of SiO_2-NPs were added to the MB solution.

On the other hand, SiO_2-NPs exhibit enhanced photocatalytic activity under UV light. The absorbance intensity was down to 2.4 (a. u.), which was 3.0 (a. u.) in the dark for 0.15g SiO_2-NPs, revealing increased dye removal efficiency compared to the dark condition (**Figure 7b**). The nanoparticles likely generate reactive species (e.g., hydroxyl radicals), initiating redox reactions that degrade MB molecules. However, the adoption of dominant dye degradation is observed in every one of the studied conditions. Thus, these results suggest adsorption-driven interactions between MB molecules and SiO_2-NPs, facilitated by the high surface area and active sites of the nanoparticles. **Figure 7c** demonstrates a direct correlation between SiO_2-NPs concentration and dye removal efficiency (*E*), achieving up to 83.99% under UV light at 0.6 g nanoparticle loading. It is noted that a marked improvement in degradation efficiency under UV light at a lower concentration of 0.15 g SiO_2-NPs was observed, while it remained insignificantly changed at higher concentrations (0.3 g and 0.6 g). This phenomenon may be attributed to several factors, including limitations on UV light penetration, particle aggregation, saturation of adsorption sites, and so on. In particular, the increase in degradation efficiency at low concentration (0.15 g) is notable and may be due to the optimal dispersion of SiO_2-NPs nanoparticles, and efficient penetration of UV light. However, further increases in concentration (0.3 g and 0.6 g) may originate from aggregation, optical limitations, or active site saturation, resulting in no significant improvement in *E*. Optimizing nanoparticle dispersion and

controlling the reaction conditions could mitigate these issues to enhance efficiency further.

Notably, the raw sand exhibited a limited adsorption capacity, with low surface reactivity, and required an extended contact time under neutral conditions (pH = 6–7). Nevertheless, it achieved a moderate methylene blue (MB) removal efficiency of 60% or higher under more favorable conditions. Specifically, these conditions included a high adsorbent dosage of 500 g/L, a prolonged contact time of 45 minutes or more, and an acidic pH of 4; however, this resulted in significantly poorer reusability compared to SiO_2 nanoparticles (Halim et al. 2015).

