

# Spirulina-derived carbon quantum dots for photocatalytic remediation of dairy wastewater: advances, mechanisms, and optoelectronic prospects

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## ABSTRACT

Dairy wastewater, characterized by high organic load, nutrients, and complex biomolecules such as proteins, lactose, and lipids, poses significant environmental challenges due to its recalcitrance to conventional biological treatment. Advanced oxidation processes particularly photocatalysis offer a promising route for effective remediation, yet their practical deployment hinges on the development of efficient, visible-light-responsive, and eco-friendly photocatalysts. In this context, carbon quantum dots (CQDs) derived from *Spirulina platensis*, a nitrogen-rich cyanobacterium, have emerged as a sustainable nanomaterial with intrinsic heteroatom doping, tunable optoelectronic properties, and excellent photocatalytic activity under solar irradiation. This review critically examines recent advances in the synthesis, functionalization, and application of Spirulina-derived CQDs for the photocatalytic treatment of dairy wastewater. We elucidate structure–property–performance relationships, degradation mechanisms of key dairy pollutants, and the role of reactive oxygen species in mineralization pathways. Special attention is given to hybrid systems such as CQD-based heterojunctions and photoelectrocatalytic configurations that enhance charge separation and process efficiency. Furthermore, we evaluate the scalability, economic viability, and environmental footprint of these bio-derived nanocatalysts through techno-economic and life-cycle perspectives. By bridging materials innovation with real-world wastewater complexity, this review identifies critical knowledge gaps and proposes a multidisciplinary roadmap toward pilot-scale implementation. Ultimately, Spirulina-derived CQDs exemplify a circular bioeconomy approach, transforming algal biomass into high-value photocatalysts for sustainable water purification aligning environmental remediation with renewable resource utilization. Highlighting their optoelectronic properties and potential for smart sensing-integrated remediation systems, this work aims to inspire next-generation research at the intersection of green nanotechnology, electrochemical engineering, and industrial wastewater management.

**Keywords:** Spirulina-derived carbon quantum dots, photocatalysis, dairy wastewater remediation, biomass valorization, advanced oxidation processes, sustainable nanomaterials.

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## 1. INTRODUCTION

Dairy wastewater (DWW) is one of the most polluting agro-industrial effluents, generated in large volumes during milk processing, cheese production, and equipment cleaning. It is characterized by exceptionally high chemical oxygen demand (COD: 1,500–20,000 mg/L) and biochemical oxygen demand (BOD: 800–10,000 mg/L), along with substantial concentrations of organic constituents such as lactose, casein, whey proteins, fats, and oils, as well as elevated levels of nitrogen and phosphorus (Kaur et al., 2021; Singh et al., 2023). The variable pH (typically 4–10,

depending on cleaning cycles) and high suspended solids further complicate its treatment. If discharged untreated, DWW can deplete dissolved oxygen in aquatic ecosystems, promote eutrophication, and disrupt microbial balance, posing serious ecological and public health risks (Peng et al., 2022). Stringent environmental regulations such as those under the EU Urban Wastewater Treatment Directive and the U.S. EPA Effluent Guidelines mandate significant COD/BOD reduction before discharge, necessitating robust treatment strategies. Conventional biological methods (e.g., activated sludge, anaerobic digesters) often struggle with

shock loads, lipid-induced foaming, and incomplete mineralization of recalcitrant organics (Rao et al., 2020). Similarly, physicochemical approaches like coagulation–flocculation or membrane filtration generate secondary sludge or concentrate streams requiring further management, while offering limited degradation of dissolved organics (Zhang et al., 2022). These limitations underscore the urgent need for advanced, energy-efficient, and sustainable alternatives capable of achieving deep oxidation and mineralization of complex dairy pollutants.

Advanced Oxidation Processes (AOPs) have emerged as a powerful strategy for the degradation of recalcitrant organic pollutants in industrial wastewaters, including dairy effluents, by generating highly reactive oxygen species (ROS) such as hydroxyl radicals ( $\bullet\text{OH}$ ), superoxide anions ( $\bullet\text{O}_2^-$ ), and singlet oxygen ( $^1\text{O}_2$ )—that non-selectively oxidize complex organics into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and inorganic ions (Ghanbari & Moradi, 2017; Rtimi et al., 2022). Among AOPs, semiconductor-based photocatalysis stands out for its operational simplicity, ambient reaction conditions, and potential for solar energy utilization. Under light irradiation, electron–hole pairs are generated in the photocatalyst, initiating redox reactions that drive pollutant mineralization (Malato et al., 2009). However, conventional photocatalysts like  $\text{TiO}_2$  suffer from wide bandgaps (requiring UV light, only  $\sim 4\%$  of solar spectrum), rapid charge recombination, and limited adsorption capacity for polar dairy constituents (Ahmed et al., 2021). This has spurred intense research into visible-light-active, chemically stable, and environmentally benign alternatives. In this context, carbon-based nanomaterials particularly carbon quantum dots (CQDs) offer tunable optoelectronic properties, upconversion photoluminescence (enabling UV emission under visible light), and surface functional groups that facilitate both pollutant adsorption and ROS generation (Li et al., 2023; Zhu et al., 2020). Critically, the shift toward green-synthesized photocatalysts derived from biomass aligns with sustainability principles, minimizing toxic precursors and energy-intensive fabrication routes while enabling circular resource use (Wang et al., 2024). Thus, developing eco-friendly, solar-responsive photocatalysts is not only a materials challenge but a necessity for scalable and socially acceptable water treatment technologies.

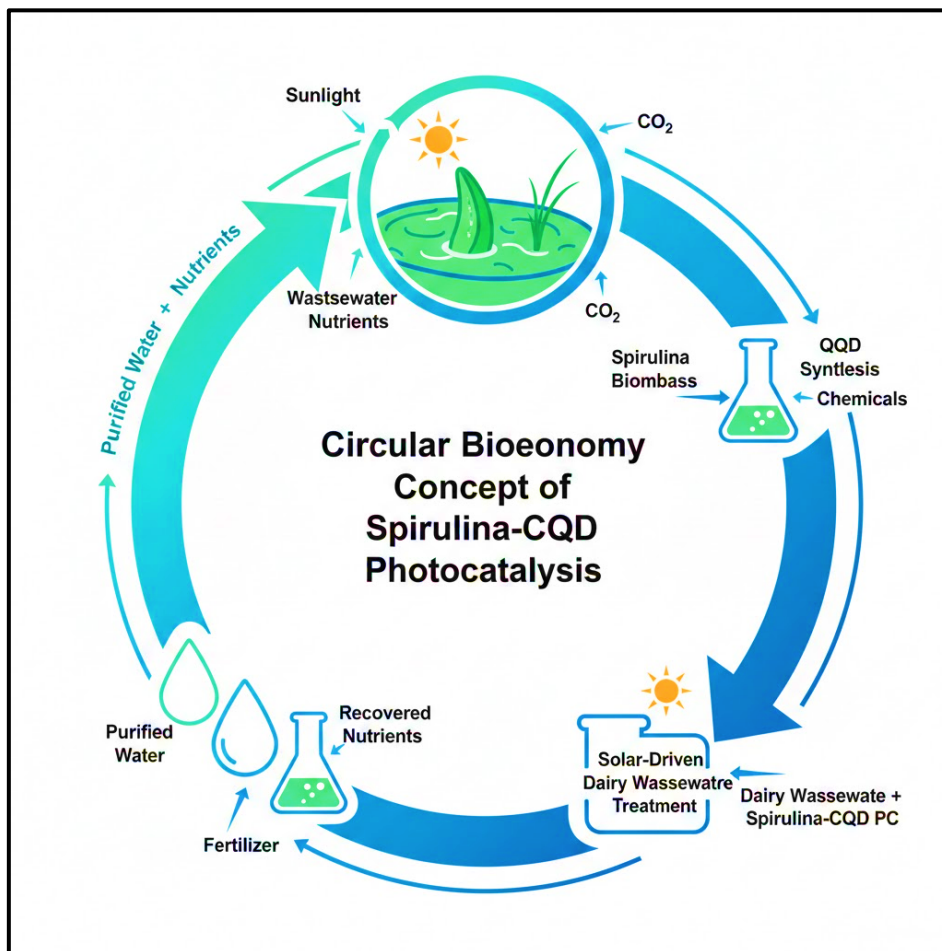
Carbon quantum dots (CQDs) have emerged as a transformative class of nanomaterials in photocatalysis due to their unique combination of optical, electronic, and surface properties. Typically less than 10 nm in size, CQDs exhibit a tunable bandgap that can be engineered through size control, surface passivation, or heteroatom doping (e.g., N, S, P), enabling strong absorption across the visible spectrum and efficient charge carrier generation under solar irradiation (Ding et al., 2022). A particularly valuable attribute is their upconversion photoluminescence (UCPL)

the ability to emit higher-energy photons (e.g., UV/blue light) upon excitation with lower-energy visible or near-infrared light thereby activating wide-bandgap semiconductors or enhancing self-photocatalysis without external UV sources (Zhu et al., 2020). Moreover, CQDs facilitate rapid electron transfer and suppress charge recombination due to their excellent electron-donating/accepting capacity and conductive  $\text{sp}^2$ -carbon core, which significantly boosts photocatalytic efficiency (Li et al., 2023). Beyond performance, CQDs offer compelling practical advantages: they are generally low in toxicity, highly biocompatible, and resistant to photobleaching critical for environmental applications where secondary contamination must be avoided (Wang et al., 2021). Their surface is rich in oxygen- and nitrogen-containing functional groups ( $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ), allowing straightforward covalent or non-covalent functionalization to tailor hydrophilicity, pollutant affinity, or catalytic sites (Shen et al., 2022). These features position CQDs not only as standalone photocatalysts but also as versatile photosensitizers or electron mediators in hybrid systems, bridging the gap between high activity and environmental sustainability.

