Clays for heterogeneous photocatalytic decolorization of wastewaters contaminated with synthetic dyes: a review

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Abstract

Photocatalysis is one of the most environment-friendly and technologically viable advanced oxidation processes. Compared to conventional thermal, biological, and physicochemical treatments, photocatalytic processes have more moderate reaction conditions and higher efficiency. They are a promising technology for the treatment of dye wastewaters, particularly those that have toxic and high organic content. Matrix-based photocatalysts have been extensively studied to enhance their efficiency. This paper is a review of recently published literature on matrix-based clay photocatalysts – e.g., bentonite, attapulgite, hydrotalcite, etc. – decolorizing dye wastewaters.

Key words: advanced oxidation process, clays, dye wastewaters, matrix-based photocatalysts

INTRODUCTION

An immense number of organic compounds are currently widely used, many of which are potent contaminants when released into freshwater ecosystems. In the majority of industrial processes water is used as a solvent, reaction or transport medium, so great efforts have been made to abate pollution from aqueous industrial waste streams since about 2000 AD. Dye wastewaters from the printing and dyeing industries are major sources of environmental contamination, for instance. Dyestuffs, slurries, dyeing aids, acids and alkalies, and fibers and inorganic compounds can all be present in dye wastewater (Wu & Wang 2012). Generally, dye wastewater is characterized by strong color, high pH, high chemical oxygen demand (COD), and low biodegradability (Wu et al. 2007). It is difficult to treat, especially with respect to color removal, using conventional processes (Bautista et al. 2008) but such wastewaters must be treated to meet discharge specifications or for recycling within the process (Levec & Pintar 2007).

High energy inputs are required, however, and there can be considerable emissions of hazardous compounds such as dioxins and furans (Debellefontaine et al. 1996). Although biological treatment is widely applied to residual wastewaters, long residence times are required for microorganisms to degrade pollutants and it is not suitable for toxic contaminants due to biomass poisoning. Other techniques like precipitation, flocculation, adsorption, air stripping, and reverse osmosis require post-treatment to dispose of the pollutants recovered (Danis et al. 1998). These limitations have encouraged researchers to develop more efficient and environment-friendly systems for such treatment.
Advanced oxidation processes (AOPs) capable of exploiting the high reactivity of hydroxyl radicals in driving oxidation have received attention as effective pre-treatment processes for less biodegradable wastewaters. They were first proposed by Glaze et al. (1987). Several technologies like Fenton, photo-Fenton, wet oxidation, ozonation, photocatalysis, etc. are included in the AOPs. In 1972, Fujishima & Honda (1972) showed the possibility of using the photo-excited semiconductor titanium dioxide (TiO₂) to split water into hydrogen and oxygen in a photo-electrochemical solar cell, and their fundamental work led to the development of a new AOP technology called heterogeneous photocatalysis, one of the most economically and technologically viable AOPs for wastewater treatment. Incineration is only suitable for highly concentrated wastewater at low flow rates, while biological treatments appear to be appropriate for high flow rate and low organic contents. Unlike other AOPs, heterogeneous photocatalysis is useful for high organic loadings at high flow rates and can cover parts of the application ranges of incineration and of biological methods. In particular, heterogeneous photocatalysis has great potential for treating effluent with high toxic contaminant content, for which direct biological treatment is not feasible.

Heterogeneous photocatalysis involves the use of a semiconductor catalyst – e.g., TiO₂, ZnO, Fe₂O₃, CdS, GaP or ZnS – irradiated with light of an appropriate wavelength, to generate highly reactive transitory species – e.g., *OH, *O₂, *HO₂ – for the mineralization of organic impurities (Chong et al. 2010; Augugliaro et al. 2012). It offers a number of advantages including ambient operating conditions, low operating costs, and complete mineralization of organic pollutants without secondary pollution, all of which have helped its wide application in wastewater treatment (Ahmed et al. 2011).

In recent years, it has been reported that matrix-based photocatalysts were quite efficient in improving the degradation rate of pollutants because the support helped to diffuse the outer photocatalyst and achieve good dispersibility, high surface area, etc (Matos et al. 2001; Liu et al. 2007). Further, such catalysis enabled easy product separation, and the recycling and reuse of the catalysts with related operating and economic advantages (Lei et al. 2006). One promising material for these systems is clay or a clay-based matrix, which is chemically inert, resistant to deterioration, commercially available in large quantities and has many industrial, catalytic and environmental applications (Liu & Wang 2007; Guo et al. 2008). Recently published literature on clay-based photocatalysts like bentonite, attapulgite, and hydrotalcite are discussed in this paper.

