

Phycoremediation of Dyes: An Overview on Mechanism, Challenges, and Prospects

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ABSTRACT

Dyes are major water pollutants as they show hazardous effects towards humans and aquatic environment. Various physical and chemical methods are used for the remediation of dyes but in the last few years, focus has been shifted towards the modern technique of remediation. Biological techniques have been exploited and utilized for the remediation of dyes as they are more sustainable, simple, and lead to the development of green technology. This review presents the different microalgal strains which are used for the remediation of dyes. It is seen that alone algal bioremediation of dyes is not an efficient and economical process. To overcome this challenge, a more advanced system, phyconanoremediation of dyes is also discussed briefly. Algal nanoparticles can achieve more remediation within few hours which makes this technique more efficient. Moreover, to make this more economical, a strategy to use the left-over biomass to produce valuable products like bioelectricity, pigments, biofuel and other medical products is also introduced. Later, challenges and opportunities are also discussed to make algal bioremediation more effective, sustainable, green, and clean technology.

Keywords : *Algal Bioremediation, Dyes, Phyconanoremediation, Challenges, Prospects.*

Introduction

Industrial effluents, domestic discharge and agro-chemical residues are the main sources of water pollution Chaukura *et al.* (2016). Industries like paints, pigments, and textiles release dyes in the water stream. Dyes are aromatic synthetic compounds and have toxic impacts on the ecosystem. Synthetic dyes are used in numerous sectors like in food, leather, cosmetics, electronic industry, pharmaceuticals, printing, plastic, etc. These dyes are seen by the naked eyes in the water bodies but are difficult to abate because of their aromatic structure. More than 3000 dyes are used in the textile, printing and various other purposes and effluent of these industries are released in an uncontrolled manner and pollute

the environment (Piaskowski *et al.*, 2018). These have harmful impact on aquatic systems because they decrease the light deep inside the sea. Thus, reducing photosynthetic activity. Many physical, chemical, and biological methods are used for the remediation of dyes like precipitation, sedimentation, adsorption, ion-exchange, bioremediation, etc. These physical and chemical methods are not efficient, eco-friendly, and economical as compared to biological methods as they utilize toxic chemicals and requires energy for the abatement of dyes. To overcome this, scientists are now moving towards the biological methods as they are eco-friendly and more effective as compare to physicochemical techniques (Devasena and Thiruchelvi, 2019). Remediation of dyes with the help of biological

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agents is known as bioremediation. Bioremediation carried out by algae is known as Phycoremediation. It is observed that phycoremediation is one of the potential techniques of remediation because of their, eco-friendly nature, ease to grow, handle, and maintain. Algae are the hyper accumulators of dyes. Moreover, algae come with an added benefit as they are the rich source of proteins, carbohydrates, lipids etc., which leads to the production of various commercial products like biofuel, medicines, pigments, natural dyes, etc. (Arora *et al.*, 2016). To make this technique more efficient, biological synthesis of nanoparticles with the help of algae is discussed. Recently, the green synthesis of nanoparticles is gaining more attention because of its efficiency, environment-friendly, simple, and expeditious rate of synthesis Kumar *et al.* (2021). This mini-review explores the biological remediation of dyes with the help of algae and discusses the more advanced and economical system of remediation of dyes. Moreover, challenges and opportunities are also briefly mentioned to make this algal-based bioremediation of dyes more economical, efficient, and promising abatement technique.

Phycoremediation of dyes and its mechanism

Algae can abate dyes with the help of three mechanisms that are biosorption, bioaccumulation, and biodegradation. In biosorption, it is observed that dyes bind to functional groups like hydroxyl, amine, thiol, etc., which are present on the surface of algae through electrostatic attraction Zohoorian *et al.* (2020). Algae adsorb chromophores on its cell surface, and it is a passive process and can be carried out by living or non-living biomass. Contrarily, bioaccumulation and biodegradation are active process and requires energy for the remediation of dyes. In bioaccumulation, dyes are accumulated inside the cell with the help of various transport proteins present on the surface of algae. On the other hand, in biodegradation, dye molecules are converted into non-toxic compounds with the help of enzymes or cell metabolites. In bioaccumulation, dyes are consumed by algae as nutrients. These methods are more economical and compatible as compared to conventional methods. The biological methods produce non-hazardous compounds and consume less quantity of water as compared to conventional methods (Chugh *et al.*, 2020).

Algae can decolorize many dyes under optimal growth conditions like pH, temperature, light, and

media. Different types of dyes have different decolorization rates. Azo dyes show a high rate of decolorization as compared to phthalocyanine (Abiri *et al.*, 2017). Ethidium bromide is remediated by *Desmodesmus subspicatus*, *Chlorella vulgaris* and *Raphidocelis subcapitata*. For complete remediation of ethidium bromide 10^{10} algae/ml is required for *Desmodesmus subspicatus* and *Chlorella vulgaris*. *Raphidocelis subcapitata* required 10^{11} algae/ml de Almeida *et al.* (2020). *Chlorella vulgaris* are able to remediate ramazol black B, Malachite green, ramazol red RR, ramazol golden yellow RNL and tectilon yellow 2G Alaguprathana and Poonkothai (2017). *Chlorella pyrenoidosa* and *spirulina maxima* dried biomass show photocatalytic reduction of methylene blue. 98.20% of methylene blue is removed by *Chlorella pyrenoidosa* and 94.19% of methylene blue is abated by *Spirulina maxima* Y. A.R. Lebron *et al.* (2019).

Chlorella marina, *Isochrysis galbana*, *Tetarselmis species*, *Nannochloropsis species*, *Dunaliella salina* and *Chlorella* species helps in the dye removal from the textile effluent. Malachite green is removed by various strains of microalgae which are *Nostoc species*, *Turbinaria conoides* and *Chlorella vulgaris*. *Spirogyra* species are used for the remediation of Acid orange 7, reactive yellow 22, basic blue 3 and basic red 46 dyes. Crystal violet is remediated by *Chactophora elegans*. *Ulothrix species* are used to adsorb methylene blue. Azo dyes are remediated by *Chlorella pyrenoidosa*, *Chlorella vulgaris*, *Spirogyra* and *Oscillatoria tenuis*. More than 30 azo dyes are completely detoxified by *C. pyrenoidosa*, *Chlorella vulgaris* and *Oscillatoria* sp. Ajaz *et al.* (2020); Hernández-Zamora *et al.* (2015). More recent studies of dye removal by microalgae are mentioned in Table 1.

Phyconanoremediation: More advance phycoremediation technique

It is observed that phycoremediation is not able to achieve complete remediation and consider to be an expensive method of treatment. To overcome this many advanced techniques, like remediation of dyes with the help of phyconanoparticles, can achieve more than 90% of remediation within 5 to 30 minutes and make algae a potential candidate for remediation. These green nano-sized particles are more eco-friendly as compared to the chemical synthesis of nanoparticles as they don't use harmful chemicals for the production of these tiny-units. Algae can synthesize nanoparticles with the help of

