Photocatalytic TiO$_2$/adsorbent nanocomposites prepared via wet chemical impregnation for wastewater treatment: A review

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**A B S T R A C T**

Recent progress on preparation of TiO$_2$/adsorbent nanocomposites (TNC) via wet chemical impregnation has been reviewed. The potential applications of TNC are growing continuously and the material is very likely to find its place in future applications of wastewater treatment. In a TNC preparation via wet chemical impregnation, electronic properties (i.e. amount of charger carrier and its lifetime) and morphological properties (i.e. particle size, surface area and crystal phase) of TiO$_2$ in as-prepared resultants are sensitively dependent on the experimental conditions during the synthesis. Currently, one major limitation in this promising area is that visible-light capacity has yet to be introduced into TNC systems. It is envisaged that this could be realized via a single wet chemical procedure without significant increase of the process complexity.

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**1. Introduction**

Long-term water shortages driven by population growth and climate change are forcing people to learn to live with less water. Manufacturing industries consume a large quantity of clean water, but until now very limited reuse has taken place. In many cases, such as meat or food processing factories, industrial wastewater streams are only slightly contaminated and contain low levels of dissolved organic compounds (DOC), e.g. polysaccharides, proteins, amino sugars, nucleic acids, humic and organic acids and cells. These dissolved organics pose a problem to the direct reuse of the lightly contaminated water without treatment, due to issues of bacterial growth, odour generation and biofouling on the utility surface. Of the current applicable treatments, adsorption process, through functionalizing the adsorbents to trap DOCs, has shown promise due to the reasonable efficacy and comparatively low costs. Highlighting its commercial viability is the fact that activated carbon (AC) adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies [1]. However, the main disadvantage of such methodology is its non-destructive nature, i.e. DOCs will be adsorbed but not decomposed; as a result, the spent or saturated
adsorbents must be regenerated before reuse, or otherwise must simply be disposed of as hazardous waste. Therefore, decomposi-
tion of the adsorbed DOCs and regeneration of the adsorbents is a very critical step to the cost-effective use of porous adsorbents and continuous large-scale operation in wastewater treatment. Several methods, based on either desorption or decomposition, have been used to regenerate the spent adsorbents, such as activated carbon [2]. For example, the most commonly used thermal or microwave treatments promote the drying and loss of highly volatile compounds below 200 °C, vaporization and decomposition of unstable compounds at temperatures between 200 and 500 °C, and the pyrolysis of non-volatile adsorbates at temperatures over 500–700 °C. In these methods, special high temperature facilities such as multiple hearth furnaces or rotary kilns are needed to desorb effectively, and usually at the expense of decreased adsorption capacity of adsorbents due to carbon loss and surface alteration after repeated regeneration cycles.

An alternative for the degradation of DOCs and regeneration of spent porous adsorbents, heterogeneous photocatalysis can effectively oxidize a wide range of organic compounds, more to its advantage, at room or moderate ambient conditions. Scientific research in heterogeneous photocatalysis began as early as the 1970s. In recent years, applications to environmental cleanup, especially water treatment, have been one of the most active areas in the heterogeneous photocatalysis [3,4]. Some other advantages of heterogeneous photocatalysis over other adsorbent regeneration methods include: (1) No dedicated post-treatment is needed since the organic pollutants can be mineralized into non-toxic by-

ion products, such as water and carbon dioxide; (2) The possibility of being activated by solar radiation could result in low energy cost; (3) Possible on-site regeneration of spent adsorbents and destruction of adsorbed organic materials; (4) Reduced loss of adsorbents due to attrition and burn-off which occurs in thermal regeneration. In the literature, materials with photocatalytic abilities could be found abundantly. These mainly belong to the metal oxide semiconductors. As the nature of wastewater purification for human consumption and more stringent water quality standards demand the minimal level of toxicity, many metal oxides with photocatalytic ability are excluded. Among those available, TiO2 nanoparticles has proven to be the most promising [5], with reported advantages of low cost, non-toxicity, greatly enhanced surface area, tunable properties which can be modified by size reduction, doping, or sensitizer, no substantial loss of photocatalytic activity after repeated process cycles, enhanced photo-induced charge transport [6] and no depletion layer formation on the surface [7]. Besides, due to the intensive research on the photocatalytic activity of TiO2, the mechanism of its purification on DOC is well understood. It usually involves the following [8]:

1. Absorption of efficient photons (\(\hbar \nu \geq \text{EG} = 3.2\text{eV}\)) by TiO2

\[
(\text{TiO}_2) + \hbar \nu \rightarrow e^-\text{CB} + h^+\text{VB}
\]

(1)

2. Oxygen ionsorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to \(-1/2\))

\[(O_2)_{ads} + e^-\text{CB} \rightarrow O_2^-\]

(2)

3. Neutralization of OH– groups by photoholes which produces OH* radicals

\[(H_2O \leftrightarrow H^+ + OH^-)_{ads} + h^+\text{VB} \rightarrow H^+ + OH^*\]

(3)

4. Oxidation of the organic reactant via successive attacks by OH radicals

\[R + OH^* \rightarrow R^* + H_2O\]

(4)

5. Direct oxidation by reaction with holes

\[R + h^+ \rightarrow R^{**} \rightarrow \text{degradationproducts}\]

(5)

Although the research in this direction began with the interest to utilize photocatalysis as a separate procedure for post-

adsorption regeneration of the spent adsorbent, it soon became evident that incorporating the photocatalytic regeneration during the adsorption process by coating TiO2 photocatalyst on the surface of adsorbents would combine the advantages of both techniques: on one hand, large surface area adsorbents work as the support of nano-sized TiO2 photocatalyst and concentrate the pollutants and intermediates around the TiO2, of which the photodecomposition rate is intrinsically low due to the limited surface area; on the other hand, nano-sized TiO2 photocatalysts can decompose the pollutants thus regenerating the adsorbents in situ. A variety of coating methods for the synthesis of TiO2/adsorbent nano-structured composites (TNC) have been reported. Some are chemical methods, such as carbonization of coal and TiO2 mixture [9], ionized cluster beam deposition [10], chemical vapor deposition [11] and wet chemical methods [12,13]. Others are physical methods, such as impregnation–desiccation [14], boiling and dip-coating deposition [15]. At the current stage, wet chemical impregnations are of great interest, i.e. hydrolysis and impregna-
tion of TiO2 precursors to adsorbents, due to their facile nature, continuous process ability, low temperature and energy costs, uniform coating with good reproducibility and adhesion, and the simplicity in controlling crystal structure/morphology and particle size by simple variations in experimental conditions, such as hydrolysis rate, solution pH and solvents.

In summary, progress on developing TNC has been made in lab-
scale synthesis particularly via wet chemical impregnation. A systematic study of different experimental conditions during these published TNC preparation is yet to be conducted. This gap has seriously hindered its optimization and commercial viability at present. In such context, the recent progress on various TNCs synthesized via wet chemical route, along with a special focus on its potential and current limitations are reviewed here. Relevant experimental conditions and properties of as-synthesized products in each study are highlighted where possible and compared in order to identify and optimize the key preparation parameters.

2. Parameters influencing wet chemical synthesis of TNC

In the literature, wet chemical assembly of TNC could be simplified as a three-module procedure, which is illustrated in Fig. 1: (1) contacting the adsorbents with the TiO2 impregnating solution for a certain period of time, (2) drying the support to remove the absorbed liquid, and (3) activating the catalyst by calcinations [16].

Relevant studies of TNC synthesis via wet chemical impregna-
tion in literature are summarized in Table 1, where key variables of the preparing conditions and corresponding as-synthesized TNC properties are listed for comparison. Each variable and its influences on the TNC prepared via wet chemical hydrolysis are further discussed in the following sections.

