

## Review Article

# Recent Review of Titania-Clay-Based Composites Emerging as Advanced Adsorbents and Photocatalysts for Degradation of Dyes over the Last Decade

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Textile industry being one of the most flourishing industries keeps growing and developing every year, and the consequences are not very pleasant. Even though its contribution towards economy of a country is indisputable, there are many pros and cons associated with it that should not be brushed aside, one of them being textile dye waste which is also growing at alarming rate. Many techniques have been designed to deal with this environmental crisis including adsorption and photodegradation of dye waste by various substances, both natural and synthetic. TiO<sub>2</sub> and clay both have gained immense popularity in this area. Over the last decade, many successful attempts have been made to design TiO<sub>2</sub>-clay-based composites to combine and make the most of their individual capabilities to degrade textile dye waste. While clay is an effective adsorbent, inexpensive, innocuous, and a great ion exchanger, TiO<sub>2</sub> provides supplementary active sites and free radicals and speeds up the degradation rate of dyes. This review summarizes various features of TiO<sub>2</sub>-clay-based composites including their surface characteristics, their role as dye adsorbents and photocatalysts, challenges in their implementation, and modifications to overcome these challenges made over the last decade.

## 1. Introduction

Color is defined as optical interpretation originating from the brain when visible light stimulates the human eye [1]. The discovery of earliest dye (aniline purple) dates back to the 1860s by W.H. Perkin who laid the foundation for worldwide production of dyes for commercial purposes [2]. Initially, the world relied on Europe for manufacture and supply of dyes, but currently, South Asia has overtaken it [3]. Gross production of dyes is expected to be 1,000,000 tons per year [4]. These dyes are used in the fabrics, processing of leather, publication, lithography, medicinal, and beauty sectors. Some of them are also used as coloring agents for food items [5]. This universal reliance of industrial sectors on dyes means that a bulk amount of dye effluents are being produced and dumped over by every industry all over the world and most of it is discarded into water bodies. It has been reported that 200 BL dye effluents are being discharged

in water per year [6, 7]. Some examples of commonly used dyes have been listed in Table 1. Most of them are used extensively in textile and chemical industries, like brilliant green, Congo red, methylene blue, and indigo carmine. Many dyes are stable towards degradation and it is hard to decompose them, resulting effluents using ordinary methods of wastewater treatment [8]. These dye effluents have been reported to cause cancer, allergies, and skin diseases; therefore, their proper treatment is inevitable [9]. Figure 1 gives a brief description of procedures involved in textile waste water treatment.

It involves various physical and chemical treatment methodologies, like coagulation, ozonation, bioremediation, filtration, photochemical degradation, and electrolysis, either individually or in combination to produce clean water. That water in turn is used for secondary purposes, like watering plants, washing, steam generators, and leaching. Some types of water treatments even produce pure water that can be

TABLE 1: List of some commonly used dyes and their abbreviations.

AAT	o-Aminoazotoluene	CR	Congo red	PPD	Paraphenylene diamine
AB	Azure B	CV	Crystal violet	PR	Procion red
AC1	Alizarin complex one	DB 291	Disperse blue 291	RB 19	Reactive blue 19
AOP	Advance oxidation process	DR 1	Dispersive red 1	RBR	Reactive brilliant red
AO7	Acid orange 7	Es	Eosin	RhB	Rhodamine B
AR 3R	Acid red 3R	GV	Gentian violet	Rh 6G	Rhodamine 6G
ARB	Acid red B	MB	Methyl blue	S I	Sudan I
ARG	Acid red G	MO	Methyl orange	SBE	Sumifix blue Exf
AV 90	Acid violet 90	MV	Methyl violet	SRhB	Sulforhodamine B
BB 41	Basic blue-41	MY	Methyl yellow	SY	Sunset yellow
Bzd	Benzidine	NBB	Naphthol blue black	Ttz	Tartrazine
CB	Conduction band	NR	Neutral red	TY	Titan yellow
Ch	Chrysoidine	OG	Orange G	TyB	Trypan blue
CN	Cyanide	OII	Orange II	VB	Valence band

