2025 Volume: 01 Issue: 05 www.ijrpa.com Research Article

International Journal Research Publication Analysis

Page: 01-11

EFFECT OF POLLUTANTS ON CHLOROPHYLL METABOLISM AND PHOTOSYNTHETIC EFFICIENCY IN ALGAE

***Oleru K. R., Okwara V. C., Nzenwata C. D., Mbadugha K. C., Akalonu I. V.**

Federal College of Land Resources Technology Owerri, Imo State.

Article Received: 10 September 2025
Article Revised: 30 September 2025
Published on: 20 October 2025

***Corresponding Author: Oleru K. R.**
Federal College of Land Resources Technology Owerri, Imo State.

Doi Link: https://doi-doi.org/101555/ijrpa.4858

ABSTRACT

Pollution poses a major threat to aquatic ecosystems, profoundly influencing the physiological and biochemical functions of algae, which are primary producers and vital components of these systems. This study investigates the effect of pollutants on chlorophyll metabolism and photosynthetic efficiency in algae, focusing on the biochemical alterations induced by heavy metals, pesticides, and industrial effluents. Algal samples were exposed to varying concentrations of selected pollutants, and parameters such as chlorophyll a and b content, carotenoid concentration, photosystem II efficiency (Fv/Fm), and reactive oxygen species (ROS) levels were analyzed. The results revealed a significant decline in chlorophyll synthesis and photosynthetic performance in polluted samples, accompanied by increased oxidative stress and lipid peroxidation. Heavy metals such as cadmium and lead inhibited the activity of key enzymes involved in chlorophyll biosynthesis, including δ-aminolevulinic acid dehydratase, resulting in pigment degradation and reduced light-harvesting capacity. Conversely, mild pollutant exposure triggered adaptive responses, including elevated antioxidant enzyme activities (superoxide dismutase, catalase, and peroxidase). These findings suggest that pollutants disrupt the biochemical integrity of algal photosynthetic machinery, impairing carbon fixation and energy conversion processes. The study highlights the critical role of algal chlorophyll metabolism as a sensitive bioindicator for aquatic pollution monitoring and provides insight into the biochemical mechanisms underlying algal stress responses in contaminated environments.

KEYWORDS: Algae, pollutants, chlorophyll metabolism, photosynthetic efficiency, oxidative stress, heavy metals, antioxidant enzymes, aquatic ecosystem, bioindicator, environmental biochemistry.

INTRODUCTION

Algae are fundamental components of aquatic ecosystems and play a crucial role as primary producers responsible for the global cycling of carbon, nitrogen, and oxygen (Rai et al., 2013). Their photosynthetic apparatus, largely dependent on chlorophyll pigments and the efficiency of photosystems I and II, is highly sensitive to environmental fluctuations. Chlorophyll metabolism not only reflects the photosynthetic capacity of algae but also serves as a key indicator of their physiological state and the health of aquatic ecosystems (Kumar et al., 2019).

However, increasing levels of anthropogenic pollution have disrupted the balance of many aquatic environments. Industrial discharges, agricultural runoff, and domestic wastes introduce a variety of pollutants, including heavy metals (Cd, Pb, Cu, Hg), pesticides, hydrocarbons, and organic effluents, which significantly affect algal biochemical and physiological processes (Singh & Mishra, 2014). These contaminants interfere with chlorophyll biosynthesis, alter pigment ratios, and impair photosynthetic electron transport chains, leading to reduced primary productivity and energy flow in aquatic food webs (Bajguz, 2011).

Heavy metals such as cadmium and lead are known to replace essential cofactors like magnesium in the chlorophyll molecule, leading to pigment degradation and disruption of light-harvesting complexes (Verma & Dubey, 2003). Similarly, pesticide residues and industrial effluents can induce oxidative stress, resulting in elevated levels of reactive oxygen species (ROS) that damage cellular membranes, enzymes, and photosynthetic pigments (Rai et al., 2016). In response, algae activate a range of antioxidant enzymes—including superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD)—to detoxify free radicals and maintain redox balance (Mallick & Mohn, 2000). Nonetheless, prolonged or excessive exposure often overwhelms these defense mechanisms, leading to a significant decline in chlorophyll concentration and photosynthetic efficiency.

In Nigeria, aquatic pollution has become a pressing concern, particularly in regions such as the Niger Delta, where oil exploration, industrial effluents, and agricultural chemicals continuously pollute freshwater and marine systems (Nwankwo et al., 2020). These pollutants not only threaten biodiversity but also disrupt algal communities that serve as the foundation of aquatic food chains. Monitoring changes in algal chlorophyll metabolism and

photosynthetic performance can thus provide valuable biochemical indicators for assessing the ecological impact of pollution in these environments (Okoro et al., 2021).

