Chapter 2

Literature Review and Research Objective

Abstract

Nowadays, textile dye emissions become a serious environmental issue imposing detrimental effects on human health and ecosystems. The toxic and persistent textile dyes need a sustainable and innovative remediation approach. In this chapter, the literature review related to the green and sustainable approaches used to synthesize nano-photocatalyst, nano-adsorbent, and hydrochar for the removal of toxic textile dye from textile effluent. Chapter 2 has been divided into three parts (1) literature review on green synthesis of TiO_2 to use as a photocatalyst. (2) literature review on green synthesis of adsorbent for adsorption of dye (3) literature review on dye removal from textile wastewater through adsorption using biomass and hydrochar as an adsorbent. Based on the literature review the research gaps have been specified and the research aim of the present thesis has been decided.

2.1 Literature review

2.1.1 Green synthesis of TiO_2 NPs to use as a photocatalyst

Several authors have reported green synthesis of TiO_2 nanoparticles using several plant extracts in the past few years. Sufficient removal and minimization of several textile dyes and other pollutants from wastewater were reported with antibacterial activity against several gram-positive and gram-negative bacteria. The available information is summarized in **Table 2.1**.

There are some studies reported in the literature about the green synthesis of TiO_2 NPs by using several plant extracts such as Baamer et al. reported the successful green synthesis of TiO_2 NPs using *Mangrove* leaves with Reactive Red 195 dye photodegradation reached 55.45% after 120 min and the zone of inhibition (ZOI) against *S. aureus*, *E. faecalis* and *V. damsela* bacteria were found to be 18,19, and 18 mm respectively [39]. Mehta et al. studied the synthesis of TiO_2

NPs by using the leaf and stem extracts of *Carissa opaca* and applied for the photocatalytic degradation of methylene blue (MB) and methyl violet (MV) and confirmed that the average particle size of TiO_2 ranged from 72.8 to 84.11 nm, with a spherical/hexagonal crystalline structure. Decolorizing efficiencies of 87.8% and 91.95% against MB, and MV dye degradation efficiencies of 82.1% and 71.9% were noted within 2 h with NPs synthesized using leaf and stem extract, respectively. Also showed antibacterial activity against *Klebsiella pneumoniae* and *Staphylococcus aureus* with a maximum ZOI of 13.3 ± 0.15 mm and 18.3 ± 0.15 mm, respectively [40]. Girigoswami et al. utilized *Solanum Tuberosum* (potato) peel extract to synthesize TiO_2 NPs and they demonstrated the enhancement of the photocatalytic activity of green synthesized TiO_2 against the bromophenol blue dye reduction after 40 min of sunlight exposure was 98% [41]. Khoiriah et al. reported the synthesis of TiO_2 NPs using *Parkia speciosa* peel extract and stated that P-TiO_2 had photocatalytic activity and completely degraded the methyl orange dye (97.99%) [42]. Yitagesu et al. used *Impatiens rothii Hook. f.* leaf extract for the synthesis of TiO_2 NPs and stated that, according to BET analysis, the specific surface area was 65 m^2/g and the average particle size from SEM and average crystallite size from XRD analysis were approximately 11 and 25 nm, respectively. The maximum photodegradation of Methylene blue dye at optimum conditions (catalyst dosage 30 mg/L, pH 10.5, initial concentration of MB 15 ppm for 100 min) has been reported to be 98% [43]. Pavithra et al. showed the synthesis of TiO_2 NPs by utilizing *Calotropis gigantean* leaf extract and reported the 96% degradation of MB dye in 60 min irradiation, due to a low recombination rate of photo-generated electrons and holes. The concentration of $O_2^{\bullet}$ and $OH^{\bullet}$ radicals in the solution was increased by the *Calotropis gigantean* plant-assisted TiO_2 NPs, which is advantageous for increasing the rate of organic compound photodegradation [44]. Bopape et al. reported the first time *Commelina benghanlensis* plant extract was used for the synthesis of TiO_2 NPs and photo catalytically degraded 65% and 82% Methylene Blue dye and pharmaceutical SSX, respectively after 120 min irradiation [45]. Rathi et al. used *Caesalpinia pulcherrima* flower extract, *Nervilia aragoana* leaf extract, and *Manihot esculenta* peel extract for the synthesis of TiO_2 NPs and they observed the MB dye degradation of 86%, 75%, and 56% after 40 min visible light irradiation, respectively. TiO_2 NPs synthesized using *C. pulcherrima* flower extract exhibited a narrow bandgap, improved morphology, enhanced degradation capacity, and superior antimicrobial potential against *E. coli, P. aeruginosa, S. aureus,* and *Candida albicans* (The values of ZOI obtained were 6, 7.2, 9, and 5 mm, respectively) [46]. Sharma et al. synthesized TiO_2 NPs using an algal extract of *Spirulina* for the adsorptive remediation of methyl orange (MO) (anionic) and malachite green (MG) (cationic) dyes. The Langmuir adsorption model yielded q_{max} values of 209.6436 mg/g for MG and 272.4795 mg/g for MO with R^2 values of 0.963 and 0.967, respectively, and the reaction fit better into the pseudo-2nd order model, according to a kinetics isotherm analysis, with R^2 values of 0.99924 and 0.99941 for MO and MG, respectively [47]. Ansari et al. studied the green synthesis of TiO_2 NPs by using *Acorus calamus* leaf extract and reported the 96.59% photocatalytic degradation of Rhodamine B (RhB) dye and also showed excellent antimicrobial activity against stain *S. aureus, B. subtilis* (gram-positive) over *E. coli, P. aeruginosa* (gram-negative) pathogenic bacteria at concentration of TiO_2 10 and 20 µg/mL was 9 ± 0.3, 10 ± 0.2 mm and 6 ± 0.2, 8 ± 0.3 mm in gram-negative and 10 ± 0.3, 12 ± 0.3 mm and 12 ± 0.4, 14 ± 0.5 mm in gram-positive bacteria, respectively [48]. Shimi et al. performed a synthesis of TiO_2 NPs by using mulberry plant leaf extract and confirmed the synthesis of anatase phase TiO_2 of spherical shape with an average crystallite size of 24 nm and band gap of 3.16 eV. Enhanced photocatalytic activity has been demonstrated by the degradation of MB dye (96%, after 120 min of UV light irradiation) followed by pseudo-first-order kinetics with the k value of 0.024 min^{-1} [49] Saka et al. reported the antifungal study of *Caricaceae* (Papaya) shell extracts mediated TiO_2 NPs and demonstrated that semi-spherical and non-spherical mono-clinic TiO_2

