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TiO_2 and ZnO as Advanced Photocatalysts for Effective Dye Degradation in Textile Wastewater

TiO_2 in ZnO kot napredna fotokatalizatorja za učinkovito razgradnjo barvil v tekstilnih odpadnih vodah

***Scientific Review**/Pregledni znanstveni članek*

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Abstract

Textile wastewater, which consist of a complex mixture of synthetic dyes and other organic and inorganic compounds derived from various wet chemical textile processes, can have a harmful effect on the environment; therefore, it must be properly treated before being discharged into municipal wastewater treatment plants and natural water bodies. In this scientific review, the main physical, chemical and biological processes for the removal of dyes from textile wastewater are presented, focusing on photocatalysis, which is a promising advanced oxidation process. The mechanism of photocatalysis is described and the methods used to determine the efficiency of photocatalytic degradation of dyes are presented. Recent studies involving single photocatalytic treatments of real textile wastewaters in the presence of TiO_2 and ZnO as catalysts are presented. The advantages of combined processes of photocatalysis in conjunction with other chemical, physical and biological treatments to increase the efficiency of wastewater treatment are discussed. Accordingly, photocatalysis combined with H_2O_2, photocatalytic ozonation, a hybrid system of photocatalysis and membrane filtration, and coupled photocatalytic-biological processes are described.

Keywords: titanium dioxide, zinc oxide, photocatalysis, dye degradation, textile wastewater

Izvleček

Tekstilne odpadne vode, ki vključujejo kompleksno mešanico sintetičnih barvil in drugih organskih in anorganskih spojin, ki izhajajo iz različnih mokrih kemijskih tekstilnih postopkov, lahko škodljivo vplivajo na okolje, zato jih je potrebno pred izpustom v komunalne čistilne naprave in naravno vodno okolje ustrezno očistiti. V preglednem članku so predstavljeni najpomembnejši fizikalni, kemijski in biološki postopki za odstranitev barvil iz tekstilnih odpadnih vod s poudarkom na fotokatalizi, ki je obetavni napredni oksidacijski proces. Opisan je mehanizem fotokatalize in predstavljene so metode za določitev učinkovitosti fotokatalitske razgradnje barvil. Izpostavljene so najsodobnejše raziskave, ki vključujejo samostojno fotokatalitsko obdelavo realnih tekstilnih odpadnih voda v prisotnosti TiO_2 in ZnO kot fotokatalizatorjev. Predstavljene so prednosti kombiniranih postopkov, ki vključujejo fotokatalizo v povezavi z drugimi kemijskimi, fizikalnimi in biološkimi procesi. Med njimi so opisani fotokataliza v kombinaciji s H_2O_2, fotokatalitska ozonacija, hibridni sistem fotokatalize in membranske filtracije ter združeni fotokatalitski-biološki procesi.

Ključne besede: titanov dioksid, cinkov oksid, fotokataliza, razgradnja barvila, tekstilna odpadna voda

1 Introduction

The textile industry is considered one of the largest water pollutants and is responsible for about 20% of global clean water pollution from various wet chemical production processes [1–3]. Wastewaters from pretreatment, dyeing, printing and finishing processes are highly polluted by complex mixtures of synthetic dyes and pigments, finishing agents, auxiliaries, heavy metals, surfactants and other chemicals, which can result in harmful effluents in the environment [4–6]. Among the effluents, synthetic dyes are classified as one of the most hazardous pollutants as they are potentially toxic, non-biodegradable and persistent [7–9]. Due to light absorption, the presence of dyes in wastewater reduces sunlight penetration, which negatively affects flora and fauna [4, 8]. Accordingly, the removal/degradation of dyes from textile wastewater is a challenging research topic for which various physical, chemical and biological processes, and their combinations have been developed and introduced (Figure 1) [4–7, 9–12].

Physical methods for removing dyes from textile effluents primarily include adsorption and membrane filtration, in which dye removal is advantageously accomplished by forces such as electrical attraction, gravity, and Van der Waals forces or physical barriers [6]. In the adsorption method, numerous suitable adsorbents are used, the best known of which is activated carbon. In addition, polymer resins and low-cost agricultural and industrial by-products such as peat, chitin, clays and fly ash are used. Membrane filtration includes microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Since nanofiltration is more effective than microfiltration and ultrafiltration, reverse osmosis is the most effective as it retains almost all substances from water [6].

Chemical methods include coagulation/flocculation, electrochemical processes, classical oxidation and advanced oxidation processes (AOP) [4, 6, 13]. Coagulation/flocculation is commonly used to destabilise particles with various coagulants such as inorganic coagulants, inorganic-organic double coagulants and synthetic polymer flocculants. A complete decolourisation is difficult to achieve with this method. Inorganic coagulants such as iron and aluminium salts are widely used in the treatment of textile wastewater; however, they have negative effects on the environment and human health [6, 14]. There are various electrochemical processes such as electrokinetic coagulation, electroflotation, electrodecantation and electrooxidation [15]. Electrons are used

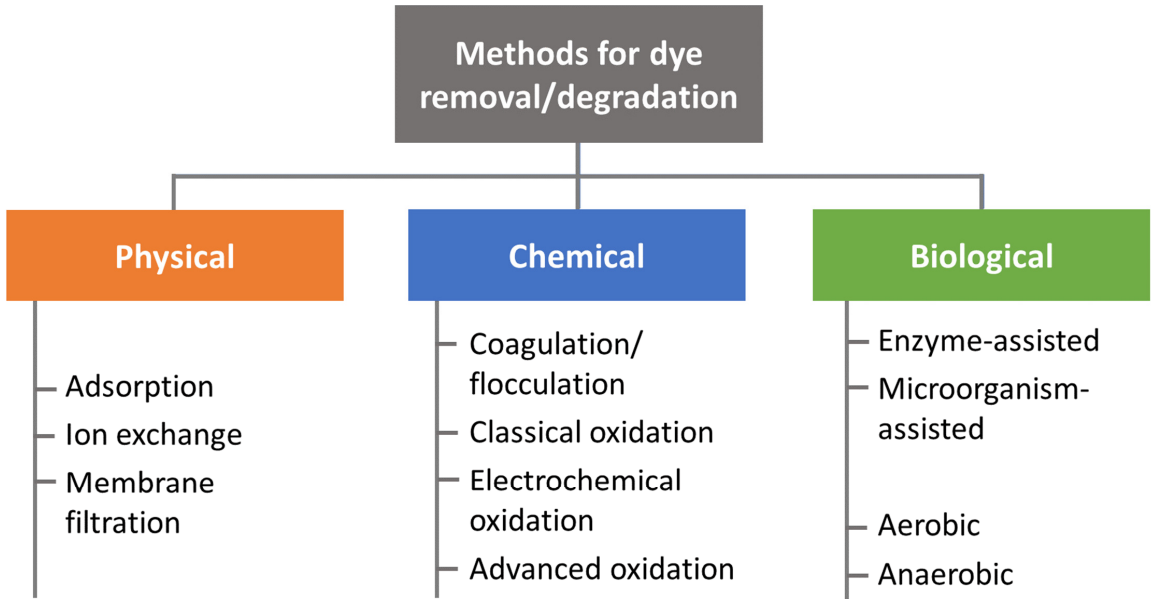

Figure 1: Methods for removal/degradation of dyes from textile wastewater

as "primary reagents," which are referred to as "clean reagents". In most cases, high concentrations of supporting electrolytes, especially NaCl, are required to achieve acceptable results; however, this leads to the generation of large amounts of environmentally harmful products [6, 15]. In the classical oxidation method, ozone (O_3), hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), chlorine dioxide (ClO_2), chlorine (Cl_2), sodium hypochlorite (NaOCl) and oxygen (O_2) are used as oxidising agents that change the chemical composition of the compound [13]. In advanced oxidation processes (AOP), reactive oxygen species (ROS) such as hydroxyl radicals (•OH) and superoxide radicals ($•O_2^-$) are usually generated and utilised. These include various methods such as the photocatalytic ozonation, Fenton process, photo-, electro- and sono-Fenton processes, and photocatalysis [2, 6, 13, 16–19]. The best known advanced oxidation process is the Fenton process, which uses a mixture of ferrous iron (typically Fe(II)) and hydrogen peroxide (H_2O_2) to generate •OH in an acidic medium. However, the Fenton process can produce chemical sludges that must be properly disposed of. Compared to the Fenton process, the advantage of the photo-, electro- and sono-Fenton processes, which combine the Fenton reaction with light radiation, electrochemical processes and ultrasound, respectively, is a higher pollutant removal rate with a lower iron dose [19–24]. Photocatalysis is considered a sustainable treatment process for the degradation of dyes from textile wastewater in the presence of photocatalysts. In this process, high efficiency of photocatalytic degradation can be achieved under mild reaction conditions in the presence of oxygen and water from the atmosphere and UV/visible light radiation without the formation of secondary impurities as the dyes are degraded to carbon dioxide and water via intermediates [2, 25].

Biological processes use biomaterials such as industrial enzymes and microorganisms for dye degradation. They can be conducted under aerobic or anaerobic conditions. These processes consist of two main steps, i.e. adsorption of dyes onto biomaterials and their degradation to non-toxic products. While peroxidase and azo reductase are the most effective industrial enzymes, bacteria, fungi, algae and yeasts are used as microorganisms. Due to the high biodegradability of biomaterials and low operating costs, biