MSW MANAGEMENT -Multidisciplinary, Scientific Work and Management Journal
ISSN: 1053-7899
Vol. 35 Issue 2, 2025, Pages: 1368-1373

A Fixed-Bed Mini Reactor for the Removal of Dye and Organic Pollutant from Synthetic Waste Water Using Graphene Oxide-Coated Stones

Sonal Panchal[1], Habib Ishaq Habib[2], Muhammad Aminu Aliyu[3], Priti Mahla[4]*
[1]Department of Microbiology, Swarrnim Startup and Innovation University, Gandhinagar-382421. Gujrat, India
[2]Department Of Veterinary Microbiology, Bayero University, Kano, (BUK), Nigeria
[3]Department Of Biotechnology, Swarrnim Science College, Swarrnim Startup And Innovation University, Gujrat, India
[4]Department of Microbiology, Swarrnim Startup and Innovation University, Gandhinagar-382421, Gujrat, India
Corresponding author: Dr. Priti Mahla;
E-mail: priti.mahla@gmail.com, drpriti.science@swarrnim.edu.in

Abstract
Increase in technologies have also caused increase in environmental issues. One of the major problems is the water pollution due to continuous discharge of effluents from textile and other related industries. In this study, a low-cost, lab-scale and environmentally compatible adsorption system had been developed for removal of crystal violet dye and organic pollutant from the waste water. A Fixed-bed mini reactor using graphene oxide-coated stones was fabricated using 50mL burette and operated under ambient conditions. A synthetic waste water was prepared containing crystal violet dye (10mg L^{-1}) and glucose (200 mg L^{-1}) to simulate mixed industrial effluents. Titration based redox method had been used to evaluate the efficiency of dye removal and organic pollutant. The results achieved a maximum crystal violet removal efficiency of 93% and COD reduction 77%. The effect of time and reusability had also been demonstrated and it showed a stable bioreactor performance. Thus, the results indicate that GO-CS based reactor offers a simple, stable, inexpensive and environmentally compatible adsorption system for the removal of dye-organic mixed waste water. The work had been novel. And not performed in a decade before.

Keywords: Graphene oxide, crystal violet, organic pollutant, fixed-bed reactor, waste water treatment

1. Introduction:

Water is one of the basic necessities of human life. Its pollution is rising significantly due to various human activities and industrialization. Improving lifestyles and Industrialization has also resulted in increasing demand of clean water both in household chores and industries (Kumari, Alam, and Siddiqi 2019)(Nemerow and Dasgupta 1990)(Ali and Aboul-Enein 2004)(Helmer and Hespanhol 1997). Water resources are therefore facing severe contamination issue leading to its unavailability to humans. Despite of use of water management strategies all over the world, these problem have become a major concern.(Agarwal, Gupta, and Agarwal 2019). Thus water pollution can be due to point and no point sources where point sources mean emission of pollutant from single source like industry and non point source means emission of pollutant from multiple sources(crini).

Textile industries are estimated to use around 2000 chemicals and dyes as colouring agents. So effluents from these industries are one of the major cause of water pollution (Amodu et al. 2015). Dyes can be classified as natural and synthetic. Being cost effective, synthetic dyes are used on regular basis in textile industries (Kant 2011)(Dahri, Kooh, and Lim 2013). Crystal violet is a basic synthetic dye also known as methyl violet10B or basic violet 3. It belongs to group of triarylmethanes.The hydrophilic nature of CV makes it an effective colouring agent to variety of cloth materials. These activity is main cause of water pollutant.(Adak, Bandyopadhyay, and Pal 2005)(Mittal et al. 2010). The fig 1. represent structure of crystal violet dye.