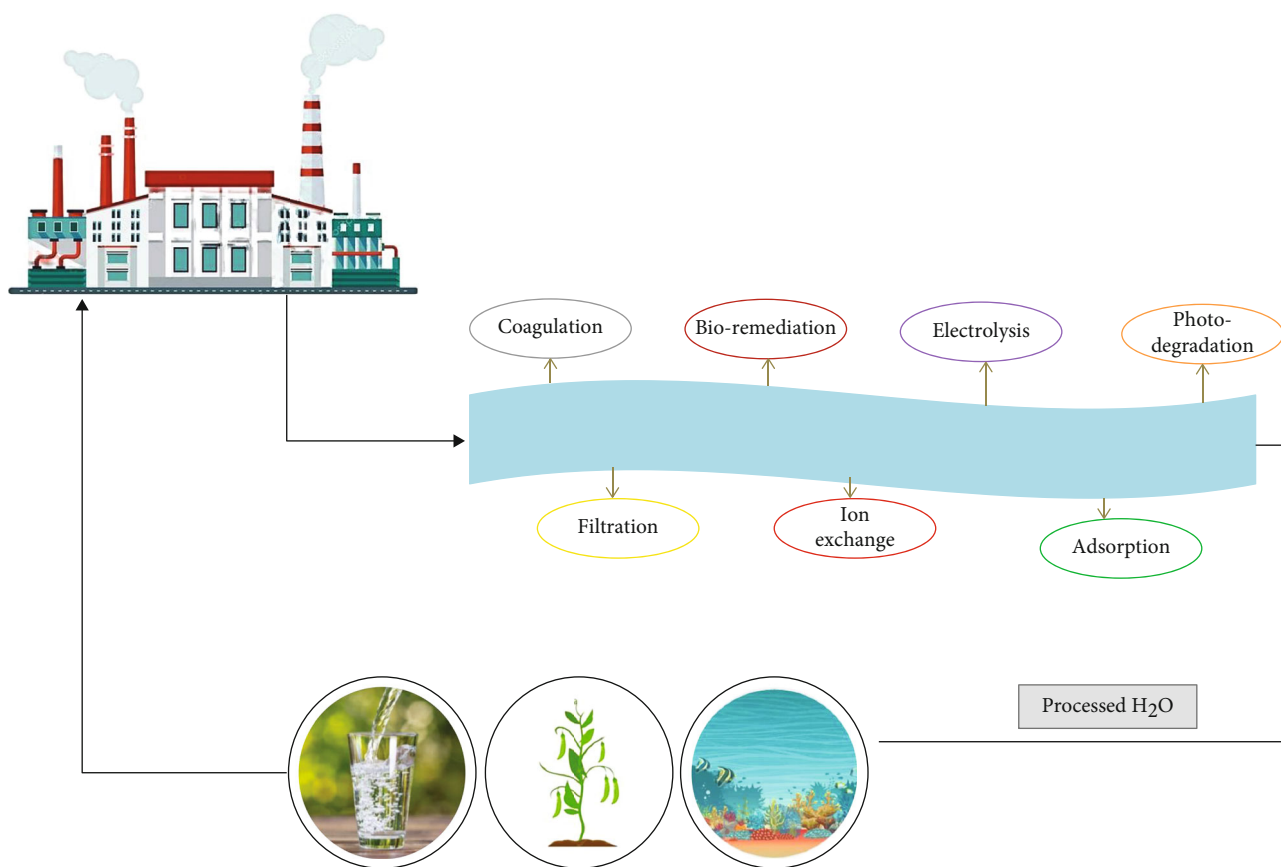


FIGURE 1: Schematic representation of textile waste water treatment plants.

used for drinking, like in Sri Lanka and Malaysia, and desalination and ion exchange processes are used to convert sewage and sea water into drinkable one.

*1.1. Toxicological Profile of Dyes.* Dye effluents mainly pollute environment in the form of water pollutants which are released into water system without treatment. It causes a significant drop in oxygen concentration of water as sulfur

hydrides screen the light from entering the aqueous streams which leads to a deleterious effects on aquatic environment. Half of these dye effluents may have chlorine in their composition which is a mutagen and cancerous in nature. Some dyes may also consist of metal ions, like Hg, Cd, As, Cr, and Pb which cannot be decomposed biologically, so they have the tendency to accumulate in our immune system, causing deterioration and inducing different maladies. Unprocessed

TABLE 2: Toxic effects of some synthetic colorants on human health.

Dyes	Toxicity	Source
DR 1	Chromosomal mutation	[11]
CV	Chronic kidney disease	[12]
DB 291	Necroptosis	[13]
AC 1	Disturbance in blood plasma proteins	[14]
CR	Skin irritant	[15]
PPD	Loss of vision	[16]
PPD	Coryza	[17]
RhB	Skin cancer	[18]
MY	Neural degeneration	[19]
S I	Imbalanced digestive system	[20]
Bzd	Urothelial carcinoma	[21]
SY	White blood cell damage	[22]
Ttz	Anxiety	[23]
AAT	Atopic dermatitis	[24]
MY	Hepatocellular carcinoma	[25]
TyB	Abnormal development	[26]
Ch	Toxicity in blood plasma	[27]
TY	Skin irritant	[28]

or partly decomposed dye pollutants are destructive for both aquatic and human life [10]. Table 2 enlists chief human maladies caused by dye pollutants.

*1.2. Degradation Methods of Dye Effluents.* Since the time, the pathological effects of dye effluents have been analyzed, and researchers have been working on various effective techniques for their decomposition and removal from wastewater. Some of these techniques have been showcased in Figure 2. They are widely explored all over the world by different researchers. Most of them were employed on industrial level for wastewater treatment or for converting sea water into pure water.

*1.2.1. Adsorption.* Amongst all these methods, adsorption has emerged as an exceptionally effective and facile method for the removal of dye effluents (Table 3) [29]. Adsorption is a physical phenomenon of separation of any element between two surfaces, e.g., liquid/solid. It can be carried out by physical or chemical means. One of its main features is regeneration of adsorbent. The adsorption potential of a substance depends on its surface area, resistance to abrasion, pore diameter and structure, etc. [30]. It is quite simplistic and economically favorable and involves swift recollection and reusability of adsorbent without needing to deal with sludge or unsafe side products. However, the success of adsorption procedure depends on performance of adsorbents which should be comprehensive in its actions. Sometimes an adsorbent may observe a very high adsorption potential but lack other important features. For instance, activated carbon is a commonly used adsorbent having a high SSA (specific surface area), void fraction, and adsorption efficiency, but its heavy price and complexed isolation

post sorption has limited its usage. Therefore, scientists have been engrossed in designing such adsorbents which are not only effective in action but also strong, durable, renewable, cost-efficient, and eco-friendly [31].

*1.2.2. Adsorption Kinetics.* The adsorption potential of an adsorbent is represented graphically using different models such as Freundlich and Langmuir [32]. These graphs are based on concentration of adsorbate adsorbed by adsorbent at constant parameters (temperature and pressure) [33].

The Langmuir model (Equation (1)) perfectly represents a single-layer adsorption unit. It is based on the assumption that dye particles when adsorbed on adsorbent arrange themselves in a single layer, all the adsorbed particles having equal amount of  $E_a$  [34]. It also suggests that single-dye particle binds per active site. Moreover, this theory overlooks the interactivity between individual dye particles [35].

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e}, \quad (1)$$

where  $Q_e$ : Adsorption potential at equilibrium ( $\text{mgg}^{-1}$ ),  $Q_m$ : Max adsorption potential ( $\text{mgg}^{-1}$ ),  $C_e$ : Conc. of adsorbed dyes at equilibrium ( $\text{mgL}^{-1}$ ),  $K_L$ : Equilibrium constant of adsorption ( $\text{Lmg}^{-1}$ ).