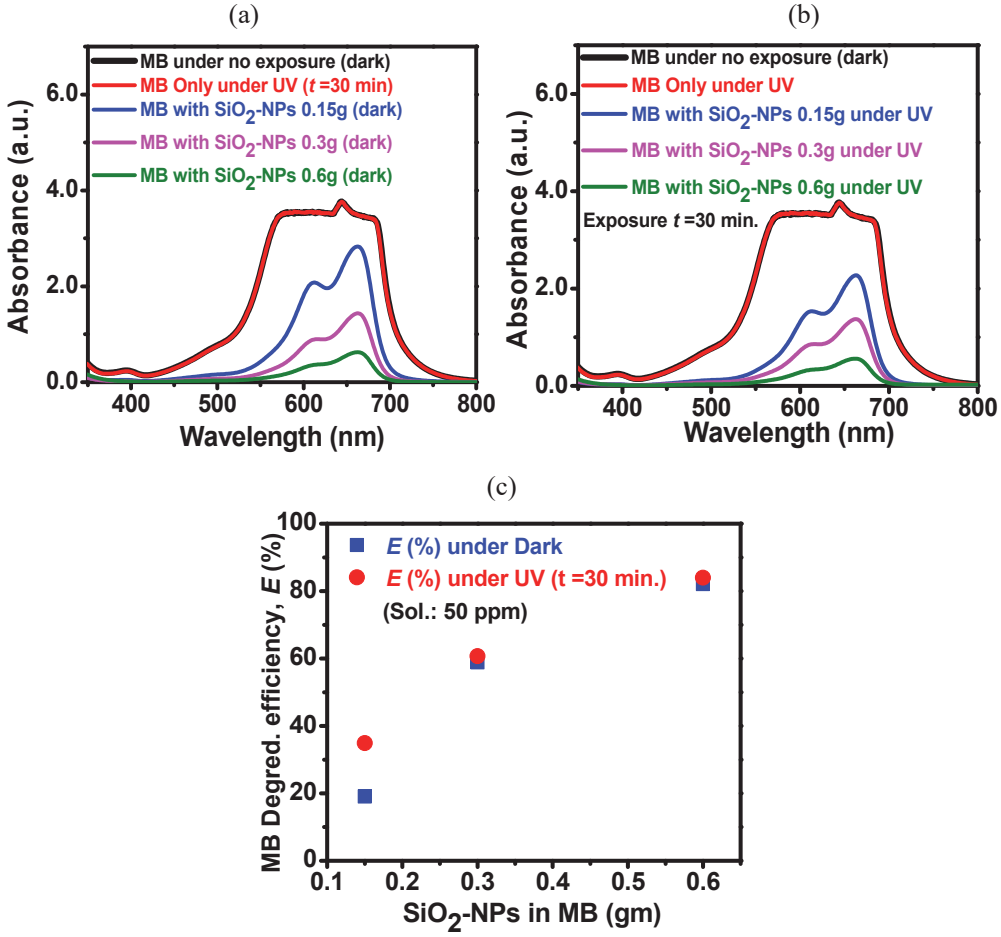

Figure 7. The absorbance spectra of SiO_2 nanoparticles added MB dye under (a) dark (b) UV and corresponding (c) dye degradation efficiency under dark and UV exposure for 30 minutes

Herein, the estimated efficiency was calculated by comparing the initial aqueous solution with the solution after the photodegradation test, highlighting the potential of SiO_2-NPs as an eco-friendly and scalable solution for industrial dye wastewater treatment, aligning with sustainable environmental remediation technologies. Dye removal was monitored using a UV-visible spectrophotometer, and efficiency was estimated as the percentage of dye color removal using **Equation 5**.

$$\text{MB removal efficiency, } E\,(\%) = \frac{(\text{Co-Ct})}{\text{Co}} \times 100 \quad \ldots\ldots (5)$$

Where Co and Ct are the initial and final dye concentration at time *t*, respectively.

(5) Reusability Performance of SiO_2-NPs

Figure 8 depicts comparative dye removal degradation efficiency for fresh and reused SiO_2-NPs for 0.6 g under both dark and UV conditions. **Figure 8a** demonstrates that fresh SiO_2-NPs achieve significant methylene blue (MB) dye removal under dark conditions, with a notable decrease in absorbance compared to the reused SiO_2-NPs. Similarly, the fresh SiO_2-NPs again exhibit superior dye degradation efficiency compared to their reused counterparts under UV conditions (**Figure 8b**). **Table 3** summarizes these findings quantitatively. However, MB dye removal efficiency improves substantially from 19.09% at 0.15 g SiO_2-NPs to 82.07% at 0.6 g under dark conditions, and from 34.92% at 0.15 g to 83.99% at 0.6 g under UV light, revealing adsorption as the dominant mechanism over photocatalysis. Upon reuse, MB removal efficiency *E* drops to 67% under dark conditions and 44.88% under UV light, underscoring a marked decline in adsorption as well as in photocatalytic performance. This decline may stem from surface fouling, optimal dispersion of SiO_2-NPs, or saturation of active sites during the initial usage cycle. Regeneration treatments, such as surface cleaning, reactivation of active sites, or the use of an advanced extraction process to reuse used SiO_2-NPs, are necessary to restore their adsorption properties. Moreover, the potential of SiO_2-NPs for wastewater treatment is evident, revealing a removal efficiency of over 80%, although further studies are required to unveil strategies to enhance their reusability for sustainable applications.

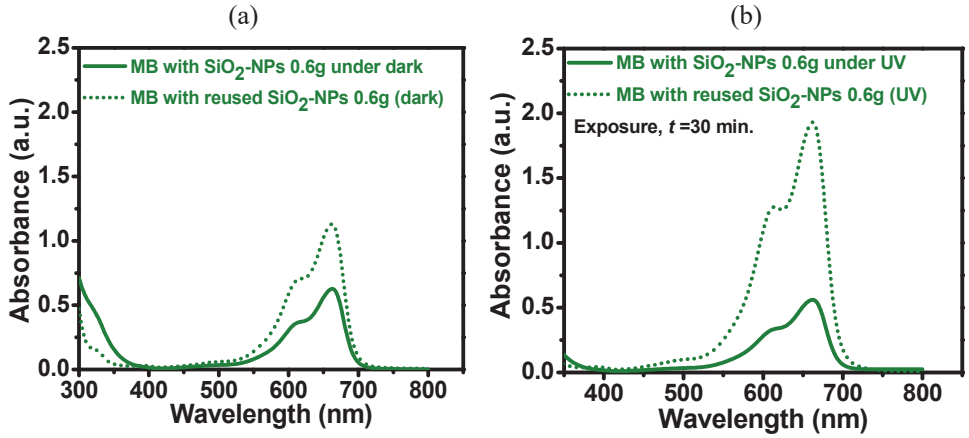

Figure 8. Absorbance spectra of fresh and reused SiO_2 NPs under (a) dark, (b) UV (*t* =30 min)