2.1. Influence of porous adsorbents

The overall performance of TNC on the DOC removal basically consists of two parts: adsorption by porous substrate and photocatalytic decomposition by nano-sized TiO2. Even with the latest progress in this field, the adsorption by porous substrates still works as the major mechanism in DOC removal, because the adsorption rate is far better than that of photodecomposition. As a result, choosing a proper adsorbent is critical to the efficient TNC synthesis for practical wastewater purification. However, to facilitate the effective photocatalysis by loaded TiO2, a balance between adsorption capacity and affinity of the TNC needs to be taken into consideration, that is, the adsorbing capacity should be
high for the DOC of target and yet the affinity should be moderate to allow the efficient diffusion of adsorbed substrates to the photocatalytic active sites. In general, the adsorption capacity and affinity of a TNC is dependent on some inherent properties of its adsorbent substrate, such as primary particle or granular size, pore size and distribution, surface area and acid–base properties. Higher adsorption capacity usually corresponds to the adsorbents of larger surface area, while the adsorption affinity associates with the microporosity and amount of surface chemical groups that are able to bind or attract the adsorbates.

In terms of the types of adsorbent substrates, most recent literature in this regard is concentrated on AC, which are known for their characteristics of large surface area, low cost, and wide pore size distribution from micro- to macro-sized pore [32]. Earlier studies seemed more interested in zeolites or molecular sieves as a group of alternative adsorbents. These contain uniformly sized pores in the range of 0.4–1.3 nm, so the materials have the ability of recognizing, discriminating and organizing molecules with precision that can be less than 0.1 nm [33]. Non-porous substrates, such as glass beads, fiberglass, silica sand, clay, etc., or less porous ones (surface areas < 200 m²/g), such as alumina ceramics and silica, were also studied among the early attempts. However, the results were far from being satisfactory in terms of photocatalytic efficiency, i.e. as-prepared TNCs possess less photocatalytic activity than the corresponding TiO₂ alone [34,35]. Pozzo et al. reviewed most of early works using non- or less-porous substrates [36]. The present work (Table 1) is in turn mainly focused on recent efforts of utilizing AC and zeolites as promising adsorbents. For these two candidates, the clear advantages of one over another as adsorbent substrate, as the TiO₂ nanoparticle loading only contributed little to the adsorbent resulting for the former, which, however, exhibited very poor dispersiveness under SEM characterization (see Fig. 2). On a more practical note, using small size TNCs in form of suspension for wastewater purification would result in the difficulty of removal and separation, whereas large granular size TNCs do eliminate this problem but, on the other hand, the large size TNCs may limit the mass transfer compared to the small size ones. Further to this complexity, the information on the primary size of the adsorbents reported in the TNC literature is largely missing in many of the studies (see Table 1), which make it impossible to cross-examine and elucidate the reported photocatalytic activities.

(1) The DOC pollutants in wastewater are often targeted to be of large molecular weight, so the favorable pore size range of adsorbents in these applications should fall into the lower range of meso-scale (2–50 nm). This renders most of zeolite adsorbents somewhat disadvantaged due to their small pore size, which could also result in undesirable plugging especially during high TiO₂ impregnation.

(2) It would be true that, depending on the targeted DOCs, the adsorbent may have different adsorption performances. In terms of adsorption selectivity on different DOCs, zeolite adsorbents are more flexible than AC due to their uniform pore size distribution. Accordingly, the repeatability of as-synthesized TNC quality based on zeolites is also superior.

(3) DOC removal by a TNC is a complex interplay between adsorption and photocatalytic decomposition. In many cases, a compromise of the adsorbent selection need to be made between ones with higher adsorption capacity and ones with lower affinity. Some early studies conducted by Yoneyama and co-workers on various adsorbent substrates have shown that TNC based on AC have most adsorption on propyzamide due to AC adsorption capacity, whereas TNC based on zeolites (Tosoh TSZ-640NAA) has the highest photocatalytic decomposition rate due to its moderate adsorption affinity [22].

(4) Adsorbents should have higher surface areas than that of loaded TiO₂ nanoparticles and should be inert with DOC. Both candidates are agreeable on this, whereas zeolites feature more desirable mechanical properties, such as attrition resistance, hardness and compressive strength.

(5) Adsorbents should possess reasonable transparency to UV–vis light sources, as light penetration to internal surfaces is one limiting factor for photocatalytic efficiency. On adsorbents side, this is dependent on pore size and its distribution. ACs featuring a wide range of macropores are more desirable in this sense as they provide easy access for the propagation of UV–vis light.

Depending on the TNC size, there are two types of operations reported in the literature: (1) fixed bed system containing large-sized TNC pellets (mm) or (2) suspension solution containing small-sized TNC powders (μm). In the form of large size pellets, the primary size of resultant TNC is usually equal to its adsorbent substrate, as the TiO₂ nanoparticle loading only contributed limited changes to the size of TNC in most of these studies. Evidently, low size ratio of porous adsorbent to TiO₂ nanoparticles could result in a decrease of resultant TNC surface area, but could significantly improve the TiO₂ coating dispersiveness on the adsorbent surface. In a study of Carpio et al., they prepared two types of TNC: large size pellets and small size powders [25]. The authors reported a negligible difference of surface area between the adsorbent and the corresponding TNC resultant for the former, which, however, exhibited very poor dispersiveness under SEM characterization (see Fig. 2). On a more practical note, using small size TNCs in form of suspension for wastewater purification would result in the difficulty of removal and separation, whereas large granular size TNCs do eliminate this problem but, on the other hand, the large size TNCs may limit the mass transfer compared to the small size ones. Further to this complexity, the information on the primary size of the adsorbents reported in the TNC literature is largely missing in many of the studies (see Table 1), which make it impossible to cross-examine and elucidate the reported photocatalytic activities.

Functional groups on the surface of adsorbents such as mineral matter and oxygen content may also influence the adsorption process through changing the hydrophilicity, as hydrophilic surface characteristics (like most zeolites compared with AC) can preferentially adsorb water or polar organic components. Therefore, competition of effective adsorption between different organic pollutants and solvent molecules implies the importance of selection of the adsorbents for target DOCs. In the literature, the nature of the surface groups on adsorbents can be modified by thermal (under O₂, NH₃ or inert gases) or wet chemical impregnation (i.e. treated with acid or base). Most relevant studies reported utilizing the unmodified adsorbents, and yet the authors fail to characterize or specify the relevant information of surface group on their starting adsorbents before assessing the as-prepared TNC performance. These adsorbent surface character-
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<th>Studies</th>
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<th>BET [m²/g]</th>
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<tr>
<td>Sampath et al. [17]</td>
<td>Mordenite</td>
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<td>Ti(OCH(CH₃)₂)₄</td>
<td>HCl</td>
<td>3</td>
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<td>659</td>
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<td>HNO₃, NaOH</td>
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<td>HNO₃, NaOH</td>
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*Calcinations were carried out in air if not otherwise specified.*
istics could even have influences on the crystallization and size of TiO₂ species somehow during the impregnation of hydrolyzed TiO₂ precursors to the adsorbents.

2.2. Influence of TiO₂ precursors

Choosing different types of TiO₂ precursors plays an important role in preparation of TNC via wet chemical impregnation. Many mainly fall into two groups: titanium alkoxides and inorganic titanium, such as titanium chloride and titanium sulfate. In their study Harada et al. observed that the presence of Cl⁻ ions on the surface of AC promotes the aggregation of titanium oxides species, and the formation of rutile TiO₂ phase instead of anatase form. As one of two common TiO₂ species, rutile generates fewer charge carriers with lower lifetimes than that of an anatase type TiO₂, when in the same nano-sized particles form with the same crystalline quality and reactive surface properties [37]. On the other hand, the SO₄²⁻ presence on TiO₂ has been reported to show higher photocatalytic activity than pure TiO₂ [38–40]. It is envisaged that using titanium sulfate as precursor could be advantageous, although this effect during the wet chemical impregnation to different adsorbents still needs further investigation.