MSW MANAGEMENT -Multidisciplinary, Scientific Work and Management Journal
ISSN: 1053-7899
Vol. 35 Issue 2, 2025, Pages: 1368-1373

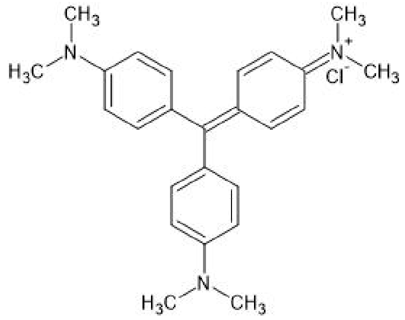

Fig 1. Chemical structure of crystal violet dye

Organic pollutants also have similar impact on environment and human as dyes. These pollutants mostly include Persistent organic pollutants (POPs) which are polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs), pesticides, various additives, and pharmaceutical and cosmetics (Richardson and Kimura 2019)(Jones and De Voogt 1999). These POPs enter food chain via different human activities and pose health issue. Consequently they are found in all the water bodies (Dang, Walters, and Lee 2012) (Hopf, Ruder, and Succop 2009).

Conventional waste water treatment are proving to be inadequate due to cost, maintenance, toxicity and many other factors. So researchers are in search of new technologies more affordable in terms of expense, time, and toxicity. And these research have given rise to a most promising technology known as Nanotechnology(Shukla, Khan, and Daverey 2021). Graphene based materials are recently discovered nanoparticles yet it has shown its application in almost all the fields like electronics, medicines etc(Akere et al. 2022). Graphene oxide is one such materials which is promising nanomaterial. And it is showing promising results in the remediation of environment as well. High surface area of graphene oxide provides active sites for reactions with various chemicals. These property is base for degrading various chemical and organic pollutant in waste water(Anegbe et al. 2024). Graphene oxide is a 2-D carbon nanoparticle with functional oxygen containing groups such as carbonyl, epoxy, hydroxyl(Parvez et al. 2014).

This paper comprises of lab scale reactor using stones coated with graphene oxide. The waste water had been made in the laboratory containing dye crystal violet and glucose for COD estimation. The effect of time and reproducibility of the reactor was also determined. The results show that GO-CS can effectively remove dye and reduce organic pollutant from simulated waste water. Thus, this interprets use of graphene oxide as a promising nanomaterial in remediation of environmental pollutants.

2. Materials and Methods

2.1 Materials

The graphene oxide was synthesized using Hummer's method. And it was characterized by various instrumentations in Sicart, Anand, Gujrat, India. Crystal violet dye and glucose were used to prepare synthetic waste water. Distilled water had been used in entire work. Small uniform size stones were collected from nearby construction site for immobilization of graphene oxide. All the chemicals were of analytical grade.

2.2 Preparation of synthetic waste water

For safety purpose, synthetic waste water had been prepared in the laboratory itself. The composition of the synthetic waste water is mentioned in the table 1. below

Table 1. Composition of synthetic waste water

Components	Concentration
Crystal violet	10 mg L^{-1}
Glucose	200 mg L^{-1}
Distilled water	1 L
pH	6.5 – 7.0

2.3 Preparation of GO-CS

The stones from a nearby construction site had been collected. It was then treated with 0.1M HCL to remove any surface impurities and then washed with distilled water and dried at 80°C. Graphene oxide suspension 2 g L^{-1} was

MSW MANAGEMENT -Multidisciplinary, Scientific Work and Management Journal
ISSN: 1053-7899
Vol. 35 Issue 2, 2025, Pages: 1368-1373

prepared by ultrasonication. The stones were then immersed into the suspension for 24h. The stones were then dried at 80°C for 1h to obtain a graphene coated stones. The parameters required for the graphene oxide coated stones are mentioned in table 2.