Table 1. Phycoremediation of dyes

Algae	DYE	Removal Efficiency	References
<i>Chlorella vulgaris</i>	Naphthol Green B	98.5%	Abd Ellatif <i>et al.</i> (2020)
	Brazil Wood	99.5%	Abd Ellatif <i>et al.</i> 2020)
	Orange G	99.5%	Abd Ellatif <i>et al.</i> (2020)
	Methylene Blue	83.04±2.94%	Chin <i>et al.</i> (2020)
<i>Anabaena oryzae</i>	Crystalline Violet	97.4%	Ibrahim <i>et al.</i> (2021)
<i>Wollea saccata</i>	Malachite Green	93.3%	Picchio <i>et al.</i> (2020)
<i>Chara vulgaris</i> L.	Methyl Red	70%	Mahajan and Kaushal (2020)
<i>Enteromorpha intestinalis</i>	Malachite Green	99.63%	Hamouda <i>et al.</i> (2020)
<i>Haematococcus pluvialis</i>	Malachite Green	66.5- 95.2%	Liu <i>et al.</i> (2018)
<i>Spirogyra</i> sp. and <i>Oscillatoria</i> sp	Red and Blue dye.	<i>Spirogyra</i> sp.: 78.29% of blue dye and 64.21% red dye. <i>Oscillatoria</i> sp.: 76.48% of blue dye and 62.63% of red dye	Brahmbhatt and Jasrai (2016)
<i>Iridaea cordata</i>	Crystal Violet and Methylene Blue	CV: 75% MB: 90%	Escudero <i>et al.</i> (2017)
<i>Fucus vesiculosus</i>	Methylene Blue and Eriochrome Black T	MB: 99.28%; EB T: 99.44%	Yuri Abner Rocha Lebron <i>et al.</i> (2019)
<i>Ulva fasciata</i> and <i>Sargassum dentifolium</i>	Methylene Blue	Individually, <i>Ulva fasciata</i> : 97% <i>Sargassum dentifolium</i> : 85.6% And in Combination: 99.2%	Moghazy <i>et al.</i> (2019)

metal precursors, and then these purified nanoparticles are used for the abatement of dyes which makes this technique eco-friendly and more efficient Iravani *et al.* (2014). Nanoparticles show maximum removal efficiency due to their unique physical, chemical, and magnetic properties. It is reported that as we go down the scale, surface-to-volume ratio increases, and quantum and tunnelling effect is changed. They have numerous adsorption sites because of these special features. These nano-sized particles help in the excellent abatement of dyes within few hours Saravanan *et al.*(2021). Green synthesis of phyconanoparticles takes place with the help of two pathways i.e., intracellular and extracellular synthesis. In intracellular synthesis, reducing agents which are present inside the cell are used to produce nanoparticles. On the other hand, in extracellular synthesis, enzymes or other bioactive compounds are released by algal cells are used for the reduction of metal ions into zero-valent nanoparticles Chaudhary *et al.* (2020). There will be no need for reducing or stabilizing agents as algal functional groups will initiate, synthesize, and stabilize the nanoparticle itself. Thus, making it an en-

vironment-friendly and cost-effective technique Negi and Singh (2018).

Chlorella vulgaris synthesizes silver nanoparticles that can remediate 96.51% methylene blue within three hours Rajkumar *et al.* (2021). Silver phyconanoparticles are also able to remediate methyl red (Husain *et al.*, 2019), methyl orange and congo red Aboelfetoh *et al.* (2017). On the other hand, gold phyconanoparticles are also used in the photocatalytic degradation of dyes. *Sargassum tenerrimum* can synthesize 5-45 nm gold nanoparticles which are used for the abatement of Rhodamine B and Sulforhodamine 101 Ramakrishna *et al.* (2016). To make this phyconanoremediation more economical, one can use the left-over biomass for the production of various commercial by-products like biofuel, pigments, biofertilizer, nutraceuticals, cosmetic products, therapeutic proteins and other medicines Hu *et al.* (2019). Moreover, these nanoparticles can be recycled and re-used for remediation or for other applications which make this process, more efficient, economical as well as a promising approach for the remediation of dyes as shown in Fig. 1.

Challenges and Prospects

Phycoremediation is an outstanding mechanism for the remediation of dyes. Despite various methods, still it is seen that dyes are not completely or quickly remediated by the microalgae. For complete bioremediation, more advanced technologies like genetic engineering, metabolic engineering or protein engineering could play a significant role in it. To make the phycoremediation process more efficient, it is important to carry out studies on the gene level and modify the genetic make-up of the microalgae to enhance the efficacy of the process. With the complete genomic studies, it will be possible to make the biomarkers for the contaminated site. CRISPR-Cas 9 tool can be used to make this process more efficient. Toxicological studies of the intermediates produced after transforming the dyes should be done along with the characterization of the strains. However, the cost-efficacy of this process is still an issue faced by sponsors and scientists. This is the major challenge faced by this technology for the commercialization or scale-up of this process. So, more studies should be carried out in the commercialization of this process to make this process more environment friendly and economical at the same time. The strain should be selected not only for maximum remediation of dyes but also able to accumulate maximum by-products like lipids, proteins, pigments, etc. Strain should have lower nutrient re-