2.3. Influence of TiO₂ loading and location

An increased amount of TiO₂ loading could also lead to augmentation of overall TNC photocatalytic activity. However, there is a bottleneck situation where penetrations of the light irradiation are blocked by excessive TiO₂ loading itself, and so are the adsorbent pores. Lu et al. reported a negligible effect of increasing TiO₂ loading on photocatalytic activity, after the loading exceeded 5 wt% in their as-prepared TNC [41]. This indicated an existence of optimal values of TiO₂ loading for maximized
economical uses of TNC and energy. In the literature, there is a great discrepancy between TiO₂ loadings and their optimal values on photocatalytic activity of TNC reported in different studies, even when the same types of adsorbents are used. Apart from the missing information on the primary size of adsorbents they used, this was likely to arise from the failure to specify the TiO₂ loading dispersiveness of their as-prepared TNC in most studies. With the same TiO₂ loading, better dispersiveness (i.e. thinner TiO₂ layer) would reduce the blockage of light irradiation, and would improve the diffusion rate of adsorbates to the TiO₂ photoactive sites by shortening the diffusion length. This also signifies the necessity of the dispersiveness screening of TiO₂ loading after the TNC preparation, which can be done by microscopic characterization techniques, such as TEM and SEM. Finally, a note should be taken preparation, which can be done by microscopic characterization techniques, such as TEM and SEM. Finally, a note should be taken of the dispersiveness of TiO₂ nanoparticles formation on a TNC: for instance, Takahashi et al. observed an undesirable formation of amorphous TiO₂ occurring at a layer thickness of less than 50 nm [42]. This would no doubt damage the photoactive quality of TNC resulant as well.

The location of TiO₂ loading, i.e. at the surface or in the bulk, is also anticipated to influence the photocatalytic activity to a certain extent. Due to the small size of TiO₂ nanoparticles, their loading could literally enter from macro- to micro-pores. Since penetration of either UV or visible light into the inside pores is less likely, especially for small pores (<5 nm), effective loading is preferably located on the surface, or in macropores in case of high TiO₂ loading. High loading in micropores also leads to plugging and will thus impair the adsorption capacity.

2.4. Influence of solvents and pH value

In some TNC preparations reported, alcohol solvents (such as 2-isopropional, ethanol, etc.) or their aqueous solution, were chosen mainly due to volatility higher than that of using water alone. This could facilitate the evaporation and the following drying treatments. Nevertheless, excessive use of alcohol or high alcohol-to-TiO₂ precursor volume ratio should be prevented, as it could shrink the body of colloidal formation and make it denser and less porous [43]. This could lead to poor crystallinity of TiO₂ nanoparticles formation at the later stage. As for using water alone, addition of a certain amount of acid is crucial to obtain a stable colloidal solution and to preserve the particles in their nano-sized form. This catalytic effect is brought about by the electrical charging of the hydroxide particles by proton adsorption, which hinders the gel agglomeration. Acid addition is also likely to have a potential linkage to the TiO₂ phase transition during the hydrolysis: Zhu et al. reported that high acid concentration (2.0 M) favored the formation of rutile phase TiO₂ during the hydrolysis of TiOSO₄·xH₂O (see Fig. 3) [44]. The follow-up investigations in this aspect are still coming. In terms of the acid type, HNO₃ is preferable to HCl due to avoiding the possible implication of an unfavorable Cl⁻ ion effect on TiO₂ crystal formation.

In parallel with its catalytic effect on TiO₂ colloidal formation, the addition of proper acids also manipulates the pH value of solvent. The pH requirement could vary to a great degree when impregnating the hydrolyzed TiO₂ precursor to different adsorbents. For example, when preparing a TNC on a zeolite substrate, pH should not be kept too low to avoid the potential acid-leaching of the zeolite and thus destruction of its porous crystal structure [45]. The structural change could affect not only the adsorption but also the photocatalytic activities of a zeolite-based TNC resultant. Xu and Langford reported a detrimental effect of lower zeolite crystallinity on the photocatalytic activity of their as-prepared zeolite TNC, although the adsorption of that alone was not significantly affected by the zeolite crystal change [19]. Detailed explanation of the former through structural investigation of the as-prepared TNC was absent in the study, though the authors speculated that it may be attributed to the lessen stabilizing effect of zeolite rigid framework on reactive species (i.e. OH⁻ and O₂⁻), and decreased oxygen adsorption on TNC, of which the latter is believed to be essential to the electron accepting process on the TiO₂.

2.5. Influence of post assembly treatments

As discussed previously, the photocatalytic activities of TiO₂ nanoparticles are closely correlated to their electronic (i.e. amount of charger carrier and its lifetime) and morphological properties (i.e. particle size, surface area and crystal phase). Post assembly treatment, such as drying and calcinations, are necessary to remove most of the organic residues on the surface and moisture, and also most likely have an impact on the photocatalytic activities of the resultant TNC. Generally, the processes involving high temperature steps (>500 °C) would be considered unfavorable for the impaired photocatalytic performance of TiO₂, because their surface areas decrease with temperature due to the grain (i.e. crystallite size) growth or nanoparticles agglomerating effect throughout the treatment process. In addition, high temperature (>70°C in air) facilitates the phase transition of TiO₂ from anatase-to-rutile crystalline phase, which is also not preferable for the preparation of efficient TNC. As a result, the recommended temperature when calcining TiO₂ gel alone should not be higher than 400 °C, where the anatase phase of TiO₂ is predominantly formed. However, a temperature that is too low (<200 °C) would also be detrimental to the quality of TiO₂ crystallinity, which is deeply related to its electronic properties (i.e. less and shorter charger carrier lifetimes) and certainly should be prevented. Nevertheless, aforementioned standards could be varied to a certain degree in presence of absorbent substrates. For example, Xu and Langford observed the presence of zeolites substrate shifted the TiO₂ phase transition temperature to a higher range and inhibited the growth of TiO₂ crystallites [19]. The authors attributed it to the crystallinity of zeolite, although a detailed explanation of the effect was lacking. Relatively few investigations have been undertaken of this aspect so far, so it certainly merits further research.
High temperatures also induce the loss of adsorption capacity on adsorbent side through surface or structural alterations. This may cause more damages to the overall performance of a TNC on DOC removal since it is mainly driven by the adsorption capacity. Especially when preparing an AC-based TNC, in addition to the temperature control, general practices also require protective gases, such as nitrogen, to avoid unnecessary carbon loss. Some of the ambient gases are also likely to affect the calcination temperature on TiO₂ crystal phase transition. These effects deserve a more comprehensive investigation. For example, using protective hydrogen gas alone reportedly confined the complete anatase-to-rutile phase transition temperature of a TiO₂ between 525 and 550 °C, which is much lower than that (700 °C) in the presence of air [46].

Compared to the investigations of calcination effects on the photocatalytic activities of TiO₂ nanoparticles, the drying process and its corresponding influence in the wet chemical preparation of TNC have received far less attention. However, as an improvement to the traditional procedure (i.e. air, <100 °C, atmospheric pressure), some advantages of drying under the supercritical conditions were indeed addressed in the literature. Such changes mainly affected the specific surface of TiO₂ nanoparticle resultants. It is well known that supercritical conditions would contribute to the maintaining of a pore structure identical to that in the gel due to the absence of surface tension [47]. One instance is that Boujday et al. reported a 23 times surface areas enlargement of the TiO₂ resultants through hydrolyzing a titanium isopropoxide precursor within their drying conditions (supercritical CO₂, >35 °C, 70 bar) [48]. Nevertheless, the augmentative effects on electronic properties of the resultants were somewhat compromised, as the charger carriers generated on the samples dried under supercritical condition were fewer and had shorter lifetimes. In addition, these observations were obtained in the absence of adsorbent substrates. Future efforts are needed on this particular aspect to justify this promising technique when preparing a TNC.