Table 2. Physical properties of GO-CS

Parameters	Value
Reactor volume	50mL
Packed bed volume	30-35mL
Stone size	2-4mm
Stone mass	45-50 g
GO loading	10 mg GO/g stone
Total GO in reactor	450 mg

The graphene oxide loading was calculated using the equation:

$$mGO = mcs - ms$$

Where,

m_s = mass of the stones before coating

m_{cs} = mass of the GO coated stones

The GO loading was then expressed as the mass of GO per unit mass of stone

$$GO\ loading = mGO/ms\ (mg\ g - 1)$$

2.4 Designing a Fixed bed mini reactor system

A lab scale mini reactor had been developed using a 50mL glass burette. GO-CS were then placed in the reactor with a glass wool in both the layers to prevent go washout. The packed bed volume was approximately 30-35 mL. The mass of GO-CS was 55 g. The experiment had been performed under optimum condition. The reactor had been operated under gravity driven downward flow.

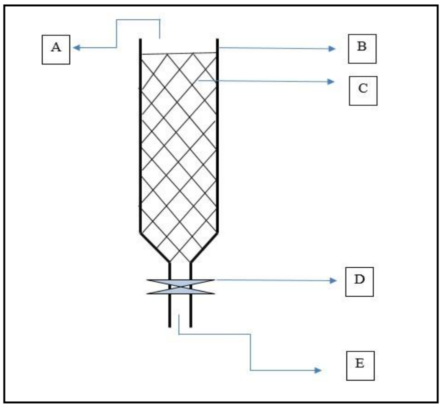

Fig 2. Schematic representation of down flow fixed-bed reactor (A) untreated wastewater; (B) cotton plug (C) packing material; (D) rubber bungs; (E) treated effluent

2.5 Experimental procedures

Approximately 30mL of synthetic waste water was introduced in the reactor. The mixture was allowed to remain in contact for different time intervals. A control had been run with the uncoated stones. After the treatment, the effluent had been removed for analysis. All the experiments had been conducted in triplicates.

2.5 Analytical method

After the fixed time interval (10, 20 and 30min), 1ml of effluent had been removed and analysed for removal of CV and glucose using standard titration based method. The reduction measurements in the titration before and after treatment were used to evaluate the removal efficiency. Experiments had been performed in triplicate and mean value had been considered to confirm reproducibility.

2.6 Calculations

Removal efficiency was calculated using the equation:

MSW MANAGEMENT -Multidisciplinary, Scientific Work and Management Journal
ISSN: 1053-7899
Vol. 35 Issue 2, 2025, Pages: 1368-1373

$$Removal\ \% = Co - Ce/Co \times 100$$

Where,
Co- Initial concentration of the titrant
Ce- final concentration

The adsorption capacity of the graphene oxide was calculated using:

$$q = \frac{(Co - Ce)V}{mGO, reactor}$$

Where,
q = adsorption capacity
V = volume of waste water treated
mGO = mass of graphene oxide in the reactor

3. Result and Discussion

3.1 Characteristic of GO-CS

The coating had been successfully done on the stones. The graphene oxide was uniformly immobilised in the stones. Thus many active sites are available for the adsorption activity. The average GO loading was found to be 10 mg g^{-1}.

3.2 Effect of contact time

The effect of contact time on the pollutant removal is shown in the Table 3. As the contact time increased, the efficiency of removal increased. At 30 min, the maximum removal efficiency was observed. It showed 93% for crystal violet and 77% for organic matter. This suggest that the active oxygen functional groups in the graphene oxide is promising as an adsorbing agent.

Table 3. ***Effect of contact time on removal efficiency of crystal violet and organic matter***

Contact Time (min)	CV Removal (%)	Organic Matter Removal (%)
10	54 ± 0.3	55 ± 0.4
20	76 ± 0.8	63 ± 0.2
30	93 ± 0.5	77 ± 0.3