quirements and can be able to survive in the robust conditions. More research should be carried out in the field of chemical modification, biomimetic systems, on the effect of tolerance of dyes and to see the influence of dyes on different valuable products. So, that this promising technique will become more cost-effective and more sustainable powerful tool for remediation of dyes. Genetic engineering can be used to enhance the adsorption of dyes over the surface by altering the gene responsible for the expression of protein on the cell surface or enhances the activity of enzyme responsible for dye tolerance and for the accumulation of some by-products. Further studies are required to develop a technology that simultaneously detects as well as abate the dyes from the environment. Still, a lot needs to be understood in the multi-disciplinary field to make this process a successful technique for remediation of dyes on the large scale.

Conclusion

Algal bioremediation of dyes is sustainable, economical, clean, and green technology as compared to traditional processes. Dyes show hazardous effects on humans, flora, and fauna due to their synthetic aromatic nature. These pollutants are released by various industries like textiles, dyeing, printing. Microalgae are the hyperaccumulator of the dyes, CO_2 , and are the source of O_2 in the aquatic atmo-

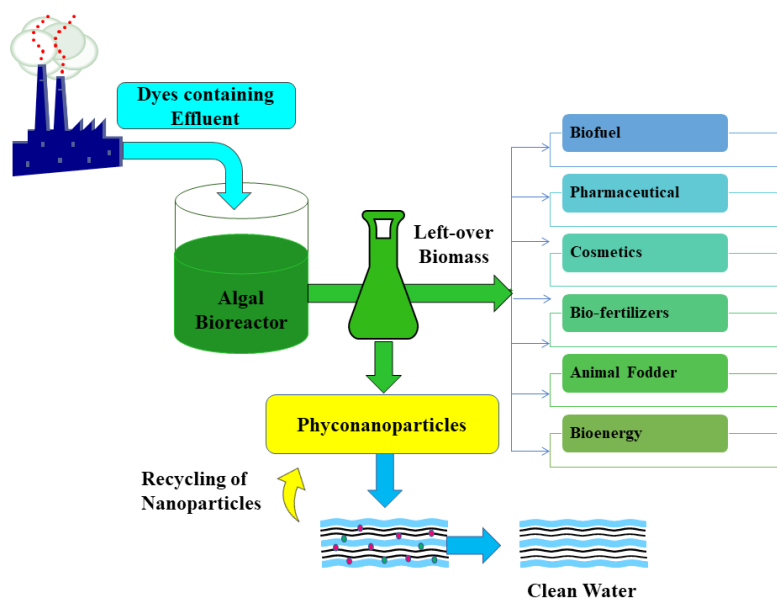


Fig. 1. Economical Phyconanoremediation of Dyes

sphere. Dyes are abated by different mechanisms of action which are biosorption, bioaccumulation, and biodegradation. It is observed that alone phycoremediation is not an effective technique. To overcome, more advanced system, green synthesis of nanoparticles helps in the maximum remediation of dyes within few hours due to their unique properties. These phyconanoparticles are easy to synthesize, maintain and are environment-friendly. Moreover, to make this technique more economical, leftover biomass can be used to produce other economical by-products. Algal species can produce various innovative by-products like biodiesel, biomethane, organic fertilizers and pharmaceutical products. This will make this technique more sustainable, efficient, and economical. Despite all these features, still more studies are required to understand the full abatement mechanism of phyconanoparticles, tolerance of algae towards dyes, effects of dye on the accumulation of different by-products, etc. This will make phycoremediation a powerful tool for the remediation of dyes.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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