Table 3. The dye removal efficiency of fresh and reused SiO_2-NPs under dark and UV exposure

MB Degradation efficiency of SiO_2-NPs, *E* (%)			
Fresh		**Reused**	
Dark	UV (*t*= 30 min.)	Dark	UV (*t*= 30 min.)
82.07	83.99	67.76	44.88

(6) Dye Removal Mechanism

Figure 9 illustrates the degradation mechanism of methylene blue (MB) dye on silica nanoparticles (SiO_2-NPs), emphasizing adsorption-dominant interactions. The absorption spectra indicate minimal changes under UV exposure compared to the dark condition, suggesting that the degradation of MB dye predominantly occurs via adsorption rather than photochemical processes. The

dense active sites on the synthesized SiO_2-NPs, extracted from river sand play a crucial role in this process. As observed, the maximum adsorption efficiency of SiO_2-NPs reached approximately 80%, highlighting their efficacy in removing MB dye from wastewater. The adsorption behavior aligns well with the Temkin isotherm model, which accounts for the interaction between the adsorbent and adsorbate, suggesting that adsorption energy decreases linearly with increasing coverage. Kinetic studies further confirm that the MB dye adsorption follows a pseudo-second-order model, indicating chemisorption as the rate-limiting step. In addition to these studies, the absorption characteristics of MB dye in both dark and UV exposure with varying concentrations of SiO_2-NPs support this possible mechanism involving multiple interactions as follows (Hani et al. 2023).

(i) *Electrostatic attractions*: The positively charged MB molecules interact with negatively charged silanol groups (-Si-O^-) on the surface of SiO_2-NPs.

(ii) *Hydrogen bonding*: The amine groups in MB form hydrogen bonds with silanol and oxygen groups present on the silica surface.

(iii) *n–π Interaction*: π-electrons from the aromatic rings of MB interact with the oxygen atoms on silica.

The high adsorption capacity and simplicity of SiO_2-NPs synthesis, utilizing an abundant and inexpensive resource such as river sand, make this material a promising candidate for removing persistent organic pollutants from industrial wastewater. The adsorption-dominant mechanism demonstrated in this study reinforces the versatility of SiO_2-NPs for sustainable wastewater treatment solutions, minimizing environmental impacts and contributing to cleaner water resources. These findings are consistent with earlier reports on nano-silica extracted from dune sand using sol-gel methods (Hani et al. 2023).

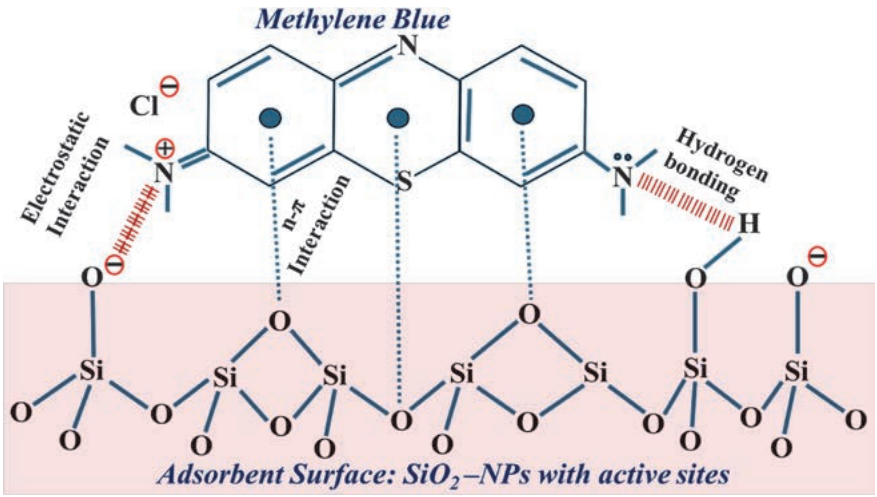

Figure 9. Mechanism of MB dye degradation under an adsorption-dominant process by river sand-derived SiO_2-NPs