Contrary to the Langmuir model, the Freundlich model (Equation (2)) represents an adsorption theory where dye particles are adsorbed and arrange in more than one layer and this arrangement is nonlinear [36]. Mostly, the Freundlich model is used where more refined adsorbents with enlarged surfaces and better pore morphology are being studied for adsorption or to describe the adsorption of extremely reactive organic dyes [37]. Although these equations are perfectly applicable at low pressure, the values become more uncertain at high pressure [38].

$$Q_e = K_F (C_e)_n^1, \quad (2)$$

where  $Q_e$ : Adsorption potential at equilibrium ( $\text{mgg}^{-1}$ ),  $K_F$ : Adsorption potential ( $\text{mmolg}^{-1}$ ),  $C_e$ : Conc. of adsorbed dyes at equilibrium ( $\text{mgL}^{-1}$ ),  $n$ : Constant of adsorption strength.

Both these models have been used to study kinetics of adsorption for various adsorbents [39–41]. Some other models that have also been proved quite successful are Temkin [42] and Henry's [43]. Koyuncu and Okur used all these four models to study adsorption potential of C2M1 for AV 90 dye where the Freundlich model proved to be superior than others having highest correlation factor ( $R_2 > 0.94$ ) [44], while Kulasooriya et al. investigated adsorption potential of brick clays for SBE dye where the Langmuir model showed better results, max adsorption potential being  $1667 \text{ mg kg}^{-1}$  [45].

*1.2.3. Parameters for Effective Adsorption of Dyes.* The process of adsorption is dependent on parameters like pH, heat, and quantity of adsorbent. Different parameters have different impact on different adsorbents. Some conditions could be more ideal for one adsorbent but not for others.

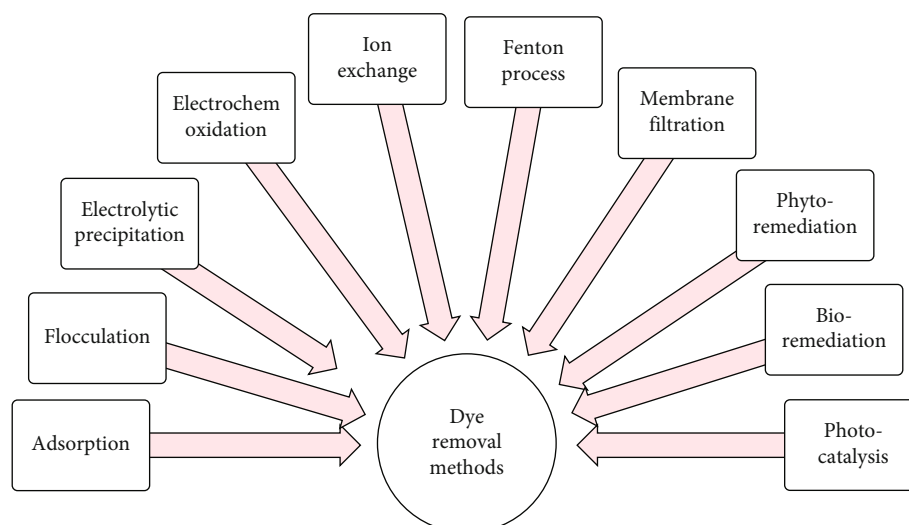


FIGURE 2: Degradation methods of dye effluents.

TABLE 3: Shortcomings of dye removal techniques.

Sr. no.	Method	Shortcomings
1	Flocculation	Sludge formation
2	Electrolytic precipitation	Time consuming
3	Electrochemical oxidation	Expensive due to electricity usage
4	Ion exchange	Only effective for selective dyes
5	Fenton process	Excessive formation of anions
6	Membrane filtration	Unstable and expensive
7	Phytoremediation	Not permanent treatment
8	Bioremediation	Impedes microbial development
9	Photocatalytic degradation	Source of light required which is expensive

Therefore, optimum parameters are decided for every adsorbent on hit and trial basis.

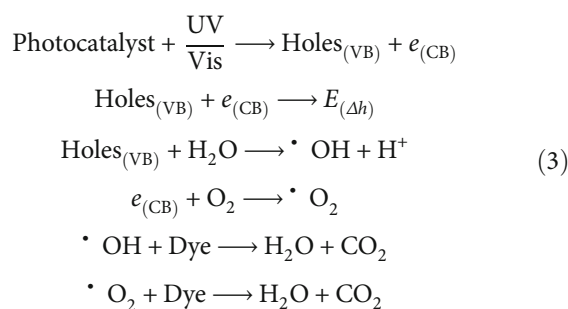
(1) *Temperature.* Adsorption is either exothermic or endothermic so temperature is a major parameter here. In an endothermic procedure, the value of  $Q_{\max}$  rises at higher temperature due to enhanced motion of the dye particles and increased active sites of adsorbents [46]. However in some cases, value of  $Q_{\max}$  falls at higher temperature as motion of dye particles slows down and adsorption is exothermic [47].

(2) *Quantity of Adsorbent.* Usually, the greater the quantity of adsorbents, the greater the number of active sites available and hence the higher is adsorption potential [48]. However, financially feasible adsorbents are those that show higher potential with minimum quantity [49].

(3) *pH.* pH is another major parameter that impacts adsorption procedure determined by pzc (point of zero charge). pH can control rate of ionization of the adsorbents. Cationic dyes show lower adsorptions at lower pH and higher adsorp-

tion at higher pH, while it is opposite for anionic dyes [50]. Cationic dyes show greater adsorptions if pH of solution is higher than  $pH_{pzc}$ , while it is opposite for anionic dyes [51].

1.2.4. *Photocatalysis.* Unlike adsorption, photocatalysis is an advanced technique which has been proved as an effective remediation for waste water treatment. This procedure does not require the usage of any strong chemical specie, so the chances of production of hazardous side products are very little. Photocatalysis is powerful enough to decompose otherwise highly stable dyes into harmless products [52]. The fundamental principle of photocatalysis involves the contact between dye pollutants and their loading onto the photocatalyst. The dye pollutants get adsorbed on its exterior where redox reactions transpire as a result of generation of electrons from conduction band (CB) and holes from valence band (VB). The resultant products finally detach from the photocatalyst and are discarded into the aqueous media [53]. The reaction mechanism can be simplified as follows:



Various studies have proved that photocatalysis is a highly efficient and result-oriented technique for degradation of dyes.