**PRINCIPLES OF HETEROGENEOUS PHOTOCATALYSIS**

Heterogeneous photocatalysis is based on a complex sequence of reactions, the underlying principles of which are well established (Mills & Le 1997; Fujishima et al. 2000). The basic photophysical and photochemical processes involved are illustrated in Figure 1 (Sud & Kaur 2012) and are often represented by the following chain reactions (Gaya & Abdullah 2008; Chong et al. 2010):

\[
\text{Photocatalyst} + \text{hv} \rightarrow \text{Photocatalyst}(e^- + h^+) \tag{1}
\]
\[
\text{Photocatalyst}(h^+) + H_2O \rightarrow \cdot\text{OH} + H^+ \tag{2}
\]
\[
\text{Photocatalyst}(e^-) + O_2 \rightarrow \cdot\text{O}_2^- \tag{3}
\]
\[
\cdot\text{O}_2^- + H^+ \rightarrow \cdot\text{HO}_2 \tag{4}
\]
\[
\cdot\text{HO}_2 + H^+ + \text{Photocatalyst}(e^-) \rightarrow H_2O_2 \tag{5}
\]
\[
H_2O_2 + (\text{Photocatalyst})e^- \rightarrow \cdot\text{OH} + \text{OH}^- \tag{6}
\]
When a semiconductor is illuminated, electrons \((e^-)\) are excited from the valence band (VB) to the conduction band (CB). Electrons raised to the CB correspond to missing negative charges (holes \((h^+)\)) in the VB. Both the \(e^-\) and \(h^+\) then migrate to the surface where they can initiate redox reactions with other chemical species adsorbed on the semiconductor. The photo-generated holes oxidize the hydroxyl groups or water molecules to produce \(•OH\) radicals while the corresponding electrons reduce the DO to superoxide radical anions \((\cdot O_2^−)\) \((Rajeshwar et al. 2008)\), which react with \(H^+\) to form \(•HO_2\) which decomposes rapidly to \(•OH\) \((Casbeer et al. 2012)\). The \(•OH\) radical, a very strong oxidizing agent (standard redox potential +2.8 V vs. normal hydrogen electrode) oxidizes the surface adsorbed organic pollutant into readily biodegradable compounds \((Lim et al. 2011)\).

The first important factors in photocatalytic reactions is the absorption of photons to create \(e^-/h^+\) pairs. The incident light energy must exceed the semiconductor band gap energy, if an electron is to be photo-excited from the VB to the CB \((Rajeshwar et al. 2008)\). The second is the \(e^-/h^+\) trapping or recombination rates, since the recombination timescale of \(e^-\) and \(h^+\) is of the order of nanoseconds \((Fujishima et al. 2000)\). It is extremely important to provide adequate scavengers for these charge carriers in the aqueous system to obtain favorable photocatalyzed reactions \((Zang & Farnood 2008)\).

Clays have the potential to contribute to all fundamental methods of enhancing photocatalytic activity. Moreover, because of their very large surface-to-volume ratio (specific surface), clays can adsorb a wide range of synthetic organic compounds. Hence, the development of clays is an innovative approach to improve the application of semiconductor nanomaterials in heterogeneous photocatalysis.

**PHOTOCATALYTIC DEGRADATION OF SYNTHETIC DYESTUFFS BY CLAYS-BASED PHOTOCATALYSTS**

Clayey materials have received a lot of attention as potential commercial adsorbents due to their low cost, abundant availability, easy accessibility, environment-friendly nature, and surface reactivity. The focus is on clay minerals because of their structural variability, chemical stability and high specific
surface (Hajjaji et al. 2013). Clays have been used as natural, cost-effective adsorbents and supporters for catalysis in wastewater treatment.