Table 4 illustrates the adsorption capabilities of various silica-based materials for methylene blue (MB) dye removal in wastewater treatment applications. Herein, the microwave kiln-assisted alkali fusion-derived SiO_2 nanoparticles from Padma River sand demonstrated an impressive adsorption capacity of 83.9 mg/g under UV irradiation compared to previous reports (Samy et al. 2023; Dhmees et al. 2018; Qin et al. 2017; Cui et al. 2017; Cisneros-Trejo et al. 2024; Riyanti et al. 2020; Jamhour et

al. 2023; Elizondo-Villarreal et al. 2024; Hani et al. 2023). Notably, the achieved adsorption capacity value surpasses or competes closely with most conventional sol-gel processed silica-based adsorbents, such as mesoporous SiO_2 from rice straw (71.4 mg/g), mesoporous silica via TEOS solution (34.23 mg/g), dune sand (25.0 mg/g), chitosan (20.9 mg/g), silica sand (3.3 mg/g), TEOS+PEDS (73.49 mg/g), Bioscaffolds Petal Cells (74.0 mg/g), and materials like blast furnace slag-based silica nanoparticles (80.8 mg/g). This enhanced adsorption behavior can be attributed to particle morphology, high surface area, controlled porosity, and improved surface reactivity imparted by microwave-assisted synthesis and the avoidance of high temperatures and complex processing steps and conditions. Moreover, it is evident that the direct utilization of low-cost, silica-rich river sand as a precursor material utilizing a simpler, faster, and greener synthesis route exhibits strong potential for large-scale wastewater treatment and pollutant remediation. Future work could focus on photocatalysis and environmental sensing technologies, and further detailed studies focusing on properties (physical, chemical, and optical), surface functionalization, composite development, and extended applications would provide a deeper understanding of this preliminary outcome-based observation.

Table 4. A summary of the adsorption capabilities of different adsorbent materials for MB dye removal/ adsorption for wastewater treatment

Material	Adsorption/Removal capacity (mg/g)	Synthesis process, Source materials	References
Mesoporous SiO_2	71.4	Rice straw, Sol-gel	Samy et al. 2023
Silica nanoparticles	80.8	Blast furnace slag, Sol-gel	Dhmees et al. 2018
Mesoporous silica	34.23	One-pot solution, *TEOS*	Qin et al. 2017
2D mesoporous SiO_2	74.0	Bioscaffolds Petal Cells	Cui et al. 2017
Porous SiO_2	73.49	Sol-gel, *TEOS+PEDS*	Cisneros-Trejo et al. 2024
SiO_2-composite	20.876	Sol–gel, Chitosan	Riyanti et al. 2020
Nano Silica	3.28	Sol-gel, Silica sand	Jamhour et al. 2023
SiO_2 Nanoparticles	150	Sol-gel, a diluted *Na*-silicate	Elizondo et al. 2024
Nano Silica	25.0	Sol–gel, Dune Sand	Hani et al. 2023
SiO_2-Nanoparticles	83.9 (under UV)	Microwave-assisted alkali fusion, river sand	Present work

4. Conclusion

The green extraction and transformation of local river sand into silica nanoparticles (SiO_2-NPs) and their subsequent application for treating wastewater contaminated with methylene blue (MB) were successfully performed. The experimental study demonstrated a removal efficiency of over 83% for 50 ppm MB under UV light and 65% in dark conditions. The extracted SiO_2-NPs exhibited excellent adsorption and reusability properties, showcasing a significant dual impact on environmental conservation. Extracting excess sand deposited on local riverbanks, transforming it into silica, and applying it for dye removal from toxic industrial wastewater not only provides an eco-friendly approach to silica extraction but also addresses critical environmental challenges through sustainable wastewater treatment. The findings align with green chemistry principles, offering practical solutions for industrial waste remediation by utilizing natural resources that pose challenges to daily livelihoods and ecosystems. By leveraging abundant, locally available resources, the study highlights a cost-

effective pathway for advancing green technology while conserving natural ecosystems. Additionally, it provides a scalable and environmentally conscious strategy, contributing to a zero-carbon future and promoting sustainable development by mitigating one environmental threat through the sustainable use of another.

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