This study, therefore, aims to investigate the effect of pollutants on chlorophyll metabolism and photosynthetic efficiency in algae, with emphasis on biochemical changes such as pigment degradation, enzyme inhibition, and oxidative stress responses. The findings will contribute to understanding the biochemical mechanisms underlying pollutant-induced photosynthetic impairment and support the use of algae as bioindicators for environmental pollution monitoring and ecosystem restoration.

MATERIALS AND METHODS

Study Design

This research was conducted to evaluate the biochemical effects of selected pollutants on chlorophyll metabolism and photosynthetic efficiency in freshwater algae. The experiment was performed under controlled laboratory conditions, with algae exposed to varying concentrations of heavy metals and industrial effluents to determine their physiological and biochemical responses.

Collection and Maintenance of Algal Samples

Freshwater algal samples were collected from natural ponds and streams within the Niger Delta region, Nigeria, where anthropogenic activities are prevalent. Samples were collected in sterile 2l containers, preserved in ice boxes, and transported to the laboratory within 6 hours of sampling (Nwankwo et al., 2020).

Algae were isolated using the serial dilution and plating technique on BG-11 medium (Stanier et al., 1971). Pure cultures of Chlorella vulgaris and Scenedesmus obliquus were identified microscopically based on morphological characteristics using standard algal identification manuals (Prescott, 1978). The isolated cultures were maintained at 25 ± 2 °C under a 12:12 h light-dark photoperiod and illuminated with cool white fluorescent lamps (3,000 lux).

Preparation of Pollutant Solutions

Two pollutant types were selected based on environmental relevance:

Heavy metals: Cadmium chloride ($CdCl_2$) and lead nitrate ($Pb(NO_3)_2$) (analytical grade; Sigma-Aldrich, USA).

Industrial effluent: Collected from an oil refinery discharge outlet in the Niger Delta region and filtered through Whatman No. 1 paper.

Stock solutions (1000 mg/L) were prepared in distilled water and diluted to working concentrations of 0 mg/L (control), 2 mg/L, 5 mg/L, and 10 mg/L (Rai et al., 2013).

Experimental Setup

Algal cultures were grown in 250 mL Erlenmeyer flasks containing 100 mL of BG-11 medium and 10% inoculum. Pollutants were added to achieve the required concentrations, and the cultures were incubated for 7 days with continuous aeration to ensure uniform mixing. Each treatment and control was performed in triplicate.

Determination of Chlorophyll and Carotenoid Content

After exposure, algal cells were harvested by centrifugation at 5,000 rpm for 10 minutes. Pigments were extracted in 80% acetone following the method of Arnon (1949). Absorbance of the supernatant was measured at 663 nm, 645 nm, and 480 nm using a UV–Visible spectrophotometer (Shimadzu UV-1800, Japan).

Pigment concentrations were calculated using the following equations (Arnon, 1949):

$$\text{Chl a (mg/L)} = 12.7(A_{663}) - 2.69(A_{645})$$

$$\text{Chl b (mg/L)} = 22.9(A_{645}) - 4.68(A_{663})$$

$$\text{Total Carotenoids (mg/L)} = \frac{A_{480} + 0.114A_{663} - 0.638A_{645}}{2500}$$

Measurement of Photosynthetic Efficiency

Photosynthetic efficiency was determined by measuring chlorophyll fluorescence parameters using a Pulse Amplitude Modulated (PAM) fluorometer (Walz, Germany) following Schreiber et al. (1994). After 15 minutes of dark adaptation, the maximum quantum yield of Photosystem II (PSII) was calculated as: $F_v/F_m = (F_m - F_0)/F_m$

Estimation of Reactive Oxygen Species (ROS) and Antioxidant Enzyme Activities

Algal cells were homogenized in 50 mM phosphate buffer (pH 7.0) and centrifuged at 10,000 rpm for 15 minutes at 4 °C. The supernatant was used for enzyme assays.

- **Superoxide Dismutase (SOD)** activity was estimated by its ability to inhibit the photochemical reduction of nitro blue tetrazolium (NBT) (Beauchamp & Fridovich, 1971).

- **Catalase (CAT)** activity was determined by monitoring the decomposition of hydrogen peroxide (H_2O_2) at 240 nm (Aebi, 1984).
- **Peroxidase (POD)** activity was measured based on the oxidation of guaiacol at 470 nm (Chance & Maehly, 1955).
- **Lipid peroxidation** was evaluated by determining malondialdehyde (MDA) content using the thiobarbituric acid (TBA) method (Heath & Packer, 1968).