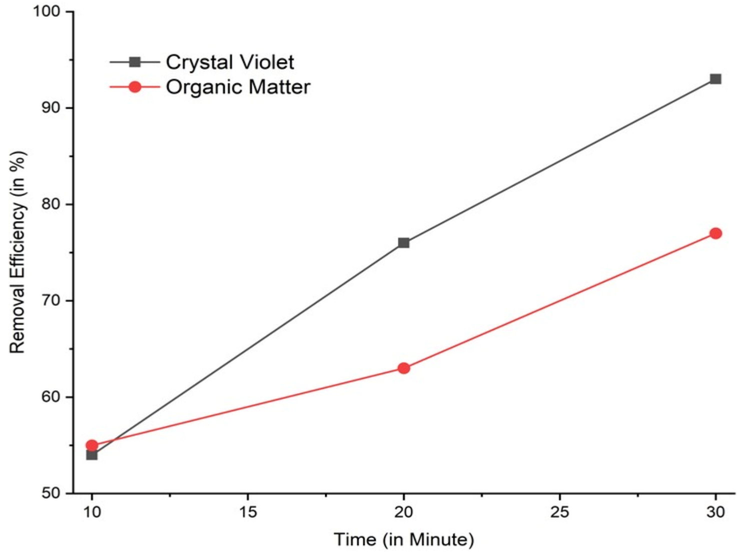

Fig 2. Effect of contact time on removal efficiency of crystal violet and organic matter

3.3 Comparison of CV and Organic Removal

The removal efficiency of CV and organic matter suggest that graphene oxide active sites can interact more with the CV structure providing more OH site to CV

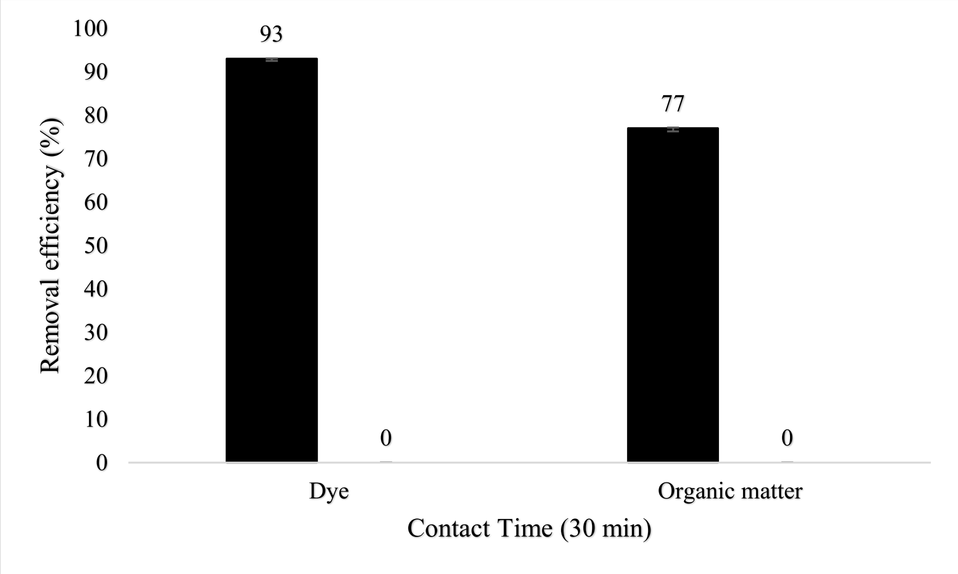

Fig 3. Comparison of removal efficiency of dye and organic matter

Conclusion

The fixed bed mini bioreactor had been successfully developed. The treatment of synthetic wastewater evaluated the removal efficiency of crystal violet to 93% whereas of organic matter to 77%. This result suggest that graphene oxide has a promising application as an adsorptive material and can be used in the regular basis in the industries to decontaminate the water prior to its discharge. Also the reactor developed gives an effective system for pollutant removal with good stability and reusability. In a whole, the immobilised graphene oxide system can be considered potential for environmentally sustainable waste water treatment.

