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Advancement in Green Synthesis of Titanium Dioxide : Photocatalytic and Larvicidal Activities – A review

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Abstract
Nanotechnology is a fast expanding field with several applications in science, engineering, healthcare, pharmaceutical, and other areas. Nanoparticles (NP) are frequently produced through a variety of physical and chemical methods. Recently, green synthesis technologies that are more simple, sustainable, and cost-effective have been developed. The environmentally friendly/sustainable synthesis of titanium dioxide nanoparticles (TiO_2 NPs) has been in great demand in the previous quarter. Bioactive components found in organisms, such as plants, facilitate the processes of bio-reduction and restriction. This review described green synthesis of TiO_2 NPs, the photocatalytical uses, and managing the larvicidal activity of disease-spreading mosquitoes. Various natural reducing agents including proteins, enzymes, phytochemicals, and others, are involved in the synthesis of TiO_2 NPs. Current research findings and future concerns in a viable platform based on biologically meditated TiO_2 nanostructures for industrial applications.

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INTRODUCTION

Nanotechnology is growing rapidly due to the numerous benefits that are felt and provide alternatives in all fields. The theoretical and conceptual realization of nanotechnology is becoming clearer and its promise of superiority is sensed(Mayegowda et al., 2023). The foundation of nanotechnology is always discussed by researchers, who were initiated by Michael Frady, a researcher on nanoparticle synthesis in 1857, then decades later became the basis for metal synthesis. Along with the need for applications in various fields and the intensification of the development of synthesis, green synthesis is currently a favorite of researchers because it is environmentally friendly, non-toxic, and economical (Sethy et al., 2020), as well as has no by-products, uses safe solvents, uses plant extracts as bioreductors(Castillo-Henríquez et al., 2020; Sunny et al., 2022), and so do perceived applicatives such as TiO_2 nanoparticles as shown in Figure 1.

Nanoparticles consist of two groups, organic nanoparticles and inorganic nanoparticles. Organic nanoparticles consist of liposomes, chitosan, ferritin, dendrimers and others. Inorganic nanoparticles are divided into three groups: metal nanoparticles; semiconductor nanoparticles; and magnetic nanoparticles. NPs TiO_2 are the most efficient light absorbers, absorbing 3-4% of solar energy. There are widely used as photocatalysts for hydrogen production and the breakdown of dyes and other hazardous chemicals in water.

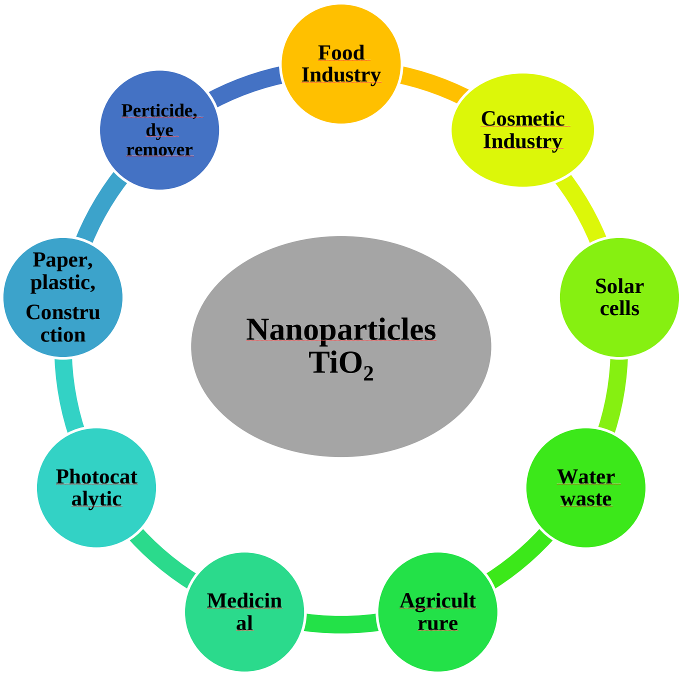

Figure 1. Application of TiO_2 nanoparticles (Rani and Shanker, 2020a)

Larvicidal activity, especially on disease-spreading mosquitoes such as Aedes, development is so rapid and cannot be separated from negative impacts, examples of diseases caused by Aedes mosquitoes such as dengue fever, cikukunya and others, from previous studies plant extracts and green synthesis of TiO_2 nanoparticles have a role in dealing with larvicidal activity (Amutha *et al.*, 2019; Narayanan, Devi, *et al.*, 2021; Narayanan, Vigneshwari, *et al.*, 2021; Balaraman, Balasubramanian and Liu, 2022) this is due by the secondary metabolite content possessed by the capping agent.