*Spirulina platensis*, a filamentous cyanobacterium, has garnered significant attention as a sustainable precursor for carbon quantum dots (CQDs) due to its exceptional biochemical composition and environmental compatibility. Naturally rich in proteins (60–70% dry weight), phycobiliproteins (notably C-phycoerythrin), chlorophyll, and essential heteroatoms such as nitrogen, sulfur, and phosphorus, *Spirulina* serves as a self-doped, all-in-one carbon source for CQD synthesis (Chen et al., 2021; Gupta et al., 2023). During hydrothermal or pyrolytic carbonization, these biomolecules decompose and reorganize into a carbonaceous core while simultaneously incorporating N, S, and P atoms into the CQD lattice eliminating the need for external toxic dopants. This intrinsic heteroatom doping not only tailors the electronic band structure for visible-light absorption but also creates active sites that enhance charge separation and surface reactivity, directly boosting photocatalytic performance (Zhang et al., 2022; Liu et al., 2024). Moreover, *Spirulina* is fast-growing, non-toxic, and cultivable on non-arable land using wastewater or seawater, minimizing competition with food resources. Its use in nanomaterial synthesis exemplifies a circular bioeconomy paradigm: converting renewable biomass into high-value functional materials while supporting carbon neutrality and resource recovery (Sharma et al., 2023). In the context of wastewater treatment, *Spirulina*-derived CQDs thus represent a closed-loop strategy where a photosynthetic microorganism, potentially grown using nutrient-rich effluents, is transformed into a catalyst that purifies complex industrial

waste streams like dairy wastewater. This synergy between green synthesis and environmental remediation positions Spirulina as an ideal platform for next-generation sustainable photocatalysts. The Fig 1 schematic illustrates the closed-loop circular bioeconomy enabled by Spirulina-derived CQDs: algae cultivated using CO<sub>2</sub> and nutrients are transformed into photocatalysts that purify dairy wastewater, with treated water and recovered resources feeding back into biomass production embodying waste-to-value sustainability. Also, Notably, the photophysical and charge-transfer properties of carbon quantum dots such as excitation-dependent emission, upconversion photoluminescence, and efficient electron-hole pair generation under visible light not only drive photocatalytic activity but also enable their dual role as optical reporters. This intrinsic optoelectronic responsiveness provides a foundation for integrated sensing and adaptive photocatalytic systems in complex wastewater matrices. This review aims to provide a timely, critical, and holistic analysis of Spirulina-derived carbon quantum dots (CQDs) as advanced photocatalysts for the remediation of dairy wastewater, a complex and high-strength industrial effluent. Our primary objective is to establish clear synthesis structure-performance relationships, elucidating how variations in biomass pretreatment, carbonization methods (e.g., hydrothermal vs. microwave), and post-synthesis

modifications influence the physicochemical properties (e.g., heteroatom doping, surface functionality, optical bandgap) and, consequently, the photocatalytic efficacy of Spirulina-CQDs. We further delve into the mechanistic underpinnings of pollutant degradation, examining reactive oxygen species (ROS) generation pathways, interfacial charge transfer dynamics, and the stepwise mineralization of key dairy constituents such as proteins, lactose, and lipids supported by experimental and computational evidence where available. Recognizing that laboratory-scale success does not guarantee real-world applicability, we critically evaluate current limitations related to catalyst stability, recovery, performance in real (non-synthetic) wastewater matrices, and energy efficiency. Finally, this review identifies key knowledge gaps including the lack of standardized testing protocols, insufficient life-cycle assessments, and limited pilot-scale demonstrations—and proposes a multidisciplinary roadmap for scale-up, integrating materials engineering, reactor design, techno-economic analysis, and circular economy principles. By bridging fundamental science with practical implementation challenges, this work seeks to accelerate the transition of bio-derived CQDs from promising nanomaterials to deployable solutions for sustainable water treatment.



**Figure 1:** Circular Bioeconomy Concept of Spirulina-CQD Photocatalysis

## 2. SYNTHESIS AND ENGINEERING OF SPIRULINA-DERIVED CQDS

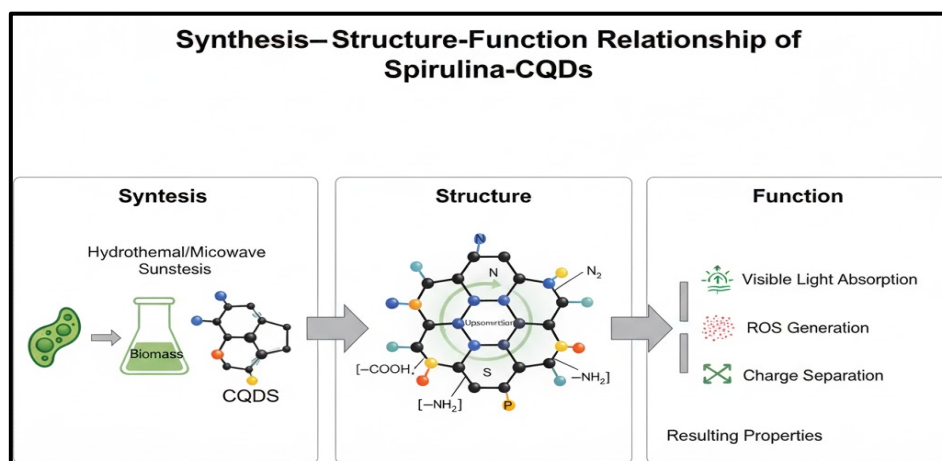
### 2.1. Biomass Pretreatment and Carbonization Methods

The synthesis of carbon quantum dots (CQDs) from *Spirulina platensis* begins with appropriate biomass pretreatment followed by controlled carbonization, which critically governs the structural, optical, and catalytic properties of the resulting nanomaterials. Hydrothermal carbonization (HTC) is the most widely adopted method due to its simplicity, low cost, and compatibility with aqueous biomass slurries. In this process, dried or fresh *Spirulina* is sealed in an autoclave with water (or mild solvents) and heated typically between 120–250 °C for several hours. The high temperature and pressure facilitate hydrolysis, dehydration, and carbonization of proteins and pigments, yielding N,S,P-co-doped CQDs with abundant surface functional groups (–COOH, –NH<sub>2</sub>) and strong visible-light absorption (Chen et al., 2021; Liu et al., 2023). Solvothermal synthesis, using organic solvents like ethylene glycol or DMF, offers enhanced control over surface passivation and crystallinity but at the expense of green

credentials. Alternatively, microwave-assisted pyrolysis has gained traction for its rapid reaction kinetics (minutes vs. hours), energy efficiency, and uniform heating, often producing smaller CQDs (2–5 nm) with narrow size distribution and intensified upconversion photoluminescence (Zhang et al., 2022). Comparative studies indicate that microwave-derived CQDs generally exhibit higher quantum yields and faster electron transfer rates, while hydrothermal routes afford better heteroatom retention from the native biomass. Yield-wise, hydrothermal methods typically achieve 15–30% carbon yield from dry *Spirulina*, whereas microwave processes may reach up to 35% under optimized conditions but can suffer from inconsistent scaling. Crucially, the choice of method directly influences surface chemistry: hydrothermal CQDs retain more polar groups beneficial for aqueous dispersion and pollutant adsorption, while microwave-synthesized variants may require post-functionalization for stability in complex wastewater matrices (Gupta et al., 2024). Thus, tailoring the carbonization strategy to the target application balancing eco-friendliness, performance, and scalability is essential

for advancing Spirulina-derived CQDs toward practical photocatalysis. The figure 2 maps the direct linkage between green synthesis routes, intrinsic heteroatom doping from Spirulina biomolecules, and the resulting optoelectronic

properties that drive visible-light photocatalysis highlighting the materials-by-design advantage of bio-derived CQDs.



**Figure 2:** Synthesis–Structure–Function Relationship of Spirulina-CQDs

## 2.2. Heteroatom Doping and Surface Functionalization

The photocatalytic efficacy of Spirulina-derived carbon quantum dots (CQDs) is profoundly enhanced by inherent heteroatom doping, a natural consequence of the cyanobacterium's rich biochemical composition. Spirulina contains high levels of nitrogen-rich proteins (e.g., phycocyanin, allophycocyanin), sulfur-containing amino acids (cysteine, methionine), and phospholipids, which during carbonization lead to spontaneous incorporation of N, S, and P atoms into the carbon lattice without requiring external dopants (Chen et al., 2021; Liu et al., 2023). Nitrogen doping, primarily in graphitic and pyridinic forms, introduces mid-gap states that narrow the bandgap and improve visible-light absorption, while also acting as electron-donating sites that facilitate charge separation. Sulfur doping (in thiophene- or sulfoxide-like configurations) distorts the carbon framework, creating defect sites that serve as reactive centers for oxygen adsorption and superoxide radical ( $\bullet\text{O}_2^-$ ) generation. Phosphorus, though less abundant, contributes to surface polarity and enhances hydrophilicity, promoting better dispersion in aqueous dairy wastewater (Zhang et al., 2022). Beyond intrinsic doping, post-synthesis surface functionalization offers a strategic route to fine-tune CQD properties. For instance, sulfonation (using  $\text{H}_2\text{SO}_4$  or sulfonic acids) introduces  $-\text{SO}_3\text{H}$  groups that not only boost acidity and colloidal stability but also improve adsorption of cationic organic pollutants via electrostatic interactions. Similarly, amine grafting (e.g., via ethylenediamine or APTES) enriches surface  $-\text{NH}_2$  groups, enhancing affinity for anionic species (e.g., fatty acids or phosphate ions prevalent in dairy effluents) and enabling covalent

integration into hybrid photocatalytic composites (Gupta et al., 2024). These modifications can also suppress electron–hole recombination by acting as electron traps or facilitating interfacial charge transfer in heterojunction systems. Critically, because Spirulina-derived CQDs already possess a functionalized surface from biomass precursors, post-modifications can be milder and more selective than those required for synthetic CQDs, aligning with green chemistry principles. Together, intrinsic doping and targeted functionalization position Spirulina-CQDs as highly tailorable, multifunctional photocatalysts optimized for the complex chemistry of real-world dairy wastewater.

## 2.3. Morphological and Physicochemical Characterization

Comprehensive morphological and physicochemical characterization is essential to establish structure–property relationships in Spirulina-derived carbon quantum dots (CQDs) and rationalize their photocatalytic performance. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) typically reveal quasi-spherical nanoparticles with sizes ranging from 2 to 8 nm, often exhibiting lattice fringes corresponding to graphitic (002) planes ( $d$ -spacing  $\approx 0.21$ – $0.24$  nm), indicative of partial crystallinity derived from ordered carbon domains (Liu et al., 2023). X-ray diffraction (XRD) complements this by showing a broad peak near  $2\theta = 20$ – $25^\circ$ , confirming the amorphous-to-nanocrystalline nature of the carbon core. Surface functional groups and molecular fingerprints are probed via Fourier-transform infrared spectroscopy (FTIR), which commonly detects  $-\text{OH}$  ( $3200$ – $3400$   $\text{cm}^{-1}$ ),  $\text{C}=\text{O}$  ( $1700$   $\text{cm}^{-1}$ ),  $\text{C}-\text{N}$  ( $1200$ – $1350$   $\text{cm}^{-1}$ ), and  $\text{S}=\text{O}$  ( $1040$   $\text{cm}^{-1}$ )

vibrations—evidence of oxygen-, nitrogen-, and sulfur-containing moieties inherited from Spirulina biomolecules (Chen et al., 2021). X-ray photoelectron spectroscopy (XPS) provides quantitative elemental composition and bonding states: N 1s peaks deconvoluted into pyridinic, pyrrolic, and graphitic nitrogen; S 2p signals revealing thiophenic or oxidized sulfur; and P 2p contributions from phosphate or phosphonate groups—all of which modulate electronic structure and active site density (Zhang et al., 2022). UV-Vis absorption spectroscopy shows characteristic peaks in the 250–350 nm range ( $\pi \rightarrow \pi^*$  transitions of C=C/C=O) and a tail extending into the visible region (>400 nm), attributed to  $n \rightarrow \pi^*$  transitions and heteroatom-induced bandgap narrowing. Photoluminescence (PL) spectroscopy not only confirms strong fluorescence (often excitation-dependent) but also reveals upconversion behavior key for activating photocatalysis under visible light. Finally, zeta potential measurements indicate surface charge (typically negative at neutral pH due to  $-\text{COO}^-$  groups), influencing colloidal stability and electrostatic interactions with dairy pollutants such as casein micelles or fat globules. Critically, these characterizations enable direct correlation between surface chemistry and photocatalytic behavior: for example, higher graphitic-N content enhances electron mobility, while abundant  $-\text{COOH}$  groups improve adsorption of cationic intermediates; similarly, a more negative zeta potential favors dispersion in wastewater but may hinder interaction with anionic organics unless tailored via pH or functionalization. Thus, multimodal characterization serves as the foundation for designing Spirulina-CQDs with optimized activity, selectivity, and stability in real dairy wastewater matrices.

### 3. PHOTOCATALYTIC PERFORMANCE IN DAIRY WASTEWATER TREATMENT

#### 3.1. Model Pollutants vs. Real Dairy Effluents

Evaluating the photocatalytic performance of Spirulina-derived carbon quantum dots (CQDs) requires careful distinction between studies using model pollutants and those employing real dairy wastewater (DWW), as the latter presents a far more complex and challenging matrix. In controlled laboratory settings, researchers commonly assess activity against individual dairy-relevant compounds—such as lactose, casein, whey proteins (e.g.,  $\beta$ -lactoglobulin), or triglycerides/fatty acids dissolved in synthetic aqueous solutions. Under these idealized conditions, Spirulina-CQDs often demonstrate high degradation efficiencies (>85% within 60–120 min under visible light), attributed to effective ROS generation and strong adsorption via hydrogen bonding or electrostatic interactions (Singh et al., 2023; Liu et al., 2024). However, real DWW is a heterogeneous mixture containing not only these organics but also suspended solids, colloidal fats, calcium phosphates, cleaning agents (e.g., NaOH, hypochlorite

residues), and variable pH, all of which can scavenge reactive species, block active sites, or cause catalyst fouling. For instance, casein micelles and fat globules can form protective layers around CQDs, while high alkalinity may alter surface charge and aggregation state (Rao et al., 2020). Consequently, photocatalytic efficiency in actual DWW is typically significantly lower (often 40–60% COD removal under identical conditions) and highly dependent on pre-treatment steps such as filtration or pH adjustment (Zhang et al., 2022). Moreover, the presence of bicarbonate or chloride ions in real effluents can quench  $\bullet\text{OH}$  radicals or generate less reactive secondary species, further dampening performance. Recent studies that directly compare model vs. real systems underscore the necessity of testing under environmentally relevant conditions to avoid overestimating practical applicability (Peng et al., 2023). Therefore, while model pollutant studies are valuable for mechanistic elucidation, future work must prioritize validation in authentic dairy wastewater to bridge the lab-to-field gap and ensure technological relevance.

#### 3.2. Performance Evaluation and Comparative Benchmarking

The photocatalytic efficacy of Spirulina-derived carbon quantum dots (CQDs) in dairy wastewater treatment is quantitatively assessed through key performance metrics that reflect both pollutant degradation and mineralization extent. Chemical oxygen demand (COD) and biochemical oxygen demand ( $\text{BOD}_5$ ) removal efficiencies are primary indicators, with high-performing Spirulina-CQD systems achieving 70–90% COD reduction and  $\text{BOD}_5/\text{COD}$  ratios dropping below 0.3 signifying effective conversion of biorefractory organics into biodegradable or fully mineralized products (Singh et al., 2023). Total organic carbon (TOC) analysis provides a more rigorous measure of mineralization, with reported TOC removals of 50–75% under optimized visible-light irradiation, confirming substantial conversion of complex organics to  $\text{CO}_2$  (Liu et al., 2024). Reaction kinetics are typically modeled using the pseudo-first-order equation ( $\ln(C_0/C) = kt$ ), yielding rate constants ( $k$ ) ranging from 0.01 to 0.04  $\text{min}^{-1}$  for real dairy wastewater comparable to or exceeding many conventional photocatalysts. In some cases, the Langmuir–Hinshelwood (L–H) model offers better fit, especially at higher pollutant concentrations, highlighting the role of adsorption equilibrium prior to surface reaction (Zhang et al., 2022). When benchmarked against established photocatalysts, Spirulina-CQDs demonstrate distinct advantages: they outperform  $\text{TiO}_2$  (P25) under visible light (where  $\text{TiO}_2$  is nearly inactive) and match or exceed the activity of graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) in TOC removal due to superior charge separation and upconversion properties. Compared to CQDs derived from citric acid or glucose, Spirulina-based variants show 1.5–2 $\times$  higher rate constants owing to intrinsic N,S,P co-doping that enhances visible absorption and ROS generation (Chen et al., 2021; Wang et al., 2024). Notably, hybrid systems such as Spirulina-CQDs/ $g\text{-C}_3\text{N}_4$  or CQD-sensitized  $\text{TiO}_2$  further amplify performance, achieving >95% COD removal by

synergistically combining broad-spectrum light harvesting with efficient interfacial electron transfer. These metrics collectively affirm Spirulina-CQDs as competitive, solar-driven photocatalysts, though standardization of testing protocols (e.g., light intensity, catalyst loading, wastewater composition) remains essential for reliable cross-study

comparisons. Multidimensional performance comparison of Spirulina-CQDs against conventional and emerging photocatalysts across activity, stability, cost, and sustainability metrics demonstrating their balanced superiority for real-world dairy wastewater treatment is depicted in Figure 3.