Photocatalysis can be carried out via batch as well as continuous process as shown in Figure 3.

This review mainly focuses on progress made on clay-based  $\text{TiO}_2$  composites over the period of past decade. It summarizes the data on the synthesis and implementation

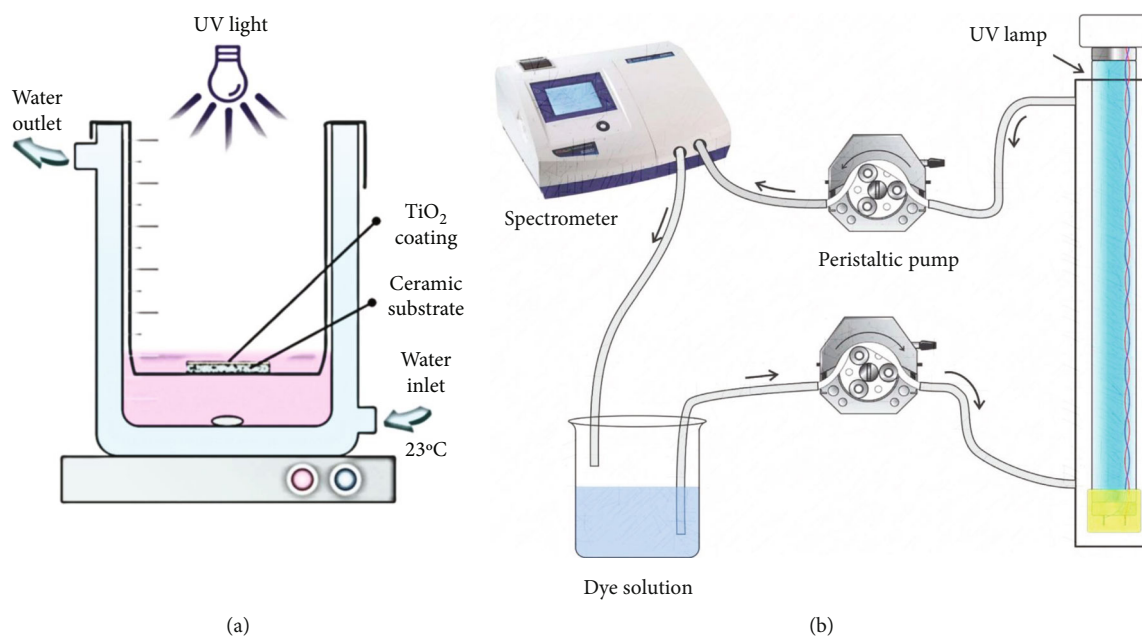


FIGURE 3: (a) Batch process setup vs. (b) continuous process setup for photocatalytic degradation of dye.

of clay-TiO<sub>2</sub> composites for treatment of industrial waste water, both as adsorbent or as a photocatalyst. A literature review based on selective experimental approaches was made which highlights the advantage of degradation of dyes by clay-based TiO<sub>2</sub> composites.

## 2. TiO<sub>2</sub> as Adsorbent and Photocatalyst and Its Limitations

TiO<sub>2</sub> is an excellent adsorbent based on its abundance, ease of excitability, modifiable physical properties, and a very fitting PCZ of 6–6.8, which enables it to adsorb dye particles [54]. TiO<sub>2</sub> is also a widely used photocatalyst owing to its degradation potential [55]. Photocatalysis obviously cannot be carried out without adsorption of dyes onto TiO<sub>2</sub>. This adsorption brings out the interaction between the dye particles and photogenerated species, which kick starts photocatalysis [56]. Thus, the photocatalytic activity of TiO<sub>2</sub> is also determined by its adsorption potential. Adsorption is a surface phenomenon which is dependent on form, area, and structural regularity of TiO<sub>2</sub> crystals [57].

TiO<sub>2</sub> is highly stable both chemically and physically and mild and inexpensive which make it a perfect photocatalyst [58]. TiO<sub>2</sub> exhibits polymorphism and its 3 mineral forms are anatase, brookite, and rutile [59, 60]. Anatase and rutile are reported to have greater photocatalytic activity. Anatase is a better photocatalyst owing to its indirect band gap that gives a greater life span to electron-hole pair, while rutile produces electron-hole pair of a shorter life span based on its direct band gap [61]. CB and VB of TiO<sub>2</sub> have a gap of 3.2 eV (anatase) and 3.0 eV (rutile) [62]. Thus, anatase has a  $\lambda_{\max}$  of 387.5 and rutile has 400 nm in UV region [63]. TiO<sub>2</sub> on photoexcitation produces a number of electrons and holes in CB and VB simultaneously. These charged species further create bunch of free radicals which forms the

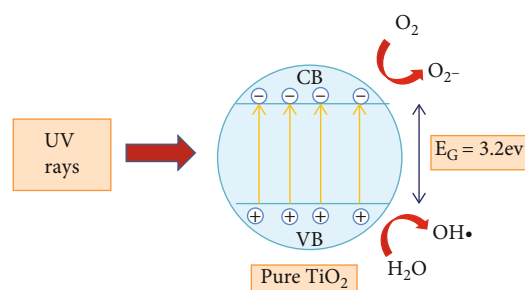


FIGURE 4: Mechanism of Photocatalytic degradation by TiO<sub>2</sub>.

core of photodegradation mechanism [64]. The mechanism is briefly explained through Figure 4 graphically.

*2.1. Drawbacks and Challenges.* However, TiO<sub>2</sub> has few drawbacks [65] that can make it less effective and various methods have been adopted to overcome them.

- (1) A very large band gap of anatase limits its ability to adsorb light in UV region only, so it cannot make proper use of spectrum. To overcome this problem, TiO<sub>2</sub> has been modified by induction of metallic [66, 67] and certain nonmetallic [68, 69] compounds which shrink the band gap as shown in Figure 5
- (2) Lesser attraction for organic dyes and lesser volume of pores per surface area reduce its adsorption potential. So adsorption capacity of organic dyes is improved by layering its surface with carbon-based organic compounds [70, 71]
- (3) Irregular distribution of TiO<sub>2</sub> particles and agglomeration of its NPs can block the active sites and hinder the interaction with incoming light. To avoid

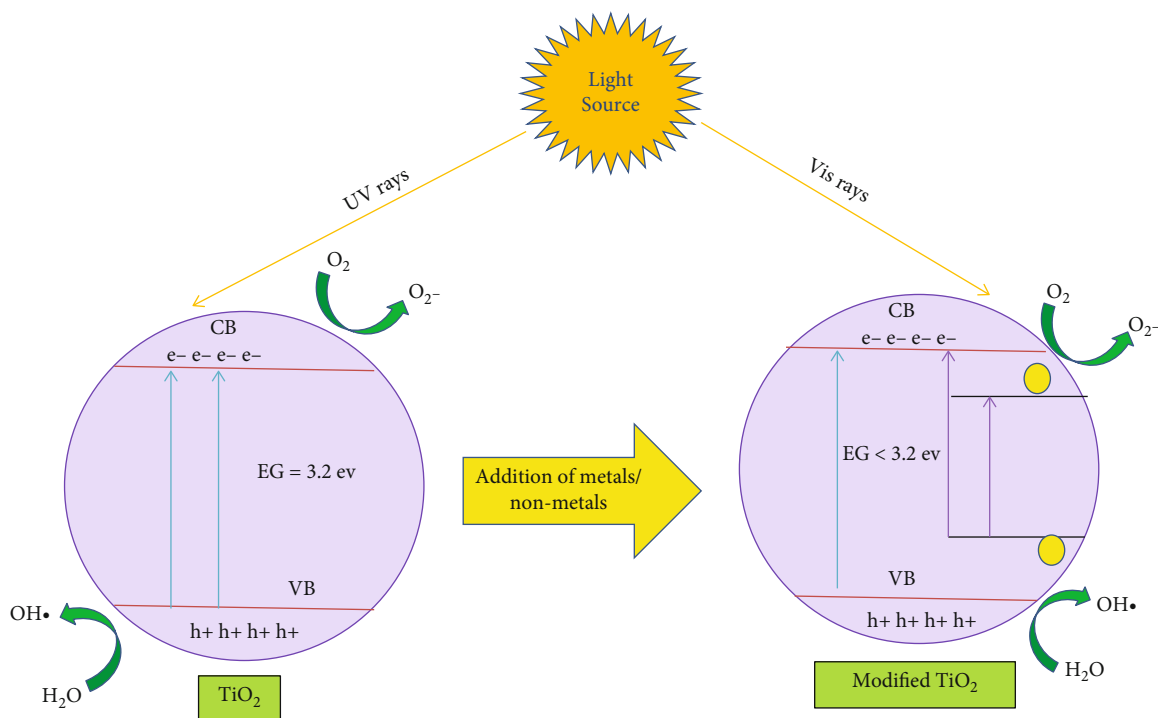


FIGURE 5: Photocatalytic activity of  $\text{TiO}_2$  vs. modified  $\text{TiO}_2$ .

this,  $\text{TiO}_2$  is immobilized with different supports which break off clustering of its particles and blockage of light [72, 73]

- (4) It often ends up making a slurry in liquid media and its regeneration gets difficult which makes its use less cost-effective. Functionalization by magnetization of  $\text{TiO}_2$  can make its recovery easier [74, 75]

**2.1.1. Clay as an Adsorbent and an Effective Support for Titania.** Clay is a mineral naturally found on earth crust. Its chief composition is finely grounded substances (mostly sheet silicates) that impart a unique plasticity in aqueous media, while it hardens up in dry conditions [76]. Clay composition involves uniformly grounded hydrated aluminosilicates. The structure of these aluminosilicates contains tetrahedral sheets of Si-O and octahedral sheets of Al. Clay has the potential to clean wastewater system up to 70% by adsorbing impurities [77]. The extent to which these impurities are adsorbed onto clay depends on how strongly they interact with natural clay and mineral oxides on its surface [78–82]. The adsorption procedure is regulated by a few factors such as nature of ions (cationic or anionic), number of ions, pH, temperature, and nature of dye being treated [83, 84].

Clays have emerged as popular supports for  $\text{TiO}_2$  for dye degradation.

- (1) Pure  $\text{TiO}_2$  has lower photocatalytic potential than clay-based  $\text{TiO}_2$  composite. Clay imparts  $\text{TiO}_2$  a larger surface area, increases the number of active sites, and hence improves its adsorption potential [85]

- (2) Cations are present in between the layers of clay structure which captures the electrons. Thus, the holes in VB of  $\text{TiO}_2$  are free and available for oxidation. This reduces the overall rate of charge recombination in  $\text{TiO}_2$ -clay composites and increases its photocatalytic potential [86]
- (3) Regeneration and recovery of  $\text{TiO}_2$ -clay composites are easier due to the presence of charged species on clay which make the composite separable from aqueous media and the reaction becomes more feasible economically

**2.2. Preparation of  $\text{TiO}_2$ -Clay Composites.**  $\text{TiO}_2$ -clay-based composites can be synthesized using various techniques as shown in Figure 6. They are reported by various researchers from all over the world with good yields and various applications.

**2.2.1. Adsorption of Dyes via  $\text{TiO}_2$ -Clay Composites.**  $\text{TiO}_2$ /stishovite clay composite was simply prepared by mixing stishovite and  $\text{TiO}_2$  and stirring with alcohol for 5–6 hours, precipitating overnight, and vacuum drying. The resultant composite was used for adsorption of MV dye. 88% of dye was adsorbed. The adsorption data shows that adsorbent's surface was covered by a single layer. Adsorption process was endothermic and it observed pseudo 2<sup>nd</sup> order. However, the recovery rate of adsorbent was not up to the mark [92].