NPs were observed, with a crystallite size of 15 nm. The series of experiments verified that the growth of the fungal strains *Fusarium spp.*, *Rosellinia necatrix*, and *Sclerotinia sclerotium* was inhibited by TiO_2 nanoparticles. The decreased dried fungal weights in the test tubes containing TiO_2 nanoparticles indicated a reduction in fungal mycelial growth as compared to the controls [50]. Shimi et al. reported another study in which *Phyllanthus niruri* leaf extract was used to synthesize TiO_2 NPs. Green synthesis of TiO_2 NPs was confirmed through characterizations and they reported the tetragonal structure of TiO_2 NPs with a band gap of 3.16 eV and calculated crystallite size of 23 nm using the Debye Scherrer equation. The TiO_2 NPs photocatalytic activity has been evaluated against MB dye under both visible and ultraviolet light irradiation and found 94.4 and 98.2% degradation of MB dye [51]. Nabi et al. studied the green synthesis of TiO_2 NPs by utilizing *Citrus Limetta* extract as a reducing and capping agent. Various characterizations verified the anatase phase formation of TiO_2 NPs with 80-100 nm particle size, spherical shape, and 3.22 eV band gap energy. Its improved photocatalytic effectiveness is demonstrated by more than 90% RhB dye degradation observed in just 80 min [52]. Achudhan et al. used several plant extracts such as twigs of *Azadirachta indica*, *Ficus benghalensis*, and a bud of *Syzygium aromaticum* for the synthesis of TiO_2 NPs and they applied the synthesized TiO_2 NPs for antibacterial and antibiofilm activities against bacteria (*Streptococcus mutans* and *Citrobacter freundii*) and fungi (*Candida albicans*). Additionally, the larvicidal activity of mosquitoes was assessed against *Aedes aegypti*, a carrier of the Zika virus. Furthermore, methylene blue, an organic dye, and paracetamol, a medicinal medication, were degraded to evaluate the photocatalytic activity of G-TiO_2 NPs. G-TiO_2 NPs showed the maximum ZOI of 16 and 14 mm against *C. freundii* and *S. mutans*, also reduced the thickness of biofilm at 100 μg/mL of G-TiO_2 NPs in both Gram-negative (*C. freundii*) and Gram-positive (*S. mutants*) bacteria (10 μm and 7 μm, respectively). The mortality of *A. aegypti* was 98% at 75 μg/mL of G-TiO_2 NPs. Additionally, the G-TiO_2 NPs demonstrated the degradation of MB dye (70%) and paracetamol (88%) [53]. Kaur et al. reported the green synthesis of TiO_2 NPs by utilizing *Lagenaria siceraria* leaf extract. They confirmed anatase phase formation and average crystallite size of 8.20 nm and particle size of 12 nm have been reported to be well controlled by the green method of TiO_2. Green synthesized TiO_2 NPs removed 98.88% of Reactive green 19 (RG19) dye more than chemically synthesized TiO_2 88.55%, because of its bigger surface area, nearly double the pore diameter, and smaller particle size [54].

In the past few years, several studies reported the synthesis of TiO_2 NPs through various plant extracts and it is seen that plant extracts can improve the photocatalytic and antibacterial activity of TiO_2 NPs.

Table 2. 1 A comprehensive analysis of various plant extracts used for the green synthesis of TiO_2 NPs and applied for textile dye degradation and antibacterial analysis.