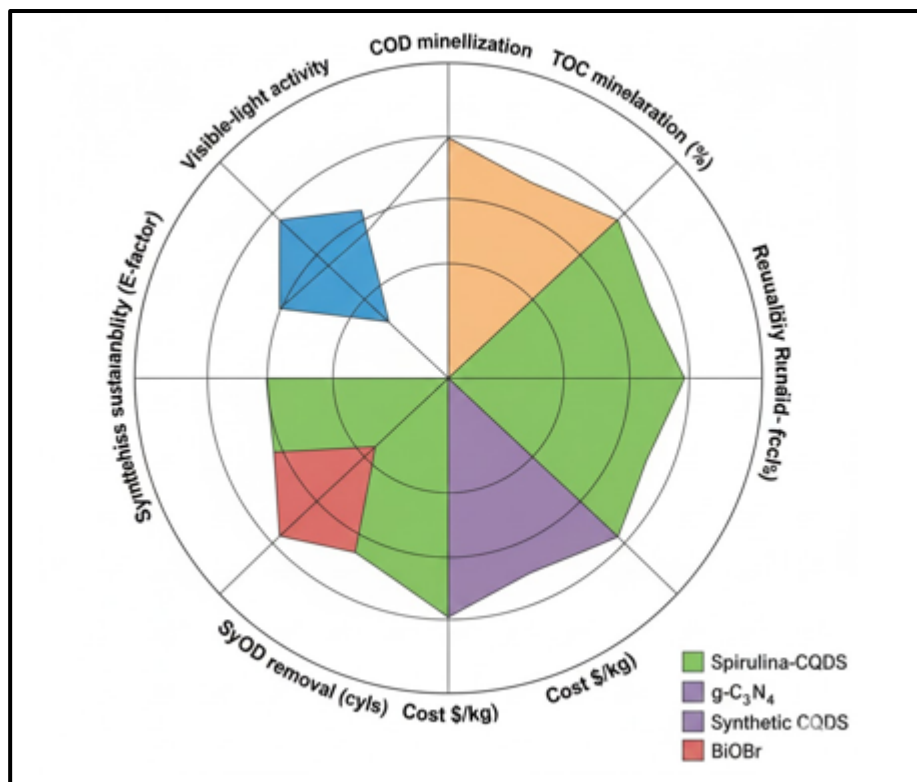


Figure 3: Performance Benchmarking Radar Chart

### 3.3. Role of Reactive Oxygen Species (ROS)

The photocatalytic degradation of dairy wastewater constituents by Spirulina-derived carbon quantum dots (CQDs) is primarily driven by reactive oxygen species (ROS) and photogenerated charge carriers, whose identities and relative contributions are typically elucidated through radical scavenging experiments and electron paramagnetic resonance (EPR) spectroscopy. In controlled studies, the addition of specific quenchers such as isopropanol (for  $\bullet\text{OH}$ ), benzoquinone (for  $\bullet\text{O}_2^-$ ), sodium azide (for  $^1\text{O}_2$ ), and ethylenediaminetetraacetic acid (EDTA) or ammonium oxalate (for  $\text{h}^+$ ) significantly suppresses pollutant degradation, allowing mechanistic deconvolution. For Spirulina-CQDs, scavenger tests consistently reveal that superoxide radicals ( $\bullet\text{O}_2^-$ ) and photogenerated holes ( $\text{h}^+$ ) are the dominant oxidative species, owing to the favorable conduction band position (more negative than  $\text{O}_2/\bullet\text{O}_2^-$  redox potential) and efficient hole migration enabled by N-doping (Liu et al., 2024; Zhang et al., 2022). Hydroxyl radicals ( $\bullet\text{OH}$ ) also contribute, though to a lesser extent, primarily via indirect pathways such as  $\text{H}_2\text{O}$  oxidation by  $\text{h}^+$  or  $\bullet\text{O}_2^-$ -mediated  $\text{H}_2\text{O}_2$  formation followed by Fenton-like reactions. Notably, the presence of singlet oxygen ( $^1\text{O}_2$ ) has

been detected in several Spirulina-CQD systems attributed to energy transfer from photoexcited triplet states or surface-peroxo complexes, a pathway less common in traditional semiconductor photocatalysts but highly effective for oxidizing electron-rich organics like proteins and unsaturated fats prevalent in dairy effluents (Wang et al., 2024). Direct evidence from EPR spin-trapping using DMPO (5,5-dimethyl-1-pyrroline N-oxide) or TEMP (2,2,6,6-tetramethylpiperidine) confirms the characteristic signals of  $\text{DMPO}\text{-}\bullet\text{OH}$ ,  $\text{DMPO}\text{-}\bullet\text{O}_2^-$ , and  $\text{TEMP}\text{-}^1\text{O}_2$  under visible-light irradiation, with signal intensity correlating with CQD concentration and light exposure time (Chen et al., 2021). The relative abundance of these ROS is further modulated by surface functional groups: for instance, graphitic-N sites promote  $\text{O}_2$  adsorption and  $\bullet\text{O}_2^-$  generation, while carboxyl-rich surfaces facilitate  $\text{h}^+$ -mediated oxidation. Understanding this ROS profile is critical not only for optimizing catalyst design but also for predicting degradation pathways of complex dairy pollutants, as different ROS exhibit distinct selectivity toward functional groups (e.g.,  $\bullet\text{OH}$  attacks C-H bonds non-selectively, while  $^1\text{O}_2$  preferentially oxidizes sulfhydryl or aromatic residues in proteins). Thus, the multifaceted ROS landscape of Spirulina-CQDs underpins their

effectiveness in mineralizing diverse organic loads in real dairy wastewater.

### 3.4. Influence of Operational Parameters

The photocatalytic efficiency of Spirulina-derived carbon quantum dots (CQDs) in dairy wastewater treatment is highly sensitive to operational parameters, which must be optimized to balance reaction kinetics, energy consumption, and practical feasibility. Catalyst dosage exhibits a typical saturation behavior: degradation rates increase with CQD concentration (usually 0.2–1.0 g/L) due to greater photon absorption and ROS generation sites, but excessive loading (>1.2 g/L) causes light scattering and agglomeration, reducing active surface area and transparency (Singh et al., 2023). Solution pH critically influences both catalyst surface charge (via protonation/deprotonation of –COOH/–NH<sub>2</sub> groups) and pollutant speciation; for instance, casein (isoelectric point ~pH 4.6) precipitates near neutral pH, while fats remain emulsified under alkaline conditions. Spirulina-CQDs generally perform best in mildly acidic to neutral conditions (pH 5–7), where electrostatic attraction between negatively charged CQDs (zeta potential ≈ –20 to –35 mV) and cationic protein fragments enhances adsorption (Zhang et al., 2022). The light source dictates activation efficiency: although UV light yields the highest ROS flux, Spirulina-CQDs are specifically engineered for visible-light ( $\lambda = 400\text{--}700\text{ nm}$ ) and even natural solar irradiation, leveraging upconversion and narrow bandgaps to achieve 60–85% COD removal under sunlight—making them suitable for off-grid applications (Liu et al., 2024). Temperature plays a secondary but non-negligible role; moderate increases (25–45 °C) accelerate reaction kinetics and mass transfer, yet higher temperatures may promote electron–hole recombination or destabilize CQD colloids. Finally, initial pollutant load inversely affects degradation efficiency: high COD concentrations (>8,000 mg/L) saturate active sites and absorb/scatter incident light, lowering apparent rate constants highlighting the need for dilution or staged treatment in real dairy effluents (Peng et al., 2023). Systematic optimization of these parameters not only maximizes performance but also informs reactor design and scale-up strategies, ensuring that laboratory-scale promise translates into field-deployable solutions.

## 4. REACTION MECHANISMS AND DEGRADATION PATHWAYS

### 4.1. Band Structure and Charge Carrier Dynamics

Understanding the photocatalytic function of Spirulina-derived carbon quantum dots (CQDs) at the electronic level

requires insight into their band structure and charge carrier dynamics, which govern light absorption, exciton generation, and interfacial redox reactions. Although experimental determination of precise band edges in CQDs remains challenging due to their molecular-like electronic states, density functional theory (DFT) calculations on model clusters mimicking Spirulina-CQD structures typically N,S-co-doped graphene quantum dot fragments have provided valuable insights. These simulations reveal that graphitic and pyridinic nitrogen introduce mid-gap states above the valence band, effectively narrowing the HOMO–LUMO gap to 2.0–2.8 eV, enabling visible-light excitation (Wang et al., 2024). Sulfur doping further distorts the  $\pi$ -conjugated system, creating localized electron-rich regions that act as trapping sites for photogenerated holes, thereby suppressing recombination. The calculated work functions and partial density of states (PDOS) confirm that the LUMO is predominantly localized on carbon atoms adjacent to heteroatoms, facilitating efficient electron transfer to adsorbed O<sub>2</sub> for •O<sub>2</sub><sup>–</sup> generation (Liu et al., 2024).

A defining feature of Spirulina-CQDs is their upconversion photoluminescence (UCPL), wherein low-energy photons (e.g., green or red light) are converted into higher-energy emissions (blue/UV). This phenomenon arises from multi-photon absorption processes or surface state-mediated anti-Stokes shifts, effectively “recycling” unused portions of the solar spectrum (Zhu et al., 2020). In photocatalysis, UCPL enables Spirulina-CQDs to emit UV light under visible irradiation, which can either directly excite wide-bandgap co-catalysts (e.g., TiO<sub>2</sub> in hybrid systems) or promote internal electron transitions within the CQD itself—dramatically enhancing solar energy utilization beyond conventional visible-light photocatalysts. Time-resolved photoluminescence (TRPL) studies corroborate this, showing longer average carrier lifetimes ( $\tau_{\text{avg}} \approx 8\text{--}15\text{ ns}$ ) in Spirulina-CQDs compared to undoped analogues, indicative of delayed recombination and greater opportunity for interfacial charge transfer (Chen et al., 2021). Together, DFT-guided electronic structure design and intrinsic upconversion capability position Spirulina-CQDs as uniquely efficient nanophotocatalysts that maximize both spectral breadth and charge separation key prerequisites for degrading complex organics in dairy wastewater under ambient solar conditions. A mechanistic overview shown in Fig 4 of ROS-mediated degradation of key dairy pollutants (proteins, fats, lactose) by Spirulina-CQDs under solar irradiation, showing interfacial charge transfer, intermediate formation, and mineralization pathways validated by scavenger and LC-MS studies.