Likewise, a  $\text{TiO}_2$ -bentonite composite was prepared by mixing  $\text{TiO}_2$  with clay and double distilled  $\text{H}_2\text{O}$  followed by stirring and drying, and the resulting composite was used for degradation of RhB via batch process and results were

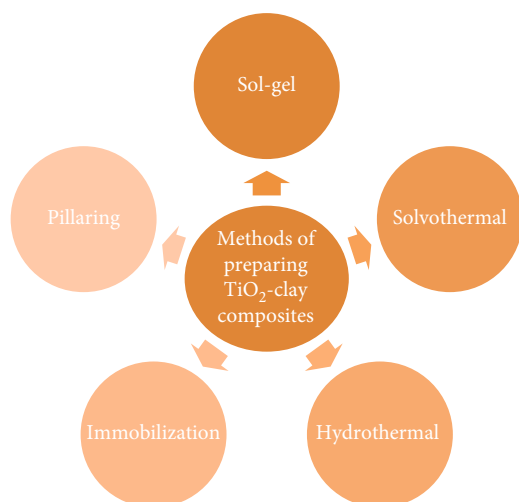


FIGURE 6: Methods of preparation of  $\text{TiO}_2$ -clay composites [87–91].

studied using the Langmuir isotherm.  $\text{TiO}_2$ -bentonite adsorbent removed up to 98.9% RhB which was higher than natural clay adsorbent [93].

$\text{TiO}_2$  has the ability to make composites with a variety of clays.  $\text{TiO}_2$ -rectorite composite was synthesized by mixing titanium butoxide/HCl suspension with rectorite/dd  $\text{H}_2\text{O}$  suspension followed by stirring, drying, centrifugation, washing, and finally drying. Then, it was magnetized with iron oxide and used for adsorption of MB dye showing max adsorption potential of  $169.20 \text{ mgg}^{-1}$ . Iron oxide was reported to increase the number of active sites by rupturing the sheets of  $\text{TiO}_2$ -rectorite composite and created large cavities which adsorbed greater number of MB molecules. Magnetization also made desorption easier [94].

The degradation potential of  $\text{TiO}_2$ -clay composites can be enhanced by incorporation of metal oxides.  $\text{TiO}_2$ - $\text{WO}_3$ -bentonite composites were synthesized through hydrothermal method by adding a mixture of  $\text{Na}^+$ -bentonite and sodium tungstate dihydrate mixture to titanium tetrachloride with constant mixing in a cold bath followed by treatment with ultrasound radiations for  $\frac{1}{2}$  hr. This mixture was heated in an autoclave with  $\text{H}_2\text{O}$  at  $443.15 \text{ K}$  for 10 h. The resultant composite was separated through filtration and washed and dried at  $25^\circ\text{C}$ . This composite was used for adsorption studies of MB dye.  $\text{WO}_3$  has been reported to escalate  $\text{TiO}_2$ 's sensitivity for gaseous species as well as improves its acidic strength and increases its affinity for dye contaminants. The unique pretreatment of bentonite with ultrasound radiations allowed a thorough disruptor of  $\text{Na}^+$ -bentonite matrix and uniform insertion and intercalation of  $\text{TiO}_2$ - $\text{WO}_3$  particles in between its layers. The adsorbent exhibited excellent adsorbent potential, a smooth desorption, and an easy recovery. Moreover, the adsorption potential of pretreated adsorbent increased by 50% possibly due to increase in number of active sites by ultrasound irradiation [95].

Mixing of  $\text{TiO}_2$  with clay and organic material like graphene imparts its tremendous adsorption properties.  $\text{TiO}_2$ -palygorskite-graphene composite was prepared via hydro-

TABLE 4: Summary of  $\text{TiO}_2$ -clay composite preparation methodologies and their consumption for adsorption of dyes in the last decade.

Adsorbent	Preparation	Adsorption	Reference
$\text{TiO}_2$ -Mnt-PAN	Spin coating	MB	[100]
$\text{TiO}_2$ -Ht	Sol-gel	MB	[101]
$\text{TiO}_2$ -Mnt-PVA	Immobilization	MB	[102]
$\text{TiO}_2$ -Knt	Sol-gel	OII	[103]
$\text{TiO}_2$ -Bnt	Sol-gel	NBB	[104]
$\text{TiO}_2$ -Knt	Impregnation	PR	[105]

thermal method, while CTAB was used as a surface active agent and adsorption of MB was studied. The studies suggest that graphene having layers of  $\text{sp}^2$  hybridized C is bestowed with a huge surface area, greater affinity for  $\text{H}_2\text{O}$ , and uniform distribution which makes it an ideal support. Likewise, palygorskite has exceptional adsorption potential owing to its enormous surface area and heat resistance. C=O groups on the surface of adsorbent provided the active sites where MB molecules were seem to be bound by H-bonds (on OH groups). The adsorbent showed commendable adsorption even after 5 recovery cycles. The max adsorption potential was  $134.59 \text{ mgg}^{-1}$  [96].

Clay composites of  $\text{TiO}_2$  can be further improved by microwave treatment.  $\text{TiO}_2$ -bentonite composite was synthesized via impregnation where bentonite was added to a water suspension of  $\text{TiO}_2$  followed by heating and stirring. The thoroughly mixed solution was subjected to microwave irradiation; the product was removed and desiccated. It was further used to study adsorption behavior using RhB and MB dyes using the Langmuir equation. Structural analysis shows that the integration of  $\text{TiO}_2$  particles onto bentonite via impregnation enhanced its adsorption potential, and  $\text{OH}^\bullet$  on  $\text{TiO}_2$  act as potential active sites and amplify the adsorption process [97].

A  $\text{TiO}_2$ -Rouge clay composite was synthesized via hydrothermal synthesis. Carefully refined and pretreated clay (with NaOH) was purified and desiccated and stored for 12 hours. Equal weight of functionalized clay and  $\text{TiO}_2$  were mixed in the presence of NaOH at  $373.15 \text{ K}$  and 5 atm. The adsorbent was used for adsorption of MB dye; it was reported to remove 91.19% dye. Morphological analysis indicates that the clay undergoes structural rearrangement post combination with  $\text{TiO}_2$  and adsorbent shows a comparatively uneven and granulated surface with multiple active sites which escalates adsorption rate [98].