S. N.	Plant used	Application	Results	References
1.	*Mangrove* leaves extract	Reactive Red 195 (RR195) dye removal and antibacterial activity	The photodegradation of RR195 obtained 55.45% after 120 min. The ZOI against *S. aureus, E. faecalis,* and *V. damsela* bacteria were found to be 18,19, and 18 mm respectively.	[39]
2.	leaf and stem extracts of *Carissa opaca*	Degradation of methylene blue (MB) and methyl violet (MV) dye, also antibacterial activities	Degradation of MB dye obtained 87.8% and 91.95%, whereas in the case of MV dye, 82.1% and 71.9%. ZOI of 18.3 ± 0.15 mm and 13.3 ± 0.15 mm against *S. aureus* and *K. pneumoniae*, respectively.	[40]
3.	*Solanum Tuberosum* (potato) peel extract	Removal of Bromophenol blue dye	Obtained 98% bromophenol blue dye reduction after 40 min of sunlight exposure.	[41]

4.	*Parkia speciosa* peel extract	Methyl orange (MO) dye removal	P-TiO_2 had enhanced photocatalytic activity with 97.99% removal of MO dye	[42]
5.	*Impatiens rothii Hook. f.* leaf (IL)	Methylene dye removal	maximum photodegradation of dye was 98% at optimum conditions (dose 30 mg/L, pH 10.5, initial concentration 15 ppm for 100 min).	[43]
6.	*Calotropis gigantea* extract	Photocatalytic degradation of MB dye	Obtained 96% degradation of MB dye in 60 min irradiation.	[44]
7.	*Commelina benghanlensis*	Photodegradation of methylene blue dye and antibiotics	65% and 82% degradation of MB dye and pharmaceutical SSX, respectively after 120 min irradiation.	[45]
8.	*Caesalpinia pulcherrima* flower extract, *Nervilia*	MB dye photocatalytic degradation, Antibacterial, and Antifungal activity	MB dye degradation of 86%, 75%, and 56% after 40 min visible light irradiation, respectively with	[46]

	aragoana leaf extract, and *Manihot esculenta* peel extract		values of ZOI obtained 9, 6, 7.2, and 5 mm, against bacteria and fungi.	
9.	Algal extract of *Spirulina*	Adsorptive remediation of methyl orange (MO) and malachite green (MG) dyes.	Langmuir model yielded a maximum adsorption capacity of 209.64 mg/g for MG and 272.47 mg/g for MO and followed 2^{nd} order kinetics.	[47]
10.	*Acorus calamus*	Antimicrobial and photocatalytic activity	Green synthesized TiO_2 NPs enhanced photocatalytic activity is responsible for 96.59% of the degradation of Rh B dye.	[48]
11.	*Mulberry* plant leaves extract	Photocatalytic MB dye degradation and Antibacterial activity	Under UV light, photocatalytic degraded 96% of MB dye in 120 min, followed by pseudo-first-order kinetics with a k value of 0.024 min^{-1}.	[49]
12.	*Caricaceae* (Papaya) shell extracts	Antifungal activity against *Fusarium spp., R. necatrix,* and *S. sclerotium*	The growth of the fungal strains *Fusarium spp., R. necatrix,* and *S. sclerotium* was inhibited by *Caricaceae* shell extracts mediated-TiO_2 NPs.	[50]

13.	*Phyllanthus niruri* leaf extract	Photocatalytic MB dye degradation	Under UV and visible light irradiation for 120 min, 98.2% and 94.4% degradation of MB dye were obtained, respectively.	[51]
14.	*Citrus Limetta* extract	Improved photocatalytic activity against RhB dye	Improved photocatalytic effectiveness is demonstrated by more than 90% RhB dye degradation observed in just 80 min.	[52]
15.	Aqueous twig and bud extracts of *Azadirachta indica twigs, Ficus benghalensis, and Syzygium aromaticum*	Photocatalytic activity Antibacterial, antibiofilm activities, and mosquito larvicidal activity	Photocatalytic activity of G-TiO_2 NPs on paracetamol and MB dye was 88% and 70%. Significantly reduced bacterial, fungal biofilm and revealed the larvicidal activity of mosquitoes against A. aegypti.	[53]
16.	*Lagenaria siceraria* leaf extract	Photocatalytic degradation of Reactive Green 19 (RG19) Dye	Green synthesized TiO_2 NPs removed 98.88% of RG19 dye more than chemically synthesized TiO_2 (88.55%).	[54]

2.1.2 Green synthesized nano-adsorbents used as nano-adsorbents for dye removal and antibacterial analysis.

Adsorption of dyes on the adsorbents has been effectively used to treat wastewater from various industries. Sustainable or green routes were used for the production of adsorbents. In recent years, several plant extracts were used to produce adsorbents and applied for textile dye degradation, and antibacterial analysis is reported in the literature. A summary of the available published articles is given in **Table 2.2**.