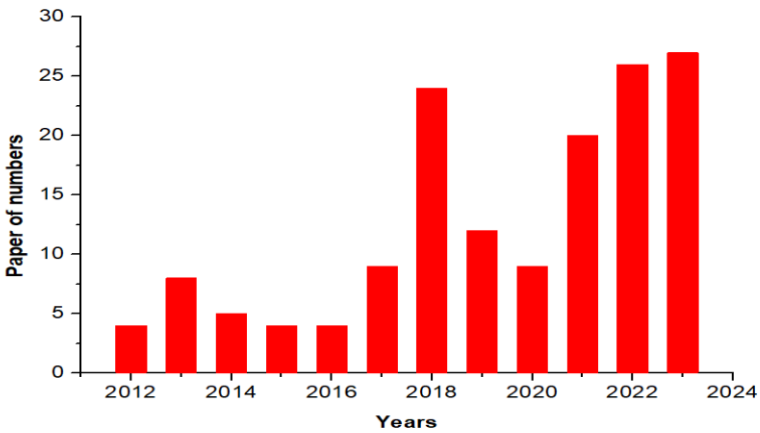

Figure 2. Histogram of green synthesis of TiO_2 nanoparticles for photocatalytic applications

The utilization and novelty review of diverse plant extracts for the manufacture of TiO2 NPs for photocatalytic applications in degrading dyes and limiting the proliferation of larvicides in disease-transmitting mosquitoes is reported in this paper. Then, in numerous tests, including one on the environment, TiO_2 NPs shown increased photocatalytic and pesticide action in handling and inhibiting the proliferation of these mosquito larvae. In general, the use of plant extracts serves as a contributor to the reducing properties of the metabolite content in plants that are present in all parts of the plant used, this is due to the presence of active functional groups from plants such as alkenyl (C-C), amides (C-N), phenolic and alcohols (O-H), amines (N-H) and carboxylates (COO)(Narayanan, Vigneshwari, et al., 2021).

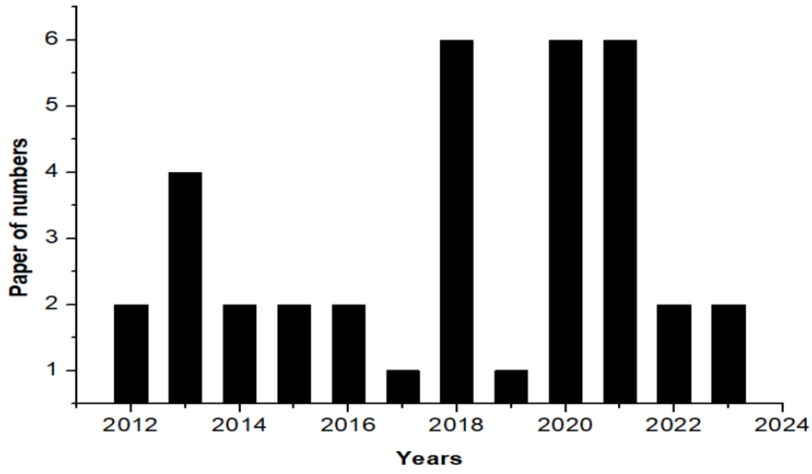

Figure 3. Histogram of green synthesis of TiO_2 nanoparticles for application of Larvicidal activity

METHOD

Green Synthesis

Green synthesis plays a key role in engineering and science today, because nanoparticles have a small size, a high surface area to volume ratio, the properties of the plants used depend on the size, and its application in all fields. The green synthesis method can provide various sources for the synthesis of TiO_2 NPs utilizing extracts such as plants, microbes and enzymes (Rani & Shanker, 2020). The plant extracts used contain secondary metabolites as bioactive compounds such as terpenoids, saponins and flavonoids, which are surface active molecules that play a role in reducing the formation of TiO_2 NPs. The extract also contains vitamins, minerals, amino acids, carbohydrates and proteins which help to regulate the size and structure of the nanoparticles produced. Secondary metabolites in plants serve a variety of functions, including bioreductor agents, capping agents, and stabilizers (Verma et al., 2022)

According to the provisions, green synthesis has been realized, one of which is in plant extracts, due to the high metabolite concentration. Figure 4 depicts a flowchart of the nanoparticle manufacturing process using plant extracts.