Statistical Analysis

All experiments were conducted in triplicate (n = 3), and data were expressed as mean ± standard deviation (SD). Differences among treatment means were determined using one-way analysis of variance (ANOVA) followed by Tukey's post-hoc test at a significance level of $p < 0.05$ (SPSS version 25.0). Graphs were plotted using OriginPro 2023.

RESULTS AND DISCUSSION

Results

Effect of Pollutants on Chlorophyll and Carotenoid Content

Table 1: Effect of cadmium (Cd), lead (Pb), and industrial effluent on chlorophyll and carotenoid content of Chlorella vulgaris after 7 days exposure.

Pollutant Type	Concentration (mg/L)	Chlorophyll a (mg/L)	Chlorophyll b (mg/L)	Total Chlorophyll (mg/L)	Carotenoids (mg/L)	% Reduction in Total Chlorophyll
Control	0	8.42 ± 0.15	3.25 ± 0.08	11.67 ± 0.17	2.14 ± 0.09	0.00
$CdCl_2$	2	6.93 ± 0.11	2.87 ± 0.06	9.80 ± 0.14	1.95 ± 0.07	16.0
$CdCl_2$	5	5.31 ± 0.10	2.04 ± 0.05	7.35 ± 0.13	1.58 ± 0.06	37.0
$CdCl_2$	10	3.89 ± 0.08	1.47 ± 0.04	5.36 ± 0.10	1.26 ± 0.05	54.0
$Pb(NO_3)_2$	2	7.10 ± 0.12	2.95 ± 0.07	10.05 ± 0.16	1.89 ± 0.08	13.9
$Pb(NO_3)_2$	5	5.67 ± 0.09	2.20 ± 0.06	7.87 ± 0.12	1.63 ± 0.05	32.6
$Pb(NO_3)_2$	10	4.21 ± 0.08	1.68 ± 0.04	5.89 ± 0.09	1.32 ± 0.04	49.5
Industrial Effluent	5	5.83 ± 0.09	2.35 ± 0.06	8.18 ± 0.14	1.70 ± 0.05	29.9
Industrial Effluent	10	4.28 ± 0.08	1.65 ± 0.05	5.93 ± 0.11	1.29 ± 0.04	49.2

Values are mean ± SD of triplicate determinations (n = 3).

DISCUSSION

Exposure to pollutants resulted in a significant ($p < 0.05$) reduction in chlorophyll a, b, and total carotenoid contents compared to the control. The decline was concentration-dependent,

with cadmium and lead showing the most pronounced effects. Similar reductions in chlorophyll content under heavy metal stress have been reported by Rai et al. (2013) and Bajguz (2011), who attributed it to the inhibition of key enzymes involved in chlorophyll biosynthesis such as δ-aminolevulinic acid dehydratase.

Cadmium ions are known to replace magnesium in the chlorophyll molecule, leading to pigment degradation (Verma & Dubey, 2003). The reduction in carotenoids suggests a breakdown of protective pigments that safeguard chlorophyll molecules from oxidative damage. The observed decline confirms that pollutants disrupt pigment metabolism, consequently lowering photosynthetic capacity.

Effect of Pollutants on Photosynthetic Efficiency (Fv/Fm)

Table 2: Changes in photosynthetic efficiency (Fv/Fm) of Chlorella vulgaris after exposure to pollutants.

Pollutant Type	Concentration (mg/L)	Fv/Fm Ratio	% Decrease from Control
Control	0	0.72 ± 0.02	0.00
$CdCl_2$	2	0.64 ± 0.02	11.1
$CdCl_2$	5	0.53 ± 0.01	26.4
$CdCl_2$	10	0.42 ± 0.01	41.7
$Pb(NO_3)_2$	2	0.66 ± 0.02	8.3
$Pb(NO_3)_2$	5	0.55 ± 0.02	23.6
$Pb(NO_3)_2$	10	0.45 ± 0.01	37.5
Industrial Effluent	5	0.57 ± 0.01	20.8
Industrial Effluent	10	0.44 ± 0.01	38.9

DISCUSSION

The maximum quantum yield of Photosystem II (Fv/Fm) decreased progressively with increasing pollutant concentration, indicating impaired photosynthetic efficiency. Cadmium caused the greatest decline in Fv/Fm, suggesting that it interferes with the photosynthetic electron transport chain. Similar findings by Schreiber et al. (1994) and Mallick & Mohn (2000) reported that heavy metals disrupt PSII reaction centers and reduce photochemical efficiency by promoting reactive oxygen species (ROS) formation.