Generally, organic molecules interact with clay surfaces through: (1) electrostatic interaction of ionic organic species with charged clay surfaces; (2) complexation of organic species with clay surfaces; for example, the π electrons of the phenyl in dioxins react with Lewis acid sites on laponite surfaces to form π electron complexes (Mao et al. 1993); (3) coordination of nonionic species, such as alcohols, ketones, pyridines, with exchangeable metallic ions on clay surfaces (Theng 1974; Shichi & Takagi 2000).

Studies of the photocatalysis of dye wastewater over clay-based photocatalysts are summarized in Table 1.

### Table 1 | Summary of studies of the photocatalysis of dye wastewater over clay-based photocatalysts

<table>
<thead>
<tr>
<th>Dye</th>
<th>Photoactive nanocomposite</th>
<th>Light source</th>
<th>Reaction time (min)</th>
<th>Degradation (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>ATT–SnO&lt;sub&gt;2&lt;/sub&gt;–TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>UV</td>
<td>30</td>
<td>99</td>
<td>Zhang et al. (2009)</td>
</tr>
<tr>
<td>MO</td>
<td>ATT–BiOCl–TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>UV</td>
<td>70</td>
<td>100</td>
<td>Zhang et al. (2015)</td>
</tr>
<tr>
<td>MO</td>
<td>ATT–TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>UV</td>
<td>40</td>
<td>99</td>
<td>Li et al. (2015)</td>
</tr>
<tr>
<td>MO</td>
<td>ATT–BiOCl–TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>visible light</td>
<td>120</td>
<td>92.57</td>
<td>Zhang et al. (2015)</td>
</tr>
<tr>
<td>MO</td>
<td>ATT–TiO&lt;sub&gt;2&lt;/sub&gt;–Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>visible light</td>
<td>180</td>
<td>94.13</td>
<td>Zhang et al. (2014)</td>
</tr>
<tr>
<td>Orange II</td>
<td>ATT–Ag&lt;sub&gt;3&lt;/sub&gt;Po&lt;sub&gt;4&lt;/sub&gt;</td>
<td>visible light</td>
<td>90</td>
<td>99</td>
<td>Ma et al. (2014)</td>
</tr>
<tr>
<td>Blue 41</td>
<td>ATT–TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>UV</td>
<td>70</td>
<td>90</td>
<td>Stathatos et al. (2012)</td>
</tr>
<tr>
<td>RhB</td>
<td>BiOCl–NiFe–LDH</td>
<td>UV</td>
<td>60</td>
<td>93.3</td>
<td>Ma et al. (2015)</td>
</tr>
<tr>
<td>MO</td>
<td>ZnCr–LDH</td>
<td>visible light</td>
<td>240</td>
<td>76</td>
<td>Liu et al. (2013)</td>
</tr>
<tr>
<td>MB</td>
<td>ZnAl–LDH</td>
<td>UV</td>
<td>60</td>
<td>90</td>
<td>Kaouther et al. (2016)</td>
</tr>
<tr>
<td>MB</td>
<td>ZnAlTi–LDH</td>
<td>visible light</td>
<td>120</td>
<td>99</td>
<td>Wang et al. (2014b)</td>
</tr>
<tr>
<td>MO</td>
<td>MgAl–LDH</td>
<td>UV</td>
<td>60</td>
<td>93</td>
<td>Sefetl et al. (2013)</td>
</tr>
<tr>
<td>MO</td>
<td>Ag&lt;sub&gt;3&lt;/sub&gt;Po&lt;sub&gt;4&lt;/sub&gt;–Ben</td>
<td>visible light</td>
<td>90</td>
<td>90</td>
<td>Rodica et al. (2009)</td>
</tr>
<tr>
<td>Orange G</td>
<td>beidellite–Bd–TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>UV</td>
<td>45</td>
<td>100</td>
<td>Rhouta et al. (2015)</td>
</tr>
<tr>
<td>CR</td>
<td>Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;–montmorillonite</td>
<td>visible light</td>
<td>40</td>
<td>86.4</td>
<td>Patil et al. (2015)</td>
</tr>
<tr>
<td>MB</td>
<td>ZnO–montmorillonite</td>
<td>visible light</td>
<td>60</td>
<td>96</td>
<td>Fatimah et al. (2011)</td>
</tr>
<tr>
<td>MB</td>
<td>kaolin–ZnO</td>
<td>UV</td>
<td>180</td>
<td>100</td>
<td>Ananthakumar et al. (2010)</td>
</tr>
<tr>
<td>Orange II</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/Portuguese clay</td>
<td>UV</td>
<td>120</td>
<td>99%</td>
<td>Hajjaji et al. (2013)</td>
</tr>
<tr>
<td>MB</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/Portuguese clay</td>
<td>UV</td>
<td>1,200</td>
<td>96.5%</td>
<td>Hajjaji et al. (2013)</td>
</tr>
</tbody>
</table>