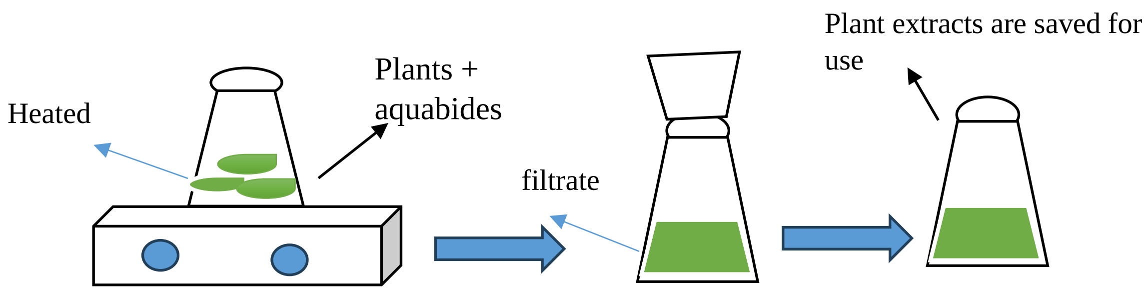

Figure 4. Schematic of the TiO_2 nanoparticle preparation process (Maurya *et al.*, 2019)

Synthesis of TiO_2 NPs

TiO_2 NPs have intriguing qualities such as photocatalytic activity, larvasdia activity, optical properties, antibacterial capabilities, and strong chemical stability, and are widely used in a variety of sectors such as catalysts, cosmetics, and others, as illustrated in Figure 1. The utilization of different plant extracts and precursors can be shown in tables 1 and 2 from prior investigations. One of the most intriguing prior studies on the manufacture of TiO_2 NPs was the utilization of *Sargassum myriocystum* extract utilizing titanium tetrabutoxide as a precursor on larvicidal action. *S. wightii* extract outperformed *A. subpictus* and *C. quinquefasciatus* in terms of mortality (LC_{50} = 26.12 and 27.28: LC_{90} = 80.89 and 82.65; $\chi 2$ = 14.321 and 19.388). In addition, NP-TiO_2 displayed excellent activity against *A. subpictus* and *C. quinquefasciatus* (LC_{50} = 4.37 and 4.68; LC_{90} = 8.33 and 8.97; $\chi 2$ = 5.741 and 4.531 mg/L).