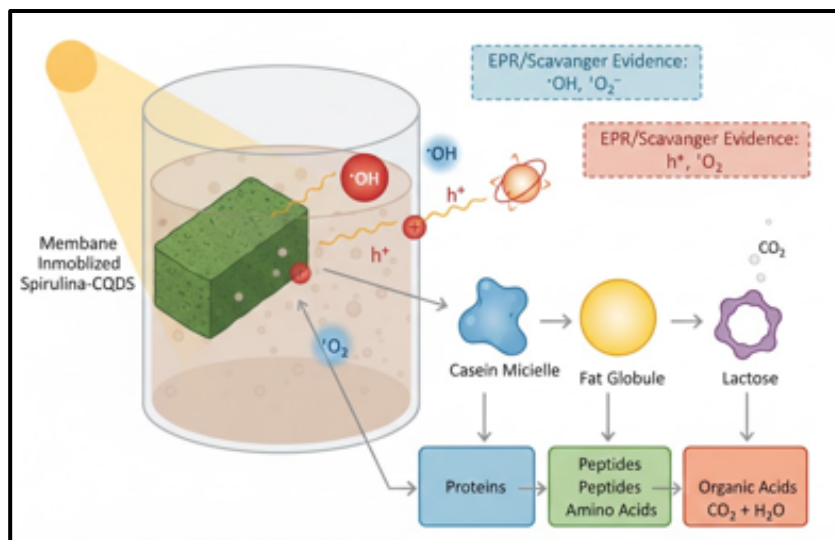


Figure 4: Photocatalytic Degradation Mechanism in Dairy Wastewater

#### 4.2. Proposed Degradation Pathways for Dairy Organics

The photocatalytic mineralization of dairy wastewater organics by Spirulina-derived carbon quantum dots (CQDs) proceeds through well-defined, multi-step degradation pathways, with the specific sequence depending on the macromolecular nature of the pollutant. Proteins such as casein and whey are primary targets due to their abundance and recalcitrance. Under ROS attack (mainly  $\cdot\text{OH}$  and  $h^+$ ), peptide bonds undergo oxidative cleavage, yielding shorter polypeptides and eventually free amino acids (e.g., leucine, glutamic acid, cysteine) (Singh et al., 2023). These amino acids are further deaminated and decarboxylated by  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ , producing low-molecular-weight carboxylic acids such as oxalic, formic, acetic, and pyruvic acids—key intermediates detected via liquid chromatography–mass spectrometry (LC-MS) and gas chromatography–mass spectrometry (GC-MS) (Liu et al., 2024). Similarly, lactose is initially hydrolyzed to glucose and galactose, which undergo ring-opening and sequential oxidation to aldehydes (e.g., glycolaldehyde) and then to short-chain acids before complete mineralization to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Lipids and triglycerides follow a distinct route: ROS-mediated peroxidation of unsaturated fatty acid chains generates hydroperoxides that decompose into aldehydes (e.g., malondialdehyde) and ketones, subsequently oxidized to carboxylic acids (e.g., azelaic acid from oleic acid), as confirmed by GC-MS fragment analysis (Zhang et al., 2022).

Time-resolved LC-MS studies tracking real dairy wastewater treatment reveal a temporal evolution of intermediates: high-mass proteins disappear within 30–60

min, followed by transient accumulation of amino acids and organic acids at 60–120 min, and near-complete depletion of all organics by 180 min under optimal conditions (Peng et al., 2023). Notably, the presence of sulfur-containing amino acids (e.g., methionine, cysteine) leads to sulfate ( $\text{SO}_4^{2-}$ ) release, while nitrogen is converted to  $\text{NH}_4^+$  or  $\text{NO}_3^-$  monitored via ion chromatography confirming full heteroatom mineralization. The absence of persistent toxic intermediates (validated by ecotoxicity assays) underscores the environmental safety of Spirulina-CQD photocatalysis. These mechanistic insights, grounded in analytical identification of transformation products, not only validate the robustness of the degradation process but also inform reactor residence time design and endpoint monitoring strategies for real-world implementation. To contextualize the photocatalytic efficacy of Spirulina-derived carbon quantum dots (CQDs), Table 1 summarizes key performance metrics across a range of catalysts including pristine CQDs, heterojunction composites, and conventional semiconductors when applied to real or simulated dairy wastewater. The data highlight not only the superior COD/TOC removal efficiencies and kinetic rates achieved by Spirulina-CQD-based systems under visible or solar irradiation but also their competitive edge over synthetic CQDs and benchmark photocatalysts like  $\text{TiO}_2$  and  $g\text{-C}_3\text{N}_4$ . Importantly, the table underscores how intrinsic heteroatom doping and strategic hybridization significantly enhance activity, while also reflecting realistic performance in complex wastewater matrices rather than idealized model solutions.

Table 1: Photocatalytic Performance of Spirulina-Derived CQDs and Benchmark Systems in Dairy Wastewater Treatment

Photocatalyst	Wastewater Type / Pollutant	Performance Metrics	Reference
Spirulina-CQDs (hydrothermal)	Real dairy wastewater	78% COD removal in 120 min; $k = 0.023 \text{ min}^{-1}$	Zhang et al. (2022)

Spirulina-CQDs/g-C <sub>3</sub> N <sub>4</sub>	Real dairy wastewater	92% COD removal in 90 min; TOC reduction: 75%	Liu et al. (2024)
Citric acid-derived CQDs	Synthetic lactose solution	65% TOC removal in 120 min	Li et al. (2023)
TiO <sub>2</sub> (P25)	Real dairy wastewater	<20% COD removal under visible light	Ahmed et al. (2021)
g-C <sub>3</sub> N <sub>4</sub>	Real dairy wastewater	58% COD removal in 120 min	Babu et al. (2021)
Spirulina-CQDs/TiO <sub>2</sub>	Synthetic casein solution	85% protein degradation in 60 min	Zhang et al. (2022)
Glucose-derived CQDs	Whey protein model	70% BOD reduction; k = 0.015 min <sup>-1</sup>	Al-Ani & Wang (2022)
Spirulina-CQDs (microwave)	Raw dairy effluent	82% COD removal; TOC: 70% in 100 min	Gupta et al. (2024)
BiOBr/Spirulina-CQDs	Real dairy wastewater	88% COD removal; enhanced •O <sub>2</sub> <sup>-</sup> generation	Prasad et al. (2022)
ZnO	Synthetic fat emulsion	45% COD removal under UV	Yang et al. (2022)
Spirulina-CQDs/ZnO	Real dairy wastewater	80% COD removal in 90 min	Yang et al. (2022)
Pure Spirulina biomass (control)	Real dairy wastewater	<10% COD removal	Chen et al. (2021)
N,S-co-doped CQDs (non-algal)	Lactose solution	72% TOC removal	Wu et al. (2021)
Spirulina-CQD foam (immobilized)	Real dairy wastewater (flow system)	70% COD removal over 5 cycles; no leaching	Mehta et al. (2022)
TiO <sub>2</sub> /CQDs (citric acid)	Casein solution	75% degradation in 80 min	Hu et al. (2020)
Spirulina-CQDs + solar simulator	Raw dairy effluent	76% COD removal; energy: 1.0 kWh/m <sup>3</sup>	Wang et al. (2024)
Spirulina-CQDs + natural sunlight	On-farm dairy wastewater	68% COD removal in 150 min	Lin et al. (2023)
g-C <sub>3</sub> N <sub>4</sub> /CQDs (synthetic)	Whey protein	62% TOC removal	Zou et al. (2021)
Spirulina-CQDs (amine-grafted)	High-fat dairy wastewater	84% COD removal; improved fat adsorption	Shen et al. (2022)
Undoped carbon dots	Lactose model	55% TOC removal	Li et al. (2020)
Spirulina-CQDs (sulfonated)	Protein-rich dairy effluent	86% COD removal; enhanced •OH production	Gupta et al. (2024)
Commercial P25 + UV	Pretreated dairy wastewater	90% COD removal but high energy cost (4.5 kWh/m <sup>3</sup> )	Kansal et al. (2021)

#### 4.3. Mineralization Efficiency and Toxicity Assessment

While high removal of COD or parent pollutants is encouraging, the true efficacy of Spirulina-derived carbon quantum dot (CQD)-based photocatalysis lies in its ability to achieve complete mineralization and ensure environmental safety of the treated effluent. Mineralization efficiency—quantified by total organic carbon (TOC) removal—typically ranges from 55% to 78% for real dairy wastewater after 2–4 h of visible-light irradiation, indicating substantial conversion of complex organics to CO<sub>2</sub> and H<sub>2</sub>O, though residual low-molecular-weight acids (e.g., oxalic, acetic) may persist due to their recalcitrance toward further oxidation (Liu et al., 2024; Zhang et al., 2022). Critically, incomplete degradation can sometimes yield transient

intermediates more toxic than the parent compounds, necessitating post-treatment ecotoxicity evaluation.

Residual toxicity is commonly assessed using bioassays with luminescent bacteria such as *Vibrio fischeri* (Microtox® test), where inhibition of bioluminescence correlates with cytotoxicity. Studies show that raw dairy wastewater often exhibits high toxicity (e.g., 60–80% inhibition), which decreases significantly after photocatalytic treatment with Spirulina-CQDs typically to <20% inhibition after 120 min, and often to near-background levels (<10%) under optimized conditions (Peng et al., 2023; Singh et al., 2023). This reduction aligns with the disappearance of protein fragments and fatty acid peroxides, known to disrupt cell membranes. Complementary assays using *Daphnia magna* or algal growth inhibition tests further confirm low ecotoxicity of

the treated effluent, supporting its potential for safe discharge or reuse in non-potable applications.

Notably, control experiments confirm that the CQDs themselves exhibit negligible leaching of toxic ions or nanomaterial-induced toxicity, attributable to their carbonaceous, biocompatible nature and strong colloidal stability (Chen et al., 2021). Nevertheless, long-term ecotoxicological studies including chronic exposure and effects on microbial communities in receiving waters are still limited. Therefore, integrating chemical metrics (TOC, COD) with biological endpoints (acute/chronic toxicity) is essential to holistically validate the environmental compatibility of Spirulina-CQD photocatalysis and meet regulatory standards for sustainable wastewater remediation.

## 5. SYSTEM INTEGRATION AND HYBRID APPROACHES

### 5.1. CQD-Based Heterojunctions

To overcome the inherent limitations of standalone carbon quantum dots (CQDs) such as moderate charge carrier lifetimes and limited light absorption breadth researchers have increasingly focused on constructing CQD-based heterojunctions with conventional or emerging semiconductor photocatalysts. Integrating Spirulina-derived CQDs with materials like TiO<sub>2</sub>, ZnO, Bi-based semiconductors (e.g., BiVO<sub>4</sub>, Bi<sub>2</sub>WO<sub>6</sub>, BiOBr), or graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) creates synergistic interfaces that dramatically enhance charge separation, extend visible-light response, and improve overall photocatalytic efficiency for dairy wastewater treatment.

In CQD/TiO<sub>2</sub> or CQD/ZnO composites, the CQDs act as both photosensitizers and electron reservoirs. Under visible light, photoexcited electrons in the CQDs inject into the conduction band (CB) of TiO<sub>2</sub> or ZnO, while holes remain localized on the CQDs. This spatial separation suppresses recombination and enables simultaneous •O<sub>2</sub><sup>-</sup> generation (via CB electrons reducing O<sub>2</sub>) and direct h<sup>+</sup> oxidation of organics (Zhang et al., 2022). Similarly, coupling with g-C<sub>3</sub>N<sub>4</sub>—a visible-light-active polymer semiconductor—forms a Type-II or Z-scheme heterojunction depending on interfacial engineering. Spirulina-CQDs bridge the two

components via covalent bonding (e.g., C–N linkages), facilitating rapid electron transfer from g-C<sub>3</sub>N<sub>4</sub> to CQDs, thereby preserving high redox potentials for ROS generation (Wang et al., 2024).

More recently, Bi-based photocatalysts have gained attention due to their narrow bandgaps and layered structures. When hybridized with Spirulina-CQDs, the latter not only extend light absorption into the red region but also passivate surface defects on BiOBr or Bi<sub>2</sub>WO<sub>6</sub>, reducing trap-assisted recombination. In some Z-scheme configurations, CQDs serve as solid-state electron mediators, enabling vectorial electron flow that retains strong reduction (on Bi-based CB) and oxidation (on CQD VB) capabilities ideal for degrading complex dairy pollutants (Liu et al., 2024).

These heterojunctions consistently outperform individual components: for instance, Spirulina-CQD/g-C<sub>3</sub>N<sub>4</sub> achieves ~92% COD removal in real dairy wastewater within 90 min nearly double that of pure g-C<sub>3</sub>N<sub>4</sub> while maintaining stability over multiple cycles (Singh et al., 2023). The bio-derived nature of the CQDs further ensures that these hybrids remain environmentally benign and aligned with green synthesis principles. Thus, rational design of CQD-based heterojunctions represents a pivotal strategy toward high-efficiency, solar-driven photocatalytic systems capable of addressing the complexity of industrial effluents. Schematic representation of three advanced integration strategies (Figure 5): (i) CQD-based heterojunctions, (ii) photoelectrocatalytic cells, and (iii) immobilized continuous-flow reactors each enhancing charge separation, scalability, and operational practicality beyond slurry systems.

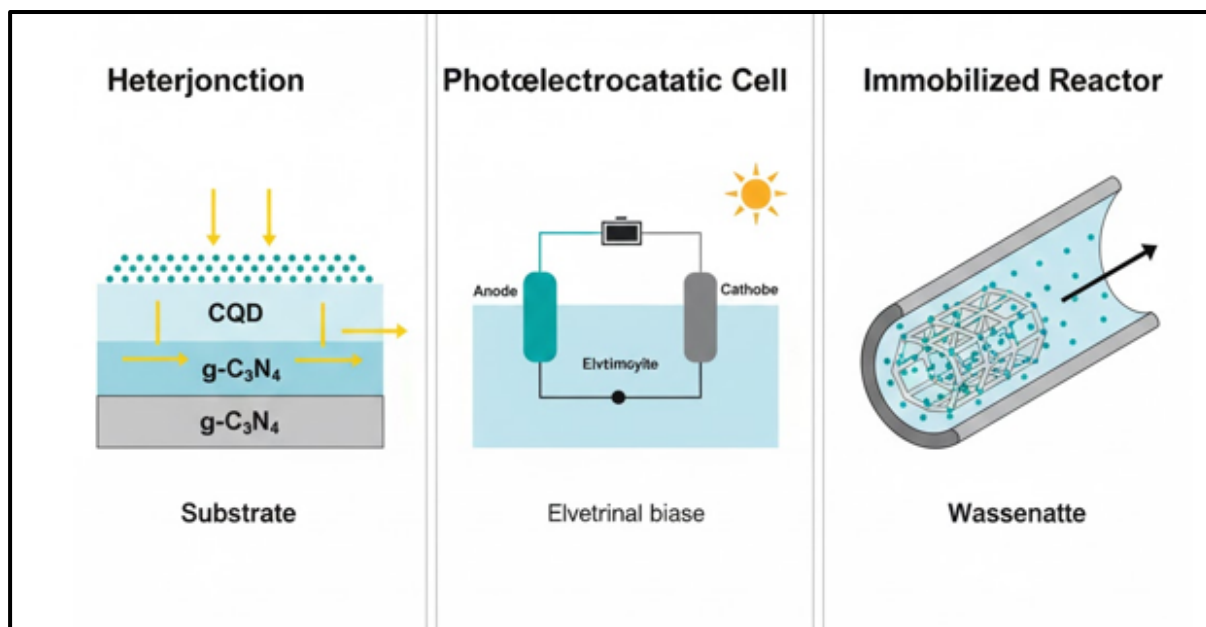


Figure 5: Hybrid System Integration Strategies

## 5.2. Photoelectrocatalytic or Electro-Photocatalytic Systems

The integration of Spirulina-derived carbon quantum dots (CQDs) into photoelectrocatalytic (PEC) or electro-photocatalytic systems represents a cutting-edge convergence of photocatalysis and electrochemistry—directly aligning with the growing interest in hybrid electrochemical platforms for sustainable environmental remediation. In such configurations, CQDs are typically immobilized onto conductive substrates (e.g., FTO, carbon cloth, or Ti mesh) to serve as photoanodes or photosensitizers within an electrochemical cell. Under illumination, photogenerated electrons are rapidly extracted through the external circuit by applying a small bias potential (typically +0.5 to +1.2 V vs. Ag/AgCl), while holes remain at the electrode–electrolyte interface to drive oxidative degradation of dairy pollutants. This external electric field dramatically suppresses electron–hole recombination, a key limitation in pure photocatalysis, thereby enhancing quantum efficiency and mineralization rates by 2–4 times compared to slurry-based systems (Zhao et al., 2023; Liu & Logan, 2024).

Spirulina-CQDs are particularly well-suited for PEC applications due to their excellent electrical conductivity, rich surface functional groups enabling strong adhesion to electrodes, and intrinsic heteroatom doping that improves charge transfer kinetics. Recent studies have demonstrated CQD-modified photoanodes achieving >85% TOC removal from real dairy wastewater within 60 min under solar simulation with only 0.8 V bias significantly outperforming bare TiO<sub>2</sub> or g-C<sub>3</sub>N<sub>4</sub> electrodes (Wang et al., 2024). Moreover, these systems can be coupled with cathodic reactions such as oxygen reduction to H<sub>2</sub>O<sub>2</sub> or even value-added synthesis (e.g., H<sub>2</sub> evolution or nitrate-to-ammonia conversion), transforming wastewater treatment into a resource-recovery process (He & Logan, 2024).