Lately, halloysite nanotubes (financially feasible clays) have enticed deep interest owing to their hollow tube-like structure, enlarged surface area, and distinctive surface features. A  $\text{TiO}_2$ -halloysite composite was doped with Fe using hydrothermal procedure and used for adsorption of RhB and MB dyes. The multilayer tubes have anionic Si-OH on the exterior side and cationic Al-OH on the interior side which attract impurities of different nature via electrostatic interactions. Moreover, they are harmless, inexpensive, easily accessible, and nonhazardous.  $\text{TiO}_2$ -Fe composites were seen to stick to the exterior of the tubes which increased

TABLE 5: Summary of preparation and photocatalytic degradation of TiO<sub>2</sub>-clay composites over the last decade.

Photocatalyst	Preparation	Photocatalysis	Source	Removal efficiency (%)	Reference
TiO <sub>2</sub> -Spt	Sol-gel	ARG	UV	99.2	[114]
TiO <sub>2</sub> -Knt	Hydrolysis	AO7	UV-Vis	60	[115]
TiO <sub>2</sub> -Rtr	Sol-gel	ARG	UV	98	[116]
TiO <sub>2</sub> -Atp-AgBr	Impregnation	MB	Solar	98.8	[117]
TiO <sub>2</sub> -Rtr	Intercalation	ARG	UV	18	[118]
TiO <sub>2</sub> -Mnt-PMMA	Emulsion polymerization/sputtering	MB	UV	29.3	[119]
TiO <sub>2</sub> -Mnt-V	Sol-gel	SRhB	Vis	67.1	[120]
TiO <sub>2</sub> -Lpt	Intercalation	ARB	UV	98.3	[121]
TiO <sub>2</sub> -Bnt-Ce	Sol-gel	NR	Solar	99	[122]
TiO <sub>2</sub> -Bnt	Pillarization	MO	UV	98.8	[123]
TiO <sub>2</sub> -Mnt	Pillarization	MB	UV-Vis	98	[124]
TiO <sub>2</sub> -Mnt	Pillarization	MO	UV	98.08	[125]
TiO <sub>2</sub> -Portuguese clay	Immobilization	MB	UV	96.5	[126]
TiO <sub>2</sub> -Mnt-Pan	Sono-chemical	AB	Vis light	59	[127]
TiO <sub>2</sub> -Ht	Low temperature	GV	Vis light	60	[128]
TiO <sub>2</sub> -Bnt	Sol-gel	AR 3R	UV	96.7	[129]
TiO <sub>2</sub> -Mnt-Ptp	Intercalation/polymerization	Rh 6G	Solar/ultrasound/UV	96	[130]
TiO <sub>2</sub> -Plg	Sol-gel	OG	UV	96	[131]
TiO <sub>2</sub> -Tunisian clay	Impregnation	RB 19	UV	99	[132]
TiO <sub>2</sub> -Mnt	Impregnation	CV	UV A	97.1	[133]
TiO <sub>2</sub> -Atp-BiOBr	In situ deposition	MO	Vis light	96.8	[134]
TiO <sub>2</sub> -Svs	Solvothermal	OG	UV	80	[135]
TiO <sub>2</sub> -Sep-Au	Sol-gel	MO	UV	90	[136]
TiO <sub>2</sub> -Plg-CdS	Hydrolysis	MB	Vis	37	[137]
TiO <sub>2</sub> -Spt-Ag <sub>2</sub> O	Sol-gel+impregnation	ARG	Vis	98	[138]
TiO <sub>2</sub> -Bnt-Fe <sub>3</sub> O <sub>4</sub>	Co-precipitation/sol-gel	MB	UV	90	[139]
TiO <sub>2</sub> -C-N-Ht	Precipitation/recrystallization	MB	Solar	95	[140]
TiO <sub>2</sub> -Y <sup>3+</sup> -Mnt	Acid-sol	MO	UV/Vis	65	[141]
TiO <sub>2</sub> -AM-Ht	Biosynthesis	MB	UV	90	[142]
TiO <sub>2</sub> -Spt	Hydrothermal	OG	UV	98.8	[143]
TiO <sub>2</sub> -Ivorian clay	Hydrothermal sol-gel	MO	UV	60	[144]
TiO <sub>2</sub> -Spt	Sol-gel	Es	UV	72	[145]

their dispersion in aqueous phase, and the greater the dispersion, greater the contact with dye contaminants present in water and hence the higher the adsorption [99].

Table 4 gives a brief summary of synthesis methodologies and application of some of TiO<sub>2</sub>-clay-based composites in degradation of dyes via adsorption.

**2.2.2. Photocatalysis of Dyes via TiO<sub>2</sub>-Clay Composites.** Mixing different phases of TiO<sub>2</sub> with clay gives amazing results in photocatalysis. A novel TiO<sub>2</sub>-kaolinite photocatalyst was prepared using various phases of TiO<sub>2</sub> which was used for photocatalytic degradation of ARG dye. According to XRD data, the photocatalyst seemed to be composed of mixtures of 3 different phases of TiO<sub>2</sub>, i.e., anatase, rutile, and brookite, in different combinations. The anatase/brookite combination was reported to have highest photoactivity. Both of them were stimulated by UV light which leads to photogeneration of free electrons in anatase. Anatase has a highly

negative CB so these electrons diffuse to brookite. These electrons undergo a series of reactions and produce •OH which oxidizes dye particles. Likewise, photoactivated holes in brookite diffuse to anatase due to its high VB potential and interact with dye particles. Thus, the mixing of different phases and resulting heterojunction between them can improve TiO<sub>2</sub>'s photocatalysis [106].

The amount of clay used in the composite plays an important role in its potential to remove impurities. A TiO<sub>2</sub>/clinoptilolite photocatalyst was prepared via sol-gel method in different ratios and used for degradation of CN and MV-2B dye. The charge on the surface was dependent on clay's ratio which is an important factor in determining the affinity of charged dye particles towards the photocatalyst. 90/10 turned out to be the best ratio; the lower the clay ratio, the higher was the surface area and photocatalysis. The lower ratio of clay also prevented accumulation of TiO<sub>2</sub> in aqueous phase and improved its recovery [107].