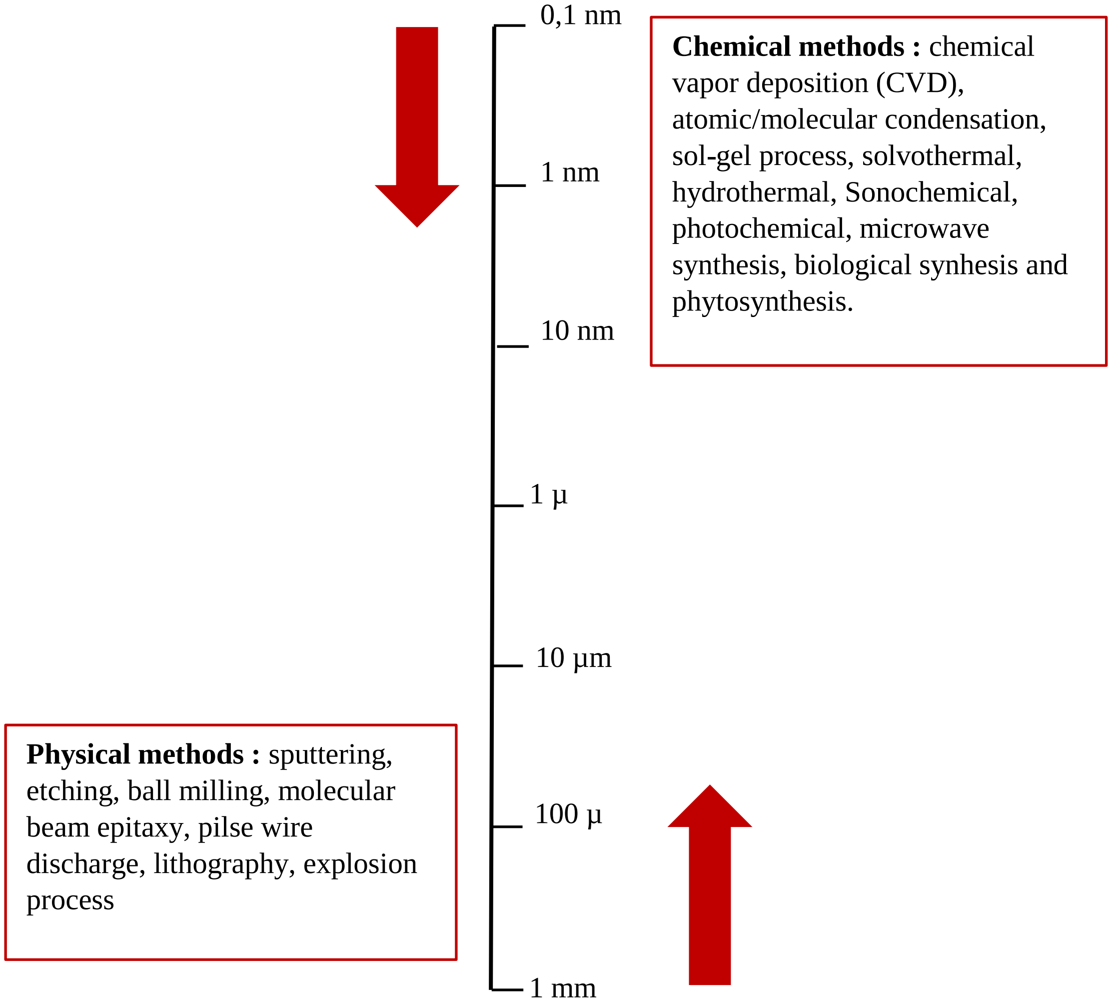

Figure 5. Nanoparticle synthesis methods.

This results described that TiO_2 NPs with *Sargassum myriocystum* extract can control vector species and photocatalytic degradation of crystal violet (90.50%) and methylene blue (92.92%) within 45 minutes (Balaraman et al., 2022). A common thread can be drawn from studies on the synthesis of TiO_2 nanoparticles from various plant extracts and precursors, namely that the use of natural materials is safer for the environment, more economical, and the process is simpler than physical and chemical methods, which are more expensive, require high energy and temperature, and cause pollution. environment. Green synthesis is based on various ideas, including lowering pollution during synthesis, being inexpensive, utilizing safe chemicals and solvents, using renewable raw materials, using derivatives, catalysis, applications for pollutant degradation, and pollution preventative (Sun et al., 2019)(Kandregula et al., 2015)

RESULTS AND DISCUSSION

Application of TiO_2 NPs

TiO_2 NPs act as a photocatalytic to accelerate the transformation, so the process is called photocatalysis (Sagadevan et al., 2021). The mechanism can be seen in Figure 6.

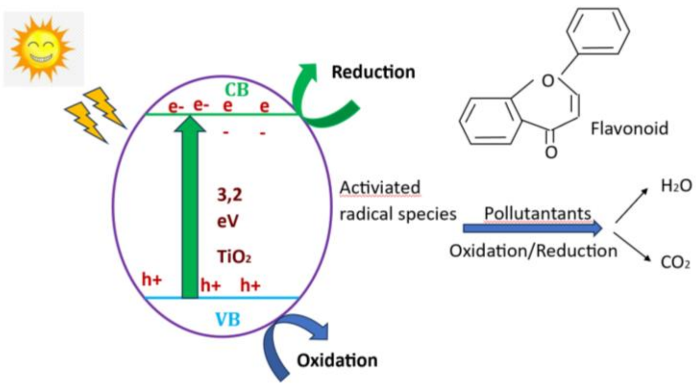

Figure 6. Photocatalytic mechanism of TiO_2 nanoparticles under light

There are several precursors used, for example $TiCl_4$ (Titanium tetrachloride), TTIP (Titanium tetra isopropoxide), $TiO(OH)_2$ (metatitanic acid or titanyl, hydroxside) tetraethylammonium perchlorate (TEAP) which can be seen in tables 1 and 2. Plant extracts are added drop by drop while constantly stirring continuously at a specified temperature, the presence of TiO_2 NPs is characterized by a shift in the color of the solution. After that, it is filtered and washed with aquabides, dried in an oven then calcined at a temperature of 400-800°C which aims to remove organic groups. The product can be applied as photocatalytic and larvicidal activities which can be seen in Tables 1 and 2.

Table 1. Photocatalytic activity

Prekursor	Plant Extract	Shape	Size (nm)	Reference
TTIP	Terminalia catappa and carissa carandas	Spherical and non agglomeration	10-21	(Rajendhiran et al., 2021)
$TiO(OH)_2$	Cola nitida	Near spherical	25.00-191.41 nm	(Akinola et al., 2020)
Tetraethylammonium perchlorate (TEAP)	hibiscus leaf crude extract	Near spherical	-	(Syahin Firdaus Aziz Zamri & Sapawe, 2019)
TTIP	Piper betel, Ocimum tenuiflorum, Moringa oleifera, Coriandrum sativum	Spherical	67-83 nm	(Pushpamalini et al., 2020)
$TiCl_4$	Malva parviflora (MP)	Near spherical	20.3-29.5 nm	(Helmy et al., 2021)
TTIP	Syzygium cumini	Spherical		
Titanium tetraisopropoxide (TTIP)	*Ageratina altissima*		20-25	(Madadi & Lotfabad, 2016)
Titanium isopropoxide (TTIP)	*Azadirachta indica*	Spherical	124	(Sankar et al., 2015)
Titanium Dioxide bulk particles (TiO_2)	*Curcuma longa*		50-100	(Abdul Jalill et al., 2016)

$TiO(OH)_2$	*Aqueous flower extract of Calotropis gigantea*		160-220	(Marimuthu et al., 2013)
$TiO(OH)_2$	*Calotropis gigantea*		10	(Marimuthu et al., 2013)
TTIP	*Nyctanthes leaves Extract*		100-150	(Sundrarajan & Gowri, 2011)
$TiO(OH)_2$	*Leaf aqueous extract of Psidium guajava*		32	(Santhoshkumar et al., 2014)
$TiO(OH)_2$	*Aqueous leaf extract of Solanum trilobatum*	Monodispersed and Spherical	70	(Ilyas et al., 2021)(Rajakumar et al., 2014)
$TiO(OH)_2$	*Aloe vera gel extract*	Spherical and Oval	80-90	(Nithya et al., 2013)
Titanium Oxysulfate	*0.3% aqueous extract of the latex of Jatropha curcas L.*	Near Spherical	23, 25-100	(Madadi & Lotfabad, 2016)
$TiO(OH)_2$	*Annona squamosa peel extract*	Spherical	23	(Roopan et al., 2012)
$TiO(OH)_2$	*Eclipta prostrata*	Polydispersed groups and spheres	23, 36–68	(Rajakumar, Rahuman, Priyamvada, et al., 2012)
Titanium dioxide (TiO_2 purity 99.0%) was	*Leaf extract of Catharanthus roseus*	Polydispersed groups and spheres	5-110	(Velayutham et al., 2012)
$TiO(OH)_2$	*Aloe vera*	Group	60	(Technology, 2016)
$TiO(OH)_2$	*Aloe vera leaves extract*	Irregular	32	(Sett et al., 2016)
$TiO(OH)_2$	*Peelextractof Citrus reticulata*	-	24	(Rajakumar, Rahuman, Roopan, et al., 2012)
Titanium tetra butoxide (Ti(OC4H9)4 97%, Sigma-Aldrich),	*Citrus sinensis and Musa acuminata Peel*	Spherical	7.3–27.3 nm and 13.4–22.4 nm,	(Olana et al., 2022)
TTIP	Leaf extract of Murraya koenigii (Curry tree)	Spherical	2-15 nm	(N. Shimpi, S. Mishra, 2020)
(Ti(OC4H9)4 97%, Sigma-Aldrich),	leaf extract *Coronopus didymus*	Spherical	13.4nm	(ur Rehman et al., 2022)
TTIP	Calotropis gigantea	Spherical	42 nm	(Prashanth, n.d.)
TTIP	Wrightia tintctoria leaf extract	Spherical	9.93 nm	(A. Muthuvel, Nejla Mahjoub Said, M. Jothibas, 2021)

TiO_2 nanoparticles are a novel option as a potential replacement for synthetic pesticides, intends to evaluate the larvicidal efficacy of the essential oils extracted.