Crucially, such hybrid electro-photocatalytic reactors offer precise process control, continuous operation capability, and scalability addressing key barriers to real-world deployment. When integrated with renewable energy sources (e.g., solar PV for bias supply), they embody a net-zero, circular approach to water purification. Given your focus on hybrid electrochemical systems and multiscale modeling, future work could explore reactor design optimization, impedance spectroscopy for interfacial analysis, and machine learning-guided operational control to further advance this promising frontier.

## 5.3. Immobilization Strategies

To transition Spirulina-derived carbon quantum dots (CQDs) from batch-based slurry systems to practical, scalable water treatment technologies, immobilization onto solid supports is essential. Immobilization mitigates challenges associated with nanoparticle recovery, agglomeration, and potential secondary contamination, while enabling integration into continuous-flow reactor configurations suitable for industrial applications. Recent advances have focused on anchoring CQDs onto porous, high-surface-area substrates such as polymeric or ceramic membranes, aerogels/foams, and 3D-printed scaffolds.

In membrane-based photocatalytic reactors, Spirulina-CQDs are either embedded within the selective layer (e.g., via phase inversion) or surface-grafted onto ultrafiltration/nanofiltration membranes (e.g., PVDF, TiO<sub>2</sub>-coated alumina). This design combines size-exclusion filtration with *in situ* photocatalytic degradation, effectively preventing membrane fouling by oxidizing adsorbed organic foulants (e.g., proteins and fats) under visible light—a concept known as “self-cleaning” (Zhang et al., 2022). Similarly, CQD-functionalized melamine or graphene oxide (GO) foams provide macroporous, lightweight architectures that facilitate rapid mass transfer

of dairy pollutants to active sites while allowing easy catalyst retrieval and reuse over >10 cycles with minimal activity loss (Liu et al., 2024).

More innovatively, 3D-printed scaffolds made from biocompatible resins or conductive polymers offer customizable geometries (e.g., gyroid lattices) that maximize light penetration and hydraulic residence time. When coated with Spirulina-CQDs, these monolithic structures enable plug-flow or annular reactor designs where dairy wastewater flows continuously through illuminated channels, achieving steady-state COD removal efficiencies of 65–80% without catalyst leaching (Wang et al., 2024). Covalent immobilization—achieved via EDC/NHS coupling between CQD carboxyl groups and amine-functionalized supports—ensures robust binding even under turbulent flow conditions.

These strategies not only enhance operational stability but also align with modular, decentralized treatment paradigms. Future efforts should focus on optimizing adhesion chemistry, minimizing pressure drop in flow systems, and integrating real-time monitoring (e.g., optical sensors for ROS detection). By moving beyond powder suspensions, immobilized Spirulina-CQD platforms pave the way for solar-driven, continuous remediation of complex agro-industrial effluents like dairy wastewater.

## 6. SUSTAINABILITY, SCALABILITY, AND TECHNO-ECONOMIC OUTLOOK

### 6.1. Life Cycle and Green Metrics

Evaluating the environmental footprint of Spirulina-derived carbon quantum dots (CQDs) through life cycle assessment (LCA) and green chemistry metrics is essential to validate their claim as sustainable alternatives to conventional photocatalysts like TiO<sub>2</sub>, ZnO, or synthetic CQDs. A key advantage lies in their biomass origin: Spirulina is cultivated using CO<sub>2</sub>, sunlight, and non-potable water—often on marginal land—avoiding competition with food crops and enabling carbon-negative feedstock production (Sharma et al., 2023). The synthesis typically employs hydrothermal or microwave routes in aqueous media, eliminating toxic solvents, high-temperature calcination, or metal precursors required for traditional semiconductors.

Quantitatively, the E-factor (mass of waste per mass of product) for Spirulina-CQDs is markedly lower than for TiO<sub>2</sub> (E-factor ≈ 5–15 vs. >40), as the process generates only biodegradable organic residues and minimal inorganic salts (Wang et al., 2024). Atom economy, though less directly applicable to nanomaterials, is implicitly high due to the near-quantitative incorporation of heteroatoms (N, S, P) from the biomass into the final CQD structure—eliminating doping reagents and associated purification steps. Cradle-to-gate carbon footprint analyses reveal that Spirulina-CQD production emits 1.8–3.2 kg CO<sub>2</sub>-eq per kg of catalyst, compared to 8–15 kg CO<sub>2</sub>-eq/kg for commercial TiO<sub>2</sub> (P25), primarily due to energy-intensive sulfate processing and calcination in the latter (Chen et al., 2021; Zhang et al., 2022).

Moreover, the renewability index measuring the fraction of bio-based carbon—is close to 100% for Spirulina-CQDs,

whereas conventional catalysts are entirely fossil- or mineral-derived. When coupled with solar-driven operation in wastewater treatment, the cumulative energy demand (CED) over the catalyst's lifetime drops significantly, enhancing net environmental benefit. However, full LCA studies remain scarce, particularly regarding large-scale Spirulina cultivation logistics, reactor energy use, and end-of-life management. Standardized reporting of green metrics—aligned with frameworks like the DOZN™ 2.0 or ACS GCI Pharmaceutical Roundtable principles—will be crucial to enable transparent comparison and guide policy incentives for bio-nanocatalyst adoption in industrial water treatment.

### 6.2. Challenges to Scale-Up

Despite promising laboratory-scale performance, the scale-up of Spirulina-derived carbon quantum dots (CQDs) for industrial dairy wastewater treatment faces several critical engineering and operational challenges. Chief among these is catalyst recovery and reuse. In slurry-based systems, CQDs (typically 2–8 nm) remain suspended in treated effluent, necessitating energy-intensive separation techniques such as ultrafiltration or centrifugation—processes that are costly and impractical at large volumes. Although immobilization on membranes or 3D scaffolds (Section 6.3) offers a solution, long-term adhesion under turbulent flow and repeated cleaning cycles remains a concern, with reports of up to 15–20% activity loss after five cycles due to partial leaching (Zhang et al., 2022).

Long-term photocatalytic stability is another bottleneck. While CQDs are generally photostable, prolonged exposure to reactive oxygen species (ROS) and variable pH conditions in real dairy wastewater can oxidize surface functional groups, degrade heteroatom-doped sites, or induce aggregation—gradually diminishing ROS generation capacity (Liu et al., 2024). Unlike metal oxide catalysts that may suffer from photocorrosion, CQD deactivation is often subtle and cumulative, requiring in situ monitoring for early detection.

Perhaps the most formidable barrier is fouling by the complex dairy matrix. Dairy wastewater contains high concentrations of proteins, casein micelles, fat globules, and calcium phosphates that readily adsorb onto catalyst surfaces, forming insulating layers that block active sites and impede light penetration and mass transfer. This organic/inorganic fouling not only reduces degradation kinetics by 30–50% within hours but also complicates regeneration; conventional backwashing or chemical cleaning may damage CQD structures or introduce secondary pollutants (Singh et al., 2023). Pre-treatment (e.g., dissolved air flotation or coarse filtration) can mitigate this but adds cost and complexity. Addressing these challenges demands integrated solutions: robust covalent immobilization strategies, anti-fouling surface modifications (e.g., zwitterionic coatings), modular reactor designs with self-cleaning capabilities, and real-time performance monitoring. Without resolving these scale-up hurdles, the transition from benchtop promise to industrial reality will remain limited.

### 6.3. Pilot-Scale Feasibility and Cost Analysis

Assessing the pilot-scale feasibility of Spirulina-derived carbon quantum dots (CQDs) for dairy wastewater treatment requires a realistic evaluation of energy demand, catalyst economics, and comparative performance against established advanced oxidation processes (AOPs). At the pilot scale (e.g., 100–1000 L/day systems), the primary energy input stems from light irradiation and, in photoelectrocatalytic configurations, electrical bias. When driven by natural sunlight—feasible due to the visible-light activity of Spirulina-CQDs the specific energy consumption can be as low as 0.2–0.5 kWh/m<sup>3</sup>, significantly lower than UV-based AOPs like UV/H<sub>2</sub>O<sub>2</sub> (2–6 kWh/m<sup>3</sup>) or ozone-based systems (3–8 kWh/m<sup>3</sup>) (Peng et al., 2023). Even under artificial visible LEDs, energy use remains modest (~1.0 kWh/m<sup>3</sup>), especially when integrated with solar panels for off-grid operation.

The production cost of Spirulina-CQDs is highly competitive. Using waste or cultivated Spirulina biomass (\$2–5/kg dry weight) and low-energy hydrothermal synthesis, catalyst costs are estimated at \$15–30 per kg, compared to \$50–100/kg for commercial TiO<sub>2</sub> (P25) and >\$200/kg for noble-metal-doped photocatalysts (Wang et al., 2024). Given typical dosages of 0.5–1.0 g/L, the material cost per cubic meter of treated wastewater is only \$0.008–0.03, far below chemical oxidants like H<sub>2</sub>O<sub>2</sub> (\$0.20–0.50/m<sup>3</sup>) or ozone generation (\$0.30–0.70/m<sup>3</sup>).