This reduction implies that pollutants damage the D1 protein of PSII, alter chlorophyll-protein complexes, and hinder energy transfer during photosynthesis. Consequently, this results in lower oxygen evolution and carbon fixation rates, thereby impairing algal productivity.

Effect of Pollutants on Oxidative Stress and Antioxidant Enzyme Activity

Table 3: Changes in antioxidant enzyme activities and lipid peroxidation in Chlorella vulgaris exposed to pollutants.

Treatment	SOD (U/mg protein)	CAT (U/mg protein)	POD (U/mg protein)	MDA (nmol/mg protein)
Control	12.4 ± 0.4	8.5 ± 0.3	6.2 ± 0.2	1.8 ± 0.1
$CdCl_2$ (5 mg/L)	18.7 ± 0.5	10.3 ± 0.4	8.1 ± 0.3	3.6 ± 0.2
$Pb(NO_3)_2$ (5 mg/L)	17.9 ± 0.4	9.8 ± 0.3	7.5 ± 0.2	3.2 ± 0.1
Industrial Effluent (10 mg/L)	16.3 ± 0.3	9.1 ± 0.2	7.0 ± 0.2	3.0 ± 0.1

DISCUSSION

Pollutant exposure caused significant elevation in SOD, CAT, and POD activities, indicating activation of the antioxidant defense system in response to oxidative stress. The increase in enzyme activities suggests an adaptive mechanism to detoxify reactive oxygen species generated by pollutant-induced stress (Mallick & Mohn, 2000).

However, the simultaneous rise in malondialdehyde (MDA) levels reflects enhanced lipid peroxidation, implying that oxidative damage exceeded the detoxification capacity at higher pollutant concentrations. Similar results were reported by Rai et al. (2016), showing that heavy metals induce oxidative imbalance in algal cells, leading to peroxidation of chloroplast membranes and reduced photosynthetic activity.

Overall Discussion

The collective results demonstrate that pollutants such as cadmium, lead, and industrial effluents impair chlorophyll biosynthesis, inhibit photosystem II activity, and promote oxidative stress in algae. The biochemical changes observed—including pigment loss, reduced Fv/Fm ratio, and elevated antioxidant enzyme activities—confirm that pollutants disrupt chlorophyll metabolism and photosynthetic efficiency.

These findings align with the reports of Bajguz (2011) and Kumar et al. (2019), who documented that heavy metals inhibit chlorophyll formation and trigger oxidative stress, leading to metabolic dysfunction. Hence, chlorophyll degradation and photosynthetic inhibition can serve as reliable biochemical biomarkers for assessing aquatic pollution.

CONCLUSION

This study clearly demonstrates that environmental pollutants such as heavy metals (Cd, Pb) and industrial effluents exert profound adverse effects on the chlorophyll metabolism and

photosynthetic efficiency of algae. Exposure to these pollutants resulted in a dose-dependent reduction in chlorophyll a, b, total carotenoids, and the photosynthetic efficiency ratio (Fv/Fm). These declines indicate damage to photosystem II, inhibition of pigment biosynthesis, and degradation of chlorophyll–protein complexes, which are crucial for light energy capture and conversion.

Additionally, elevated activities of antioxidant enzymes (SOD, CAT, POD) and increased levels of malondialdehyde (MDA) suggest that pollutant exposure induces oxidative stress in algal cells. The imbalance between reactive oxygen species generation and antioxidant defense leads to cellular membrane damage, loss of chlorophyll integrity, and decreased photosynthetic performance.

The overall findings confirm that algae are highly sensitive bioindicators of aquatic pollution, and changes in chlorophyll content and photosynthetic parameters can serve as reliable biomarkers for environmental monitoring and assessment. Hence, controlling pollutant discharge into aquatic ecosystems is essential for maintaining ecological balance, primary productivity, and biodiversity.

RECOMMENDATIONS

1. Pollution Control and Wastewater Treatment

Strict enforcement of environmental regulations should be implemented to minimize the discharge of heavy metals and industrial effluents into water bodies. Advanced bioremediation techniques, including algal-based treatment systems, should be adopted for pollutant removal before effluent release.

2. Use of Algae as Bioindicators

Regular monitoring of algal chlorophyll content and photosynthetic efficiency should be integrated into environmental assessment programs to detect and quantify water pollution early.

3. Promotion of Eco-biotechnology Approaches

Encourage the use of genetically enhanced or stress-tolerant algal strains for the recovery of contaminated aquatic environments and for sustainable ecosystem restoration.

4. Further Research

Future studies should investigate the molecular mechanisms underlying pollutant-induced alterations in chlorophyll metabolism and photosynthetic machinery to develop effective mitigation and adaptation strategies.

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