Table 2. Larvasida activity

Prekursor	Ekstrak Tanaman	Shape	Size (nm)	Reference
Solution TiO_2	leaf extract of Pouteria campechiana	Spherical	29	(Narayanan, Devi, et al., 2021)(Madadi & Lotfabad, 2016)
TiO_2 powder	Coleus aromaticus and assess the	Spherical	12-33	(Narayanan, Vigneshwari, et al., 2021)
	Sargassum myriocystum	Spherical	20 to 250	(Balaraman et al., 2022)
	Mangifera indica	Spherical	30± 5nm.	(Rajakumar et al., 2015)
Solution TiO_2	Seaweed Sargassum wightii	Spherical	25 nm	(Mathivanan et al., 2023)
$TiO(OH)_2$	Morinda citrifolia root extract	Spherical	20.46-39.20 nm.	(Suman et al., 2015)
$TiO (OH)_2$	trilobatum extract	Spherical	70 nm	(Rajakumar et al., 2014)
TiO_4	*Parthenium hysterophorus*	Spherical	20–50 nm	(Balaraman et al., 2022)(Thandapani et al., 2018)
$TiO(OH)_2$	*Mangifera indica extract*	Spherical	30±5 nm	(Rajakumar et al., 2015)
TiO_2	*Desmostachya bipinnata*	Spherical	36,4 nm	(Shyam-Sundar et al., 2023)
TiO_2	*Ledebouria revoluta*	Spherical	47 nm	(Aswini et al., 2021)
$TiCl_4$	*Aza- dirachta indica twigs, Ficus benghalensis and Syzygium aromaticum.*	Tetragonal, agglomerated	10-33 nm	(Achudhan et al., 2020)
$TiCl_4$	*leaf extract of Peepal (Ficus religiosa)*	Spherical	70,29-84,93	(Soni & Dhiman, 2020)
$TiO(OH)_2$	*Aloe ferox mill, and Commipora abyssinica (O.Berg)*	-	-	(Abutaha et al., 2022)
$TiO(OH)_2$	*Aqueous leaf extract of solanum trilobatum (purple fruited pea eggplant)*	Spherical	70 nm	(Rajakumar et al., 2014)

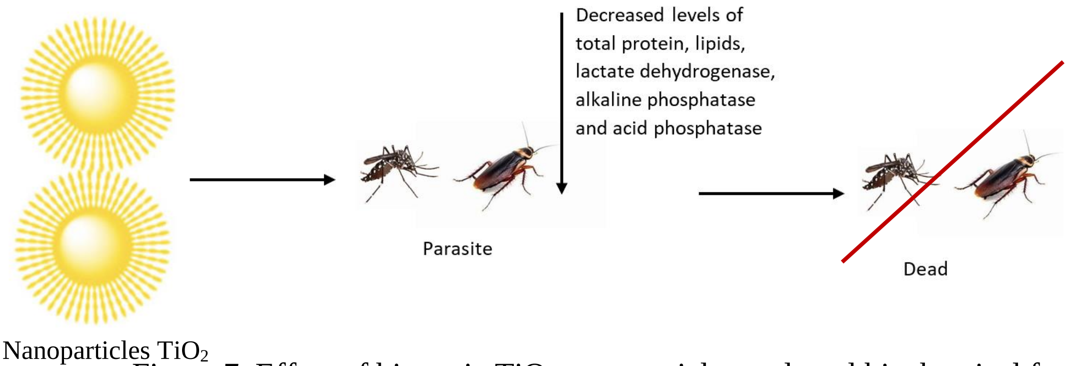

Figure 7. Effect of biogenic TiO_2 nanoparticles on larval biochemical factors

CONCLUSION

In this review, the most recent study on the topic of green synthesis of TiO_2 NPs uses natural sources that are used as photocatalytic removers of synthetic dyes and larvicidal action in disease-spreading mosquitoes. Based on the information, researchers and scientists are encouraged to broaden their investigation of nature's potential and develop effective and sustainable methodologies for synthesizing nanoparticles and their desired properties for use in a variety of scientific disciplines. This method is an approach that can be used to adjust the size, shape and structure of crystals depending on the type of source and certain parameters and considering the application. These reports open opportunities for green synthesis efforts using extracts derived from natural sources to produce materials with functions and characteristics.

RECOMMENDATIONS

Recommendations for article review to be applied in chemistry learning so as to maximize the learning process. Will provide a knowledge base for the application of photocatalysis and larvicidal activities, serving as a reference in research as a bioreductor or capping agent.

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