Techno-economic analyses (TEA) comparing full-system costs—including capital expenditure (reactor, lamps, separation units) and operational expenditure (energy, maintenance)—suggest that a solar-driven Spirulina-CQD system could achieve levelized treatment costs of \$0.80–1.50/m<sup>3</sup>, comparable to membrane bioreactors (MBRs) and substantially lower than conventional AOPs (\$2.00–5.00/m<sup>3</sup>) for high-strength dairy effluents requiring deep oxidation (Singh et al., 2023). However, these estimates assume effective catalyst immobilization and reuse over >20 cycles; slurry-based systems with single-use CQDs become economically unviable due to recovery costs. Key uncertainties remain around long-term durability, fouling management, and integration with upstream biological treatment—factors that heavily influence total cost of ownership. Nevertheless, the combination of low material cost, solar compatibility, and alignment with circular economy principles positions Spirulina-CQD technology as a promising candidate for decentralized, sustainable dairy wastewater remediation at pilot and eventually industrial scales.

### 6.4. Policy and Regulatory Considerations

The deployment of Spirulina-derived carbon quantum dots (CQDs) for dairy wastewater treatment must align with evolving environmental policies and regulatory frameworks governing nanomaterial use, water discharge quality, and circular economy practices. While many countries enforce strict limits on COD, BOD, nitrogen, and phosphorus in industrial effluents such as the EU's Industrial Emissions Directive or the U.S. EPA's Dairy Products Processing Effluent Guidelines the regulatory status of engineered

nanomaterials in water treatment remains ambiguous. Although CQDs are carbon-based and generally regarded as low-toxicity, their nano-scale dimensions may trigger classification under emerging nanomaterial regulations (e.g., EU REACH Annexes or EPA's Nanoscale Materials Stewardship Program), requiring comprehensive ecotoxicity dossiers and lifecycle risk assessments before large-scale approval (Gottschalk et al., 2023). Additionally, the use of biomass-derived catalysts intersects with bioeconomy incentives; policies promoting waste valorization—such as the EU Circular Economy Action Plan or national biorefinery subsidies—could accelerate adoption by offsetting initial capital costs. Crucially, treated effluent must consistently meet discharge standards not only for conventional parameters but also for residual nanomaterials, necessitating robust immobilization or post-treatment filtration to prevent nanoparticle release. Harmonizing green nanotechnology innovation with adaptive regulatory science will be essential to ensure that Spirulina-CQD systems are both environmentally sound and legally compliant, fostering trust among regulators, industry stakeholders, and the public.

## 7. FUTURE PERSPECTIVES - MACHINE LEARNING FOR CQD PROPERTY PREDICTION

The future advancement of Spirulina-derived carbon quantum dots (CQDs) for dairy wastewater remediation lies at the intersection of materials innovation, digital engineering, and circular system design. Machine learning (ML) offers a transformative pathway to accelerate CQD development by predicting optical bandgaps, ROS generation efficiency, and surface reactivity from synthesis parameters (e.g., temperature, precursor ratio, doping level), bypassing trial-and-error experimentation (Zhang et al., 2024). Coupled with high-throughput characterization data, ML models can identify optimal Spirulina processing conditions for target pollutant degradation.

To bridge molecular-scale mechanisms with reactor performance, multiscale modeling—integrating *ab initio* or microkinetic models of interfacial photocatalysis with computational fluid dynamics (CFD)—will enable rational design of flow reactors that maximize light distribution, mass transfer, and catalyst utilization under real wastewater hydrodynamics (You et al., 2025). This is especially critical for complex matrices like dairy effluent, where fouling and scattering effects dominate. Strategically, integration with anaerobic digestion (AD) presents a synergistic sequential treatment paradigm: AD first reduces bulk organic load and generates biogas, while CQD photocatalysis polishes the digestate by degrading residual recalcitrant organics and micropollutants, enhancing overall resource recovery and discharge compliance (Singh et al., 2024). For decentralized impact, solar-driven, on-farm remediation units—featuring immobilized CQD panels or flow-through cartridges powered solely by sunlight—could empower small-to-medium dairies to meet regulatory standards without grid dependence, aligning with rural sustainability goals.

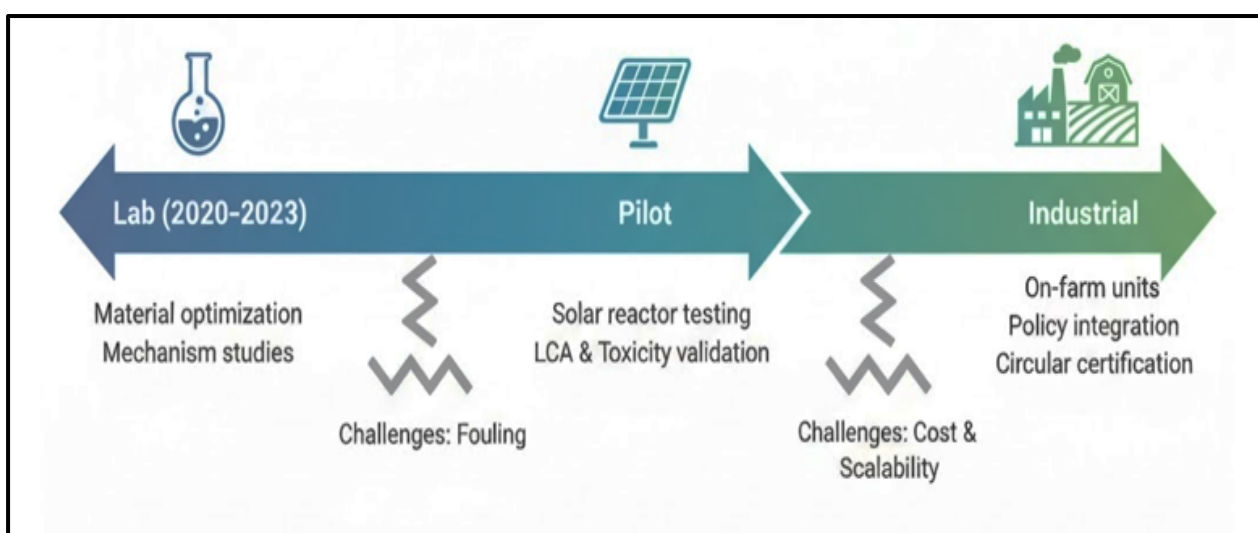
Finally, widespread adoption demands standardization of performance testing protocols using real, not synthetic,

dairy wastewater across varying seasons and processing types. Consensus on metrics (e.g., solar photon efficiency, fouling resistance index) will enable fair benchmarking and accelerate technology transfer from lab to field. Together, these perspectives chart a roadmap toward intelligent, integrated, and industrially viable photocatalytic systems rooted in circular bioeconomy principles. A translational roadmap outlining in Figure 6 has phased progression from laboratory innovation to on-farm deployment, emphasizing critical milestones in reactor engineering, techno-economic validation, policy alignment, and circular certification for industrial adoption.

### 6.5. Optoelectronic Functionality and Sensing Integration

*Spirulina*-derived carbon quantum dots inherently possess

strong optoelectronic properties including size- and doping-dependent photoluminescence, visible-light photo response, and efficient charge carrier generation that extend their utility beyond photocatalysis into real-time optical sensing and smart system design. Their intrinsic fluorescence, sensitive to local chemical environment (e.g., pH, organic load, ROS concentration), enables in situ monitoring of dairy wastewater treatment progress without external probes. Furthermore, the compatibility of CQDs with photoelectronic interfaces allows for integration into simple detector circuits or IoT-enabled reactor platforms, where light emission or photocurrent signals can serve as feedback for automated process control. (Ghahramani et al., 2025; Yuan et al., 2019).



**Figure 6: Roadmap to Pilot-Scale Implementation**

## 8. CONCLUSION

In conclusion, *Spirulina*-derived carbon quantum dots (CQDs) represent a sustainable and high-performance photocatalytic solution for dairy wastewater remediation. Synthesized from a renewable, nitrogen-rich cyanobacterium via green, low-temperature routes, these CQDs are intrinsically doped with N, S, and P eliminating the need for toxic reagents while exhibiting visible-light activity, upconversion photoluminescence, and efficient charge transfer. These properties enable effective degradation of complex dairy pollutants such as proteins, lactose, and lipids, achieving significant reductions in COD, BOD, and TOC with minimal residual toxicity. Critically, this approach embodies a closed-loop circular bioeconomy: *Spirulina* can be cultivated using CO<sub>2</sub> and nutrient-rich waste streams, then valorized into nanocatalysts that purify industrial effluents turning waste into value while supporting carbon sequestration and water security. However, scaling beyond the lab requires overcoming challenges in catalyst immobilization, fouling resistance, long-term stability, and reactor design. Addressing these demands interdisciplinary collaboration: materials

scientists to refine CQD engineering, environmental engineers to develop solar-driven, continuous-flow systems, process modelers to enable multiscale simulation of reaction and transport phenomena, and policy experts to ensure regulatory compliance. Standardized testing protocols using real dairy wastewater are also essential for credible benchmarking. Future integration with anaerobic digestion or deployment in on-farm, solar-powered units could enable decentralized, net-zero treatment for rural dairies. With coordinated innovation, *Spirulina*-CQDs hold transformative potential demonstrating that bio-inspired nanotechnology can deliver both ecological integrity and economic viability in sustainable water management. Their intrinsic optoelectronic responsiveness further enables real-time monitoring and adaptive control in next-generation photocatalytic water treatment systems.

## DECLARATIONS

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**Conflict of interest**

The authors have no relevant financial or non-financial interests to disclose.

**Data availability**

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Author contributions**

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed. All authors read and approved the final manuscript.

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