Photocatalysis degradation of synthetic dyestuffs over attapulgite-based photocatalysts

Attapulgite (ATT, also called palygorskite) is a species of hydrated magnesium aluminum silicate non-metallic mineral \([\text{H}_2\text{O}]_4(\text{Mg,Al,Fe})_5(\text{OH})_2\text{Si}_8\text{O}_{20-4}\text{H}_2\text{O}\) with special lath-like or fibrous morphology (Cao et al. 2008). Due to its unique structure and textual properties, natural ATT is widely used in adsorbents, adhesives, catalysts, and catalyst supports (Chen & Wang 2007; Fang & Chen 2010). It has a large specific surface with excellent activity and chemical adsorption properties, and some studies have shown that it can also improve the selectivity of catalysts (Wang et al. 2015).

Zhao et al. (2006, 2007) prepared silver and copper modified ATT/TiO<sub>2</sub> photocatalysts by hydrolysis. Due to the small size of the anatase (TiO<sub>2</sub>) crystals and its relatively high porosity, the composite sample exhibited much higher activity than that of pure TiO<sub>2</sub> for the degradation of methylene blue (MB).

nanocomposite particles – average size about 10 nm – were loaded successfully onto the ATT fiber surface and dispersed widely. The highest degradation rate of MO was 99% within 30 minutes. Using the same method, they produced ATP–BiOCl–TiO$_2$ as a photocatalyst. It is more effective than titanium dioxide with an average particle size of 25 nm (Zhang et al. 2015). Zhang et al. (2014) also prepared ATTiO$_2$–FexOy. Their results show that the highest degradation ratio and COD removal of MO using this catalyst were 94.13 and 90.91%, respectively. They also found that the photocatalyst could be recovered readily and that the degradation ratio was still 83.89% after 5 cycles.

Ma et al. (2014) synthesized Ag$_3$PO$_4$ particles on the surface of ATT for the sunlight-driven catalytic removal of orange II from water. They showed that the photocatalytic activity and stability of Ag$_3$PO$_4$ were significantly improved by loading it onto ATT. In addition, the silver content in the photocatalyst composite decreased from 77.3 wt% in bare Ag$_3$PO$_4$ to 18.8 in the composite, greatly reducing treatment costs. Although Ag$_3$PO$_4$ precipitates quickly in aqueous solution, it also can be applied as a coating on carriers, avoiding the aggregation of nanoparticles into micrometer-sized particles in solutions (see Figure 2).

Stathatos et al. (2012) prepared palygorskite/TiO$_2$ composite films as new photocatalysts for the photo-discoloration of basic blue 41 azo-dye in water. These nanocomposite films proved very promising as photocatalysts and highly effective in discoloring the dye, despite the small amount of immobilized palygorskite/TiO$_2$ catalyst on the glass substrates. A palygorskite/TiO$_2$ weight ratio of 3:2 proved the most efficient, and reproducible dye discoloration results were obtained after three cycles. It was also found that palygorskite showed a positive synergistic effect for the TiO$_2$ photocatalysis. Zhang et al. (2015) indicated that the enhanced separation of photo-generated electron–hole pairs in mixed rutile-anatase might be responsible for the improvement in photocatalytic activity.

**Photocatalysis degradation of synthetic dyestuffs over layered double hydroxide (LDH)-based photocatalysts**

LDHs have been studied increasingly in the last few years and widely applied in photocatalysis thanks to their stability, their ease of preparation and their low cost. LDHs can be prepared with a variety of divalent and trivalent cations, so that semiconductor materials can be obtained by choosing suitable chemical compositions. Many previous studies have shown that, at equal mass, calcination of hydro-talcite improves photocatalytic activity by the formation of metal oxide nanocrystals (Guo et al. 2001; Seftel et al. 2008). These have been used to photo-degrade many species, including phenolic compounds (Patzkó et al. 2005), pesticides (Guo et al. 2001) and dyes (Hadnadev-Kostić et al. 2012).

LDHs are a class of two-dimensional anionic clays with a structure based on brucite (M(OH)$_2$)-like layers. Parts of octahedral-M (II) cations are substituted isomorphously by M(III) cations, and the excess positive charges thus formed are compensated by the incorporation of generally hydrated interlayer anions (Vaccari 1999).

Ma et al. (2015) prepared BiOCl–NiFe–LDH photocatalysts and investigated their ability to remove Rhodamine B (RhB). In a set of three recycling rounds, RhB degradation efficiencies were 93.3, 90.1 and 87.9%, respectively.

Liu et al. (2013) prepared ZnCr- and MgAl-LDHs. These exhibited different adsorption capabilities for MB and MO due to the different colloidal properties of the LDH samples, revealed by Zeta potential measurement. The finding that organic dye elimination from solution by pristine LDH samples arises from photo-assisted degradation and adsorption, is important for the rational design and use of clay-like materials to treat sewage containing toxic compounds.

Abderrazek et al. (2016) indicated that untreated [Zn–Al] LDH offered the best photocatalytic activity. It was even better than that of commercial ZnO nanoparticles. The structure is shown in Figure 3. [Zn–Al] LDH provided decolorized 90% after 1 hour of irradiation.
Wang et al. (2014a, 2014b) synthesized ZnAlTi LDHs with different Zn:Al:Ti ratios by homogeneous precipitation using urea hydrolysis. The photocatalytic activity was evaluated by MB degradation under solar irradiation. The maximum photodegradation of MB was 99% and was achieved with a catalyst loading of 1.0 g L\(^{-1}\) from an initial MB concentration of 10 mg L\(^{-1}\), at neutral pH. A kinetic study indicated that the process was well fitted by the Langmuir–Hinshelwood model. After three cycles, the degradation of MB was still close to 90%, indicating that the photocatalyst had high stability for recycling.

Seftel et al. (2013) indicated that MgAlTi-LDH shows very strong photocatalytic effects due to the segregation of small, well defined TiO\(_2\) nanoparticles on the highly hydroxilated layered surface. Up to 93% of the MO could be removed by a TiO\(_2\)/LDH-type nanocomposite system. Controlled thermal treatment of photocatalytic systems enabled the quality of the photocatalytically active sites deposited
on the layered support to be tailored. The use of the TiO$_2$/LDHs nanocomposites offered many advantages including increased activity per unit mass, higher efficiencies at lower solid/liquid ratio, decreased reaction times, reduced agglomeration, and easier separation at the end of the processes.

**Photocatalysis degradation of synthetic dyestuffs over bentonite-based photocatalysts**

Bentonite, whose main component is montmorillonite, is abundant. It consists of twin layers of tetrahedral silica sandwiching a single octahedral alumina sheet. Bentonite is negatively charged due to the isomorphic substitutions of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral layer and Mg$^{2+}$ for Al$^{3+}$ in the octahedral layer. This negative charge is balanced by the presence of exchangeable cations (e.g., Na$^+$, Ca$^{2+}$, etc) in the lattice structure, which allow excellent performance in the adsorption of cationic contaminants by cationic exchange (Hu et al. 2006; Tahir & Rauf 2006). For example, Ag$^+$ can be spontaneously adsorbed on natural bentonite (Hefne et al. 2010), and it has been used successfully as carrier for Ag$_3$PO$_4$ for treating dye wastewaters (Özcan et al. 2005).

Silica-bentonite has large specific surface (472 m$^2$/g) and high hydrothermal stability, which makes it a potential catalyst host-material (Li et al. 2009). When loaded with TiO$_2$, its photocatalytic results
are better than those of pure TiO₂. Dvininov et al. (2009) used TiO₂-pillared montmorillonites as catalysts for Congo red (CR) dye photodegradation, under UV. The photocatalytic activity of the pillared clays is a function of TiO₂-pillar size, longer pillars enhancing the contact areas between the dye solution and photoactive species present in the interlayer space (see Figure 4). Rodica et al. (2009) studied the role of TiO₂-pillared montmorillonitic photocatalysis for the removal of CR and showed that the process efficiency was that arising from simple sorption of the dye. Rhouta et al. (2015) prepared Na⁺–beidellite–Bd–TiO₂ photocatalysts, which were, again, much more efficient than pure TiO₂. For instance, total elimination of Orange G (OG) dye from aqueous solution occurs within about 45 minutes, when using 3Cethyltrimethylammonium⁺–Bd–TiO₂.