3. Current barriers and research opportunities in TNC literature for wastewater treatment

Among the concurrent efforts along with general practices of TNC preparations reviewed heretofore, several lab-scale testings of TiO₂ photocatalytic activity using various DOCs, such as phenol, methanol, dichloromethane, propyzamide, pyridine, propionaldehyde, 4-chlorophenol, etc., were also devised in these studies. Satisfactory results have been demonstrated, along with different adsorption and photocatalysis rates. However, due to non-identical operational conditions, i.e. light sources, intensity, concentration of the DOC, amount of TNCs used and apparatus design, these results do not allow a direct comparative cross-examining across different studies at this stage. Some other limitations regarding the TNC literature that needed to be addressed before TNC attains the commercial viability of TNC include:

1. The current experimental results are still a long way from continuous operation of adsorption and photocatalytic regeneration of TNC. In principle, photocatalytic regeneration of TNCs is a three-step process: DOC adsorbrates desorption from the adsorbents, diffusion to the photoactive sites and the photocatalytic decomposition by TiO₂ photocatalysts. As discussed in Section 2.1, photocatalytic decomposition process by TiO₂ requires much longer time compared to the adsorption of DOCs by the absorbents, and such are the desorption and diffusion process of adsorbed DOCs. These have affected its feasibility for commercial applications. Several possible improvements from the TNC design point of view has been suggested in Section 2, including reduced size of adsorbent substrates and improved dispersiveness of TiO₂ coating. From the operation point of view, there are also some practical improvements regarding this issue, including the introduction of proper external heat [49] or ultrasonic waves [50] to enhance the desorption and diffusion rate of most DOC adsorbates, and the addition of oxidizing inorganics such as hydrogen peroxides, ozone, ammonium persulphate, potassium bromate and peroxydisulphate [51–53] to supply more beneficial radicals to the photo reaction system. In addition, to inhibit the electron–hole recombination of TiO₂, oxygen and its steady-state concentration in the solution system will also have a profound effect on the photodecomposition rate under ambient conditions [54,55]. However, in the wake of these problems, the possible continuous operation would be more attractive for adsorbents with faster desorption properties and for those TNCs with weak affinity to the adsorbents.

2. Compared with using TiO₂ photocatalyst alone, one advantage of TNC is found to be its large ability to collect photodecomposed intermediates and to prevent possible secondary pollution, as illustrated in Fig. 4. However, this also gives an uncertainty in modeling of TNC photocatalysis kinetics because the ongoing photocatalytic reaction by TiO₂ likely occurs with both adsorbed reactants and ones in the solution. Previously, several experimental results indicated that photocatalytic reaction rates of various DOCs over illuminated TiO₂ fitted the Langmuir–Hinshelwood (L–H) model [56–61]:

$$\frac{dc}{dt} = \frac{kKC}{1 + KC}$$

where r is the photocatalysis rate of the reactant (mg/l min), C the concentration of the reactant (mg/l), t the illumination time, k the reaction rate constant (mg/l min), and K the adsorption coefficient of the reactant (l/mg). In terms of a TNC photocatalysis model, not only does the adsorption coefficient

![Fig. 4. Reaction mode of photo-induced mineralization of propyzamide substrate over naked TiO₂ (a) and TiO₂-loaded adsorbent (b) [22].](image-url)
of the reactant, $K$, have to adjust accordingly, but also the concentration of the reactant, $C$, should be replaced by a value with considerations of both adsorbed reactants and the ones left in solution. This value is also likely dependent on the diffusion rate from the adsorption sites to the photoactive sites. Given that most of current lab-scale TNC studies with DOCs were empirical, a mechanistic model that can address the kinetics between different working processes (i.e. adsorption, diffusion and photocatalysis) is yet to be developed, as this is only explicable by understanding the underpinning science.

It is well known that the band gap energy of TiO$_2$ is intrinsically wide, between 3.0 and 3.2 eV (3.0 for rutile and 3.2 for anatase). This means plain TiO$_2$ semiconductors only absorb a small portion (5%) of the solar spectrum in the UV region. Currently, it is of great interest to find ways that TNC could possess the ability of directly utilizing visible sunlight through modification of TiO$_2$ photocatalysts. Early attempts on visible-light sensitization of TiO$_2$ mainly involved the doping of transition metal elements [62–64], which, however, has the drawbacks of requiring intensive energy and expensive ion implantation facilities. The processes increase free charge carrier trapping in bound electron–hole pairs and tend to form charge carrier recombination centers. As a result, doped TiO$_2$ resultants suffer from thermally instability, possible photo-corrosion and harmful nature of the dopants [65–67]. Moreover importantly, most cationic dopants only result in limited band gap changes, and in some cases, do increase the light absorption, but not the photocatalytic activity. As a consequence, more significant advances in this field were achieved on doping TiO$_2$ photocatalyst with non-metallic or anionic elements such as carbon, sulfur, halides, phosphor and boron. This has been reflected readily in several recent reviews [68–70]. Asahi et al. first recognized the visible-light sensitivity of TiO$_2$ with a certain amount of nitrogen dopants [71] and attributed it to the band gap narrowing effect, which was resulted from the interaction between doped N (2p) and original O (2p) states. Now nitrogen has proven to be the most effective dopant due to its similar size to oxygen and low ionization energy [72]. Most recently, Burda et al. developed N-doped TiO$_2$ via a wet chemical method (titanium isopropoxide and triethylamine as Ti and N precursors) [73–75] and claimed it had no high temperature induced surface property changes. Fine control of the nitrogen doping level was attained with the possibility of high N-content (reportedly up to 8%) compared with other methods, e.g. the sputtering and implantation [76–78], high temperature sintering TiO$_2$ under N-containing atmosphere [79–81], etc. More importantly, it is envisaged that the future visible-light sensitive TNC could be achieved within a single wet chemical procedure without any extra preparation complexity and cost, as illustrated in Fig. 5.

4. Conclusions and recommendations for future work

Development of TNC and its wastewater treatment applications are still in the very early infancy. Highlights of this technique include the higher level of overall photoactivity compared to using suspension mixture of TiO$_2$ photocatalysts and adsorbents, a large capability of scavenging degradation intermediates and potentials of directly utilizing the low cost visible-light sources. For a TNC prepared via wet chemical impregnation, electronic properties (i.e. amount of charge carrier and its lifetime) and morphological properties (e.g. particle size, surface area and crystal phase) of TiO$_2$ in as-prepared resultants are largely dependant on the experimental conditions available during the synthesis. Collectively, efforts of TNC preparation and its potential TiO$_2$ visible-light sensitization via wet chemical impregnation carried out in the literature thus far have formed a useful database for developing future visible-light sensitive TNC. Based upon the literature available from this review, recommendations regarding future efforts can be mainly two-fold. On the experimental front, visible-light sensitive TNC prepared via a wet chemical procedure, especially N-doping, should be demonstrated in a timely fashion; on the theoretical front, given that most of lab-scale TNC studies with DOCs were empirical, a mechanistic model that can address the kinetics between different working processes (i.e. adsorption, diffusion and photocatalysis) within a TNC system is yet to be developed. The optimal design of TNC is only achievable by understanding the underpinning mechanisms of these processes and their synergistic interactions.

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