Rapsomanikis et al. prepared TiO<sub>2</sub>-halloysite clay composites using sol-gel method for photocatalysis of BB41. The unique feature of this photocatalyst was that its surface was modified with Ag particles by treating composite's films with 1.0 mM AgNO<sub>3</sub> sol for 10-20 minutes followed by rinsing with double distilled H<sub>2</sub>O and drying by N<sub>2</sub> gas. Later, the Ag ions were reduced to Ag<sup>0</sup> by UV irradiation of films. These Ag particles were reported to improve TiO<sub>2</sub>'s efficiency to separate charge carrying species which led to an enhanced photocatalytic activity [108].

Even though TiO<sub>2</sub>-clay photocatalyst show a remarkable potential to degrade dyes and are economically feasible, some of them (e.g., TiO<sub>2</sub>-palygorskite) have limited applications as they can only be stimulated by ultraviolet light owing to their large E<sub>G</sub>. Various experiments have been carried out to make them responsive to visible light, some of which include hybridization and doping with other metals especially transition metals. The plasmonic effects of Ag nanoparticles enable it to improve the visible light sensitivity of TiO<sub>2</sub>-clay photocatalysts and expand their area of usage. A TiO<sub>2</sub>-Palygorskite composite was doped with Ag-AgCl particles through deposition-photoreduction method and used for photocatalytic degradation of RhB. Due to the surface plasmonic effect, Ag nanoparticles improved the photoactivity of the catalyst under visible light [109].

The sensitivity of TiO<sub>2</sub> towards light spectrum can also be broadened by merging it with other metal oxides like Fe<sub>2</sub>O<sub>3</sub> which are highly photoactive under visible light due to Fenton mechanism. Therefore, its fusion with TiO<sub>2</sub> imparts an exceptional photoactivity under natural day light, which is a mixture of ultraviolet (5%) and visible (40%) and IR light (55%). One such photocatalyst was prepared through sol-gel procedure where bentonite-supported TiO<sub>2</sub> was doped with Fe<sub>2</sub>O<sub>3</sub> and used for photocatalysis of MB. The dye was completely degraded in 2 hours. Fe<sub>2</sub>O<sub>3</sub> not only improved the photoactivity by absorption of light in visible region, but its magnetic nature also helped to retrieve and reuse the photocatalyst making it economically favorable [110].

Another such attempt to exploit visible light for photodegradation by TiO<sub>2</sub>-clay composites was made by depositing g-C<sub>3</sub>N<sub>4</sub> onto TiO<sub>2</sub>-bentonite via wet impregnation. For this purpose, TiO<sub>2</sub>-bentonite composite was mixed with highly concentrated slurry of g-C<sub>3</sub>N<sub>4</sub>, sonicated for 120 minutes, stirred overnight, and dried at 333.15 K. Samples of such composites with varying weight of g-C<sub>3</sub>N<sub>4</sub> were prepared. These composites were applied for photodegradation of RBR dye. 90% of the dye was degraded within 1.6 hour under visible light. This brilliant outcome was ascribed to strong interaction between clay and g-C<sub>3</sub>N<sub>4</sub> leading to enhanced dispersity, increased number of active sites, and their uniform distribution and better optical activity. Another reason was rate of charge recombination declined due to electron transfer from g-C<sub>3</sub>N<sub>4</sub> to TiO<sub>2</sub> and photoinduction under visible light. The photocatalyst was reusable for 5 successive cycles [111].

Incorporation of nonmetallic additives like urea into TiO<sub>2</sub>-clay composites can be quite favorable. Urea is reported to promote formation of anatase phase and con-

tributes to porosity of the TiO<sub>2</sub>-clay composite that adds to photocatalytic potential. Urea addition can also lead to shrinkage of the band gap of the TiO<sub>2</sub>-clay composite from 3.35 to 2.92 eV and makes it visible light activated. It is reported to enhance the degradation rate of dyes by 2.3 times under visible lights. Moreover, it is inexpensive and easily available which makes it even a better additive [112].

Photocatalytic degradation coupled with ultrasound treatment has been proved a very effective technique to enhance photoactivity of TiO<sub>2</sub>-clay composites. During photocatalysis, the efficiency of photocatalyst is reduced over the time due to blockage of active sites and hindrance of UV light. Ultrasonic treatment solves this problem by acting as an irradiation sources and activates TiO<sub>2</sub> to carry out sono-catalysis in the absence of UV light. Ultrasound waves also induce turbulence in the liquid phase which results in particle sizing and deagglomeration and hence increase number of active sites available. Moreover, treatment of these titania-clay composites with ultrasound waves leads to formation of supplementary OH• radicals. All these factors are reported to escalate photoactivity of titania-clay composites and speed up the removal rate of dye [113].

Table 5 gives a brief summary of synthesis methodologies and application of some of titania-clay-based composites in degradation of dyes via photocatalytic degradation.

It is evident from Tables 4 and 5 comparisons that sol-gel and coprecipitation methods are more used for synthesizing titania-clay composites as compared to other methodologies.

### 3. Conclusion

- (i) TiO<sub>2</sub> as both photocatalyst and adsorbent is extensively and effectively used for treatment of textile waste water
- (ii) The factors that limit TiO<sub>2</sub>'s efficacy of dye degradation can be overcome by using different supports like clays, silica, etc.
- (iii) Clays like rectorite, bentonite, montmorillonite, attapulgite, kaolinite, and halloysite are most commonly used as supports for TiO<sub>2</sub> using various techniques
- (iv) Clay as a support provides TiO<sub>2</sub> with a high surfaces area, porosity, improved morphology, more active sites, and better adsorption of dyes
- (v) Loading of TiO<sub>2</sub> on clays helps preventing the aggregation of TiO<sub>2</sub> and its loss to environment
- (vi) The efficacy of these TiO<sub>2</sub>-clay composites can be enhanced by further addition of various metallic and nonmetallic substances, ultrasonic irradiation, and experimenting with different phases and particle size of TiO<sub>2</sub>
- (vii) These TiO<sub>2</sub>-clay composites are energy-efficient, nonhazardous, and economically feasible

- (viii) The study on TiO<sub>2</sub>-clay-based composites and their modifications for treatment of textile waste water is a rapidly growing field of science

## Data Availability

All data related to this work is presented in results section along with references.

## Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publications of this review.

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