References

1. Adak, Asok, Manas Bandyopadhyay, and Anjali Pal. 2005. “Removal of Crystal Violet Dye from Wastewater by Surfactant-Modified Alumina.” *Separation and Purification Technology* 44(2):139–44.
2. Agarwal, Prashant, Ritika Gupta, and Neeraj Agarwal. 2019. “Advances in Synthesis and Applications of Microalgal Nanoparticles for Wastewater Treatment.” *Journal of Nanotechnology* 2019(1):7392713.
3. Akere, Taiwo Hassan, Aline M. Z. de Medeiros, Diego Stéfani T. Martinez, Bashiru Ibrahim, Hanene Ali-Boucetta, and Eugenia Valsami-Jones. 2022. “Synthesis and Characterisation of a Graphene Oxide-Gold Nanohybrid for Use as Test Material.” *Nanomaterials* 13(1):33.
4. Ali, Imran, and Hassan Y. Aboul-Enein. 2004. *Chiral Pollutants: Distribution, Toxicity and Analysis by Chromatography and Capillary Electrophoresis*. John Wiley & Sons.
5. Amodu, Olusola S., Tunde V Ojumu, Seteno K. Ntwampe, and Olushola S. Ayanda. 2015. “Rapid Adsorption of Crystal Violet onto Magnetic Zeolite Synthesized from Fly Ash and Magnetite Nanoparticles.” *Journal of Encapsulation and Adsorption Sciences* 5(4):191–203.
6. Anegbe, Bala, Ikhazuagbe H. Ifijen, Muniratu Maliki, Ita E. Uwidia, and Aireguamen I. Aigbodion. 2024. “Graphene Oxide Synthesis and Applications in Emerging Contaminant Removal: A Comprehensive Review.” *Environmental Sciences Europe* 36(1):15.
7. Dahri, Muhammad Khairud, Muhammad Raziq Rahimi Kooh, and Linda B. L. Lim. 2013. “Removal of Methyl Violet 2B from Aqueous Solution Using Casuarina Equisetifolia Needle.” *International Scholarly Research Notices* 2013(1):619819.
8. Dang, Viet D., David M. Walters, and Cindy M. Lee. 2012. “Historical Changes in Polychlorinated Biphenyls Contaminated Sediments.”

9. Helmer, Richard, and Ivanildo Hespanhol. 1997. *Water Pollution Control: A Guide to the Use of Water Quality Management Principles*. CRC Press.
10. Hopf, Nancy B., Avima M. Ruder, and Paul Succop. 2009. "Background Levels of Polychlorinated Biphenyls in the US Population." *Science of the Total Environment* 407(24):6109–19.
11. Jones, Kevin C., and Pim De Voogt. 1999. "Persistent Organic Pollutants (POPs): State of the Science." *Environmental Pollution* 100(1–3):209–21.
12. Kant, Rita. 2011. "Textile Dyeing Industry an Environmental Hazard."
13. Kumari, Priya, Masood Alam, and Weqar Ahmed Siddiqi. 2019. "Usage of Nanoparticles as Adsorbents for Waste Water Treatment: An Emerging Trend." *Sustainable Materials and Technologies* 22:e00128.
14. Mittal, Alok, Jyoti Mittal, Arti Malviya, Dipika Kaur, and V. K. Gupta. 2010. "Adsorption of Hazardous Dye Crystal Violet from Wastewater by Waste Materials." *Journal of Colloid and Interface Science* 343(2):463–73.
15. Nemerow, Nelson Leonard, and Avijit Dasgupta. 1990. "Industrial and Hazardous Waste Treatment."
16. Parvez, Khaled, Zhong-Shuai Wu, Rongjin Li, Xianjie Liu, Robert Graf, Xinliang Feng, and Klaus Müllen. 2014. "Exfoliation of Graphite into Graphene in Aqueous Solutions of Inorganic Salts." *Journal of the American Chemical Society* 136(16):6083–91.
17. Richardson, Susan D., and Susana Y. Kimura. 2019. "Water Analysis: Emerging Contaminants and Current Issues." *Analytical Chemistry* 92(1):473–505.
18. Shukla, Saurabh, Ramsha Khan, and Achlesh Daverey. 2021. "Synthesis and Characterization of Magnetic Nanoparticles, and Their Applications in Wastewater Treatment: A Review." *Environmental Technology & Innovation* 24:101924.