Fatimah et al. (2011) synthesized a ZnO/montmorillonite photocatalyst based on a natural montmorillonite from Indonesia using a sol–gel intercalation method. The photocatalyst had lower band gap energy, and the increased adsorption of MB resulted in faster photodegradation. The kinetics of the reaction obeyed the Langmuir–Hinshelwood model.

Photocatalytic degradation of synthetic dyestuffs of other clays

The layered structure and particle size of kaolin (also called halloysite) could also be beneficial in the production of high-quality and relatively cheap photocatalysts (Henych & Štengl 2013; Gómez et al. 2014) on an industrial scale. Tubular halloysite combined with nanocrystalline TiO₂ were used in the

![Figure 4](https://iwaponline.com/wpt/article-pdf/12/2/432/380777/wpt0120432.pdf)

**Figure 4** | TEM images of TiO₂-pillared montmorillonitic clay (Özcan et al. 2005).
preparation of nanocomposite films on glass substrates at 450°C via the sol-gel route by Papoulis et al. (2014). These films were promising photocatalysts and highly effective in dye discoloration. Kaolin modified with 2 wt% ZnO was found to be photoactive and degraded MB within 3 hours under UV irradiation (Ananthakumar et al. 2010).

Bouna et al. (2014) prepared TiO$_2$/stevensite as a photocatalyst. Their data indicated that the formation of Na$^+$-stevensite by the TiO$_2$ particles leads to TiO$_2$/stevensite nanocomposites with increased specific surfaces and mesopore volumes, and lower points of zero charge values. The photocatalytic activity level of TiO$_2$/stevensite nanocomposites with high Ti content was greater than that of pure TiO$_2$ sample, and increased with increasing TiO$_2$ content.

The effects of any one clay-based photocatalyst on different dye wastewaters are not the same, and neither are the intermediate products of different clay-based photocatalysts for the same dye wastewater. Hajjaji et al. (2013) indicated that the combined effects of adsorption and photocatalysis resulted in very satisfactory performances, even for mixtures with relatively low TiO$_2$ catalyst content. Titania-gel impregnated clays achieved high Orange II (OII) decolorization efficiency (up to 99%) in short times (2 hours). However, their decolorization of MB solutions was much slower (20 hours), although the final color attenuation achieved was 96.5%. Wang et al. (2014a) found that RhB on laponite underwent a stepwise N-deethylation and its decomposition was terminated once rhodamine 110 – a decomposition product – was formed, whereas the same phenomenon was not observed for RhB on montmorillonite, where the decomposition involved chromophore destruction.

CONCLUSION AND FUTURE PERSPECTIVES

In this review, an attempt has been made to integrate recent developments in the application of clays for photocatalytic treatment of colored effluents. Undoubtedly, clays hold great potential for photodegradation of dye pollutants and offer significant advantages over the commercial semiconductor photocatalysts currently available. The incorporation of clays into various semiconductors can significantly improve their photocatalytic performance because of the extended light absorption range, high adsorption capacity, increased specific surface and superior electron conductivity. Even though considerable progress has been made, there are several key technical issues that need further investigation. They are:

1. The incomplete understanding of clays’ photocatalytic enhancement mechanisms. In-depth studies are needed to elucidate these, which would, in turn, contribute to the design of clay-based photocatalysts.
2. Unlike laboratory tests using pure aqueous dye solutions, textile effluents contain different types of synthetic dyes and other substances. For example, both anionic and cationic dyes may be present simultaneously in real industrial effluents – e.g., from paper printing and textile dyeing. It is thus essential to investigate the simultaneous photodecomposition of co-existing dyes from multi-component solutions, as well as the efficacy of clays with real dye-bearing effluents.
3. Finally, very little information is available on the toxicity and/or biocompatibility of clays. Work is needed, therefore, on in vitro and in vivo interactions between clays and different living systems, if clays are to be used successfully in dye–wastewater remediation.

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