In a study, Akhi et al. reported the removal of the MB dye through adsorption by utilizing *Ophiorrhiza mungos* (Om)-mediated Ag NPs as an adsorbent. They demonstrated 88.11% removal of MB dye at the optimum condition (adsorbent dose 600 mg/L, 298 K for 1 h duration) and maximum monolayer adsorption capacity of 80.45 mg/g (Langmuir isotherm model) [55]. Shahbazarab et al. synthesized Nanodiopside ($CaMgSi_2O_6$) by utilizing a silica source from rice husk and investigated its adsorption capacity against Congo red dye, and antibacterial properties. In this study, they demonstrated the adsorption capacity (maximum) of 213.26 mg/g in 64 min contact time at optimum conditions (adsorbent value 0.006, dye concentration 65, and pH 3.7 at 61℃) and ZOI against *B. subtilis* and *E. coli* were obtained 9.8 and 9.2 mm, respectively. The adsorption of CR dye followed the Langmuir single-layer model and pseudo-second-order kinetics [56]. Ghoohestani et al. prepared a magnetic adsorbent by using a *Cordia myxa* leaf for the removal of MB dye. Prepared Fe_3O_4 had 21-32 nm sized spherical particles with 115.07 m^2/g surface area and reported an 88.8% degradation of MB dye at operating condition, dose of adsorbent 0.50 mg/mL, pH of solution 7.5, and contact time 60 min with a maximum adsorption capacity of 17.79 mg/g (Langmuir isotherm) with pseudo-second-order kinetics [57]. Norbert et al. synthesized Cu-doped CeO_2 NPs by utilizing *Murraya Koenigii* leaves extract, and confirmed the formation of Cu-doped CeO_2 NPs with highly porous structures (average particle size 20 nm, 11.21 m^2/g) through several characterizations. Cu 15% doped CeO_2 NPs are the most efficient adsorbents for Congo red, exhibiting an adsorption efficiency of 193 mg/g, and have superior antibacterial activity against the gram-positive bacteria B. *subtilis* and *S. aureus* and gram-negative bacteria *E. coli* and *P. aeruginosa* [58]. Sachin et al. reported the removal of Congo red dye lychee peel extract-mediated ZnO NPs (spherical with size of <10 nm). Observed 98.4% removal of CR dye for 120 min contact time at operating condition of 100 mg dose, pH, and initial concentration of the dye solution was 2 and 50 mg/L, respectively. They also demonstrated 34% inhibition against *B. subtilis*, 52% against *E. coli*, 58% against *P. aeruginosa*, and 32% against *S. aureus* [59]. Parimelazhagan et al. showed the degradation of Coomassie Violet Dye by using the adsorbent zinc hydroxide NPs (CG-Zn $(OH)_2$ and particle size was found to be 78 μm). They synthesized NPs using *Calotropis gigantea* leaf extract and achieved the maximum degradation (90.74%) and equilibrium dye adsorption capacity, q_e (35.12 mg/g), at 150 rpm for 24 h at 299 K and optimum pH, dye concentration, adsorbent dosage of 1.8, 225 mg/L, 5 g/L, respectively [60]. Bui et al. synthesized CuO@C nanocomposite (surface area of 17.33 m^2/g) by using the green reducing and capping agent *Combretum indicum* flower extract. They obtained adsorptive degradation of brilliant blue (BB, 71.39%), methylene blue (MB, 23.67%), Congo red (CR, 84.60%), and malachite green (MG, 83.23%), at optimum conditions. The maximum adsorption capacities were found, BB (22.8 mg/g), MB (23.154 mg/g), CR dye (11.063 mg/g), and MG (46.387 mg/g) by using nonlinear Langmuir isotherm [61]. Vinayagam et al. used leaf extract of copper pod tree to synthesize hydroxyapatite (HAp) nano-adsorbent for the removal of Acid blue 113 (AB113) dye. The optimum dye removal at operating conditions of, a dose of CP-HAp NPs 1 g/L, pH of 8, initial dye concentration 20 ppm, 120 min contact time, and 150 rpm, was obtained to be 92.72%. Adsorption of AB113 followed Freundlich isotherm (R^2 > 0.968) and pseudo-second-order kinetics (R^2 > 0.99) [62]. Rashid et al. prepared nickel oxide nanoparticles (NiO-NP) using olive tree leaves as a reducing agent, and for capping agent Dsorbitol and applied NiO-NPs for adsorption of the anion dye methyl orange (MO) and cation dye methylene blue (MB). Through various characterizations, they confirmed the formation of spherical shape and highly crystalline, and highly agglomerated NPs with a size range of (30 to 65 nm). The maximum removal of MO was 88% in 160 min contact time at optimum conditions, with an adsorbent dosage of 6 g/L, pH of 2, and initial dye concentration of 20 mg/L at 300 rpm agitation speed, while for MB dye was found to be 96% in 100 min contact time at optimum conditions, with an adsorbent dosage of 6 g/L, pH of 10, initial dye concentration of 25 mg/L at 300 rpm agitation speed [63]. Bhavyasree et al. reported the synthesis of novel CuO/C nanocomposite using the aqueous extract of *Ficus religiosa* leaves, and adsorption capacities of nanocomposite for Congo Red (CR), Methylene Blue (MB), and Coomassie Brilliant Blue (CBB) dyes are reported to be 20 mg/g, 7.582 mg/g and 15.23 mg/g respectively. They also demonstrated the CuO/C nanocomposites' antibacterial efficacy against the fungus *C. albicans* and *A. niger,* as well as the bacteria *P. aeruginosa, S. mutans, E. coli, S. aureus,* and *K. pneumonia*, and it was detected to be 29 nm, 11 nm as well as 13 nm, 12 nm, 14 nm, 16 nm, and 12 nm, respectively [64]. Kahsay et al. utilized an aqueous leaf extract of *Becium grandiflorum* for the green synthesis of ZnO NPs (average crystallite size of 20 nm). The Langmuir isotherm most accurately depicts the adsorption behavior with a q_{max} value of 143.6 mg/g and maximum removal of 71.53 % at optimum conditions (initial dye concentration and adsorbent dose were 25 mg/L, and 25 mg, respectively, at 180 min contact time). The minimum ZOI for *S. aureus, E. coli, K. pneumonia, P. aeruginosa,* and *Staphylococcus epidermidis* was 7, 6, 8, 11, and 12 mm, respectively [65]. Saruchi et al. investigated the synthesis of copper oxide by using leaf extract of *Aloe barbadensis* as a green reducing agent. They reported the highest percentage of MB dye removal of 98.89%, achieved in 210 min at 150 rpm shaking and an initial MB dye concentration of 100 mg/L at an alkaline pH. They also reported the antibacterial activity of CuO-A NPs and determined the ZOI for Pseudomonas, Klebsiella, Staphylococcus, and E. coli were, 11 mm, 12 mm, 8 mm, and 9 mm, respectively [66]. Khani et al. synthesized Cu-NPs using fruit extract of *Ziziphus spina-christi (L.)* and used it as a nano-adsorbent to remove crystal violet dye from wastewater and also explored its antibacterial activity against *S. aureus* and *E. coli*. They reported the removal of CV achieved 95.00% at the optimum conditions (adsorbent dose of 80 mg, a pH of 9.0, initial dye concentration of 35 μg/mL) for 7.5 minutes of stirring and maximum values of ZOI against *S. aureus* and *E. coli* were 1.8 ± 0.1 and 1.7 ± 0.2, respectively [67]. Sharma et al. demonstrated the removal of Gentian Violet dye by using the green synthesized silver nano-adsorbents (soil-Ag NPs) mediated from the Neem and Basil leaf extract and reported the 98.1% and 99.4% removal of Gentian Violet dye from respected plants [68].

According to the literature mentioned above, it has been observed that researchers are turning their attention toward the synthesis of nanoparticles by utilizing various plant extracts. It was reported in the literature that the synthesis process used normal operating conditions, natural reducing and capping agents (plant extract), reduced the need for harmful chemicals as reducing agents, and also minimized the production of harmful by-products, making it sustainable and environmentally friendly. Nanoparticles synthesized through plant extracts showed their excellent adsorption property against many textile dyes, and their improved antibacterial activity, which is used to completely remove the dyes or minimize the concentration of dyes also antibacterial activity improves the mineralization of textile effluents. The combination of antimicrobial, antioxidant, and adsorption properties makes these novel green synthesized nanoparticles an excellent candidate for wastewater treatment and biomedical applications. Therefore, the remarkable potential of these nanocomposites can be harnessed across various aspects of human life.

Table 2. 2 A comprehensive analysis of various plant extracts used for the green production of nano-adsorbents and applied for textile dye degradation and antibacterial analysis.

S. N.	Plant extract	Adsorbent	Applications	Results	References
1.	*Ophiorrhiza mungos*	Ag NPs	Methylene blue dye removal	Maximum dye removal was 88.11% in 1 h, and an adsorption capacity of 80.451 mg/g	[55]
2.	Rice husk	Nanodiopside ($CaMgSi_2O_6$)	Investigation of Congo red dye removal and antibacterial properties	The adsorption capacity (maximum) was 213.26 mg/g in 64 min and ZOI against *B. subtilis* (9.8 mm) and *E. coli* (9.2 mm)	[56]
3.	*Cordia myxa* leaf	Magnetic Fe_3O_4	Degradation of methylene blue dye	Maximum removal of dye 88.8% in 1 h and an adsorption capacity was 17.79 mg/g	[57]
4.	*Murraya Koenigii* extract	Cu-doped CeO_2 NPs	Congo red dye degradation, antibacterial activity	98% degradation in 35 min, maximum antibacterial activity against S. aureus strain	[58]

5.	Lychee peel	ZnO NPs	Congo red (CR) dye degradation, Antibacterial analysis	>98% in 2 h, ZnO NPs showed the highest inhibition of 58% against *P. aeruginosa.*	[59]
6.	*Calotropis gigantea* leaf	CG-Zn $(OH)_2$ NPs	Removal of Coomassie violet (CV) dye	90.74% at 150 rpm for 24 h, 299 K	[60]
7.	*Combretum indicum* plant	CuO@C nano-composite	Brilliant blue, Congo red, Malachite green, and Methylene blue degradation	71.39%, 84.60%, 83.23%, and 23.67% in 1.5 h	[61]
8.	Leaf extract of copper pod tree	Hydroxyapatite nano-adsorbent	Acid blue 113 dye	92.72% in 2 h at 150 rpm and room temperature	[62]
9.	Olive tree leaf extract	Nickel oxide NPs (NiO-NP)	Methylene blue and Methylene orange degradation	88% in 160 min for MO and 96% in 100 min for MB	[63]
10.	*Phyllanthus emblica* aqueous fruit extract	Magnesium oxide NPs (MgO NP)	Adsorptive activity against Congo Red (CR), Methylene Blue (MB), and Coomassie	Adsorption capacities for CR, MB, and CBB dyes are 20, 7.58, and 15.23 mg/g, respectively, and the highest antimicrobial	[64]

			Brilliant Blue (CBB) dyes and antimicrobial activity	performance against C. albicans (ZOI of 29 mm).	
11.	*Becium grandiflorum* leaf extract	ZnO NPs	Adsorption of methylene blue and antimicrobial activity	The maximum removal of 71.53% in 3 h with an adsorption capacity of 143.6 mg/g and maximum ZOI of 12 mm against S. epidermidis	[65]
12.	leaf extract of *Aloe barbadensis* miller	Copper oxide-Aloe vera (CuO-A) based NPs	Removal of methylene blue dye and antibacterial properties	MB dye removal of 98.89%, achieved in 3.5 h and maximum ZOI of 12 mm against Klebsiella	[66]
13.	Fruit extract of *Ziziphus spina-christi (L.)*	Cu-NPs	Elimination of crystal violet dye and antibacterial properties	Achieved optimum removal of 95.00% for 7.5 min of stirring and maximum values of ZOI against *S. aureus* and *E. coli* were 1.8 ± 0.1 and 1.7 ± 0.2, respectively	[67]
14.	Neem leaf (*Azadirachta*	soil-Ag NPs	Removal of Gentian Violet dye	Basil leaf (O. sanctum) provided 99.4% removal of Gentian Violet dye, 98.1% for	[68]

	indica) and Basil leaf (*Ocimum sanctum*)			silver nanocomposite made of Neem leaf (A. indica)	

2.1.3 Sustainable conversion of biomass into adsorbents for dye removal from wastewater

Conversion of biomass into value-added products is advantageous for the environment because waste biomass is abundantly available in the environment. There are some studies in which, Researchers converted waste biomass into biochar and hydrochar through several processes and used them as adsorbents for dye removal. **Table 2.3** shows the summary of some research work on the conversion of waste biomass into adsorbents.

Sewu et al. converted wood chips (WC), rice straws (RS), and Korean cabbage (KC) into biochar and used them as alternative adsorbents to activated carbon (AC) to remove CV and CR dye from wastewater. Pyrolysis of biomasses was done under operating conditions of nitrogen gas (N_2) flow rate at 200 mL/min, heater temperature was increased steadily for 50 min at a rate of 10°C/min, and held at 500°C for 60 min. For CR dye, the adsorption capacity of all biochars was lower than for AC. For CV dye, KC had a greater Langmuir maximum adsorption capacity (1304 mg/g) in comparison to RS (620.3 mg/g), AC (271.0 mg/g), and WC (195.6 mg/g) [69]. Rawat et al. used waste of the mentha plant to produce biochar by slow pyrolysis to remove MB (catatonic) dye from an aqueous solution. Slow pyrolysis of mentha stem powder (20-30 mm) was done at 450°C and 700°C for 2 h with an increment rate of 5°C/min. Adsorption of MB dye on BC450 and BC700 followed Pseudo-second-order were found to have maximum adsorption capacity (Langmuir isotherm) values of 86.96 and 588.24 mg/g, respectively, at ambient temperature [70]. Guo et al. utilized Oven-dried *Magnolia grandiflora* (MGL), *Magnolia denudates* (MDL), and *Michelia figo* (MFL) fallen leaves at 343K for 24 h, sieved into 0.15 mm size and used as adsorbents for the removal of MB dye from water. Fallen leaves spontaneously and endothermically adsorbed MB., fitting well with the Langmuir isotherm ($R^2 > 0.995$) and following pseudo-second-order kinetics ($R^2 > 0.992$) with the maximum adsorption capacities of 185.19 mg/g, 149.25 mg/g, and 238.10 mg/g, respectively [71]. Saniya et al. performed experiments on the carbonization and activation of *Murraya koenigii* (Curry tree) plant bark and used that activated curry tree carbon to adsorb CV dye from wastewater. The dried pieces of curry tree were treated with concentrated sulphuric acid (1:1 w/v) then dried and further heated at 170°C for 90 min in a muffle furnace. The optimum adsorption of CV dye was achieved at the adsorbent dosage (100 mg/L), Time (60 min), temperature (35°C), and dye concentration (10 ppm) and reported more than 70% removal efficiency with 35.71 mg/g maximum adsorption capacity [72]. Suwunwong et al. converted *Zea mays L.* (corncob) into biochar using pyrolysis at operating conditions of 500°C temperature with approximately 10°C/min heating rate for 2 h, and after this biochar was finally crushed and sieved (< 0.5 mm). Adsorption of MB dye on biochar (corncob) demonstrated an adsorption capacity of 16.69 mg/g. The Langmuir model adequately explained the adsorption equilibrium isotherm (monolayer sorption), and the pseudo-second-order kinetic model nearly matched the adsorption rates [73]. Saleh et al. produced hydrochar from *Quercus coccifera* acorns and then used it to remove Basic Red 18 (BR18) dye. Pure water and dried *Q. coccifera* acorns were added to the reactor. The reactor was closed and the internal pressure was increased to 100 bar. The reactor temperature was raised to 513 K and maintained for 3 h. A 72.8% hydrochar yield was obtained from the biomass. The maximum removal of BR18 dye was reported to be 88.7% through adsorption at pH 10, 45 μm particle size, 1.5 g/L of particles, 455 mg/L of dye, and 60 min followed pseudo-second-order kinetics [74]. Cuong Nguyen et al. reported the slow pyrolysis of agro-waste Wattle bark (BA), Mimosa (BM), and Coffee husk (BC) to produce biochar for the adsorption of methyl orange (MO) dye from wastewater. Chopped and oven-dried biomasses were placed in the furnace designed to heat up to 500°C and maintained for 2 h with a heating rate of 10°C/min. Biochars' maximum adsorption capacity values against MO dye derived from the Langmuir model were 12.26, 12.33, and 12.34 mg/g [75].

Wenwen Tu et al. applied a two-stage process of hydrothermal carbonization and chemical activation technology to prepare an activated hydrochar with a rich-pore structure and large surface area from sludge sewage and coconut shell and used to decolorize CR and MB dye. In this study, raw materials of sewage sludge and coconut shell were contacted as the mass ratio was 1:1 when carbonization temperature and time were at 180°C and 4 h, respectively to produce hydrochar, then produced hydrochar was impregnated with 2.5 mol/L KOH solutions and heated up to 700°C for 50 min to activate the hydrochar. The adsorption potential of activated hydrochar on CR and MB dye was demonstrated, and the maximum adsorption capacities obtained were 228.25 mg/g and 623.37 mg/g, respectively, and followed the pseudo-second-order kinetics and Langmuir model [76]. Hammud et al. produced biochar through the hydrothermal carbonization (HTC) of palm leaves and activated biochar (AHTC) with H_2O_2 oxidation of HTC biochar at 208°C. Gaseous nitrogen was used to flush the autoclave and Citric acid catalyst pellets and chopped palm leaf pieces were mixed with deionized water in the autoclave. After that, the mixture was heated for 435 min to 186-225°C. The adsorption of Malachite Green dye (MG) on HTC biochar and AHTC biochar was calculated at 25°C, activated biochar AHTC achieved an adsorption capacity of 62.80 mg/g, which was much higher than that of HTC biochar (45.59 mg/g) and followed pseudo-second-order kinetics and Langmuir model [77]. Goyi et al. used potato peel to produce hydrochar (PPH) by using the HTC process and compared the adsorption activity of hydrochar (PPH) and potato peel powder biomass (PPWP) against Congo red dye. Potato peels were dried for 48 h at 50°C in an oven, then crushed and sieved to obtain PPWP, then PPWP with deionized water was transferred into the autoclave heated at 200°C for 25 h then dried and ground to obtain PPH. The adsorption capacity of PPH (147.00 mg/g, 90 min) was reported more than PPWP (67.05 mg/g, 70 min), followed by the Freundlich model and pseudo-second-order kinetics [78].

Table 2. 3 A comparative study of dye removal from wastewater through adsorption using biomass, biochar, and hydrochar as adsorbent.

S. N.	Biomass	Dye	Process parameters	Results	References
1.	Wood chip (WC), Rice straw (RS), and Korean cabbage (KC)	Congo red (CR) and Crystal violet (CV) dye	Nitrogen gas (N_2) at 200 mL/min, temperature at 500°C at a rate of 10°C/min for 60 min	110 and 195.6 mg/g, 190.8 and 620.3 mg/g, 95.81 and 1304 mg/g, and followed Pseudo-second-order with Langmuir isotherm	[69]
2.	Mentha plant waste: BC450 and BC700	Methylene blue	Heated at 450°C and 700°C for 2 h with a rate of 5°C/min.	Adsorption capacity of 86.96 and 588.24 mg/g, and followed Langmuir isotherm with Pseudo-second-order	[70]
3.	*Magnolia denudates* (MDL), *Magnolia grandiflora* (MGL) and *Michelia figo* (MFL)	Methylene blue	Oven-dried at 343K for 24 h, sieved into 0.15 mm size	The adsorption capacity of 185.19, 149.25, and 238.10 mg/g followed Pseudo-second-order with Langmuir isotherm	[71]

4.	*Murraya koenigii* (Curry tree carbon, CTC)	Crystal violet (CV) dye	Heated at 170°C for 90 min in a furnace to complete carbonization and activation	Adsorption followed Langmuir isotherm with Pseudo-second-order and obtained 35.71 mg/g capacity	[72]
5.	corncob *Zea mays L.*	Methylene blue	pyrolysis for 2 h at ~500°C, ~10°C/min heating rate	the maximum removal efficiency was 16.69 mg/g, Langmuir isotherm, pseudo-second-order	[73]
6.	*Quercus coccifera*	Basic Red 18 (BR18) dye	Internal pressure 100 bar, reactor temperature was raised to 513 K and for 3 h	Maximum removal of BR18 dye 88.7%	[74]
7.	Wattle bark (BA), Mimosa (BM), and Coffee husk (BC)	Methyl orange (MO) dye	The furnace heated up to 500°C and maintained for 2 h with a heating rate of 10°C/min	Maximum adsorption capacity values obtained from the Langmuir model were 12.26, 12.33, and 12.34 mg/g	[75]

8.	Coconut shell and sewage sludge	Congo red and methylene blue dye	Carbonization at 180°C for 4 h and activated with 2.5 mol/L KOH solutions heated up to 700°C for 50 min	The adsorption capacities obtained were 228.25 mg/g and 623.37 mg/g, followed by the Langmuir and pseudo-second-order kinetics model	[76]
9.	Palm leaves	Malachite Green dye (MG)	HTC at 186-225°C for 435 min and activation of biochar (AHTC) with H_2O_2 oxidation at 208°C	The adsorption capacity of AHTC and HTC biochar was 62.80 mg/g and 45.59 mg/g, followed by pseudo-second-order kinetics and the Langmuir model	[77]
10.	Potato peel (biomass, PPWP) and hydrochar (PPH)	Congo red (CR) dye	HTC in autoclave heated at 200°C for 25 h	The adsorption capacity of PPH and PPWP was 147.00 (90 min) and 67.05 (70 min) mg/g, followed by pseudo-second-order kinetics and the Freundlich model	[78]

11.	Bamboo sawdust	Congo red (CR) dye	Hydrothermal reaction temperatures from 160 °C to 280 °C, reaction time 0.5 h to 6 h.	The largest adsorption capacity for Congo red is 33.7 mg/g at the equilibrium concentration of 0.1 mg/mL at 25 °C	[79]
12.	Orange peel	Cationic MB (methylene blue) and anionic MO (methyl orange) dyes	HTC in autoclave maintained at 185 °C for 18 h.	The highest biosorption capacities are 203.4 mg/g for MB and 113.3 mg/g for MO and follow Langmuir isotherm and PSO kinetic models, indicating monolayer chemisorption on a homogeneous surface.	[80]

2.2 Literature Summary and Research Gap

The textile sector is known to produce a significant amount of synthetic waste worldwide. Wastewater that has dye in it is xenobiotic, mutagenic, carcinogenic, and recalcitrant. The efficient treatment of textile effluent and the consumption of freshwater must be balanced ecologically. The goal of textile wastewater treatment methods is to remove and break down the contaminants that the textile industries release into the wastewater. These techniques utilized some hazardous chemical compounds to produce adsorbents, photocatalysts, etc, and sometimes direct use of chemicals in chemical methods of dye removal. The sustainable and ecologically friendly removal of dyes has drawn the attention of researchers in recent years. The literature review above demonstrates the sustainable and environmentally friendly manufacturing of adsorbents and nanoparticles that reduce the amount of dye in textile effluents.

A thorough assessment of the literature revealed that some aspects have not been addressed for the environmentally friendly removal of dyes from textile effluents. According to the literature, the following are the key research gaps:

- Limited studies available on the sustainable or green synthesis of nano-photocatalyst and nano-adsorbent.
- Limited studies are available on the enhancement of the antibacterial activity of green synthesized (Plant extracts) nanoparticles.
- *Tinospora cordifolia* (Giloy) plant extract reducing and capping abilities are not yet reported.
- No literature has been reported on the utilization of the *Tinospora cordifolia* (Giloy) plant for the green synthesis of TiO_2 NPs.
- No literature is reported on the green reduction of Graphene Oxide using the *Tinospora cordifolia* (Giloy) plant.

- No literature is reported on the production of hydrochar from hydrothermal carbonization of sunflower stalks.

2.3 Objectives and Aims of Research

The following objectives of the study are determined by the research gaps:

- Green synthesis of TiO_2 nanoparticles using *Tinospora cordifolia* plant extract and characterization of G-TiO_2 to confirm synthesis.

- Potential application of G-TiO_2 for photocatalysis of Acid blue 113 (AB113) dye and antibacterial activity against *Escherichia coli*.

- Green reduction of graphene oxide using *Tinospora cordifolia* plant extract and characterization to confirm reduction.

- Optimal degradation of methylene blue (MB) dye through G-rGO nano-adsorbent using response surface methodology (RSM).

- To study the antibacterial activity of G-rGO against *Staphylococcus aureus* and *Escherichia coli*.

- Sustainable production of hydrochar through hydrothermal carbonization of sunflower stalks and characterization of hydrochar.

- Potential application of sunflower stalks-mediated hydrochar as an adsorbent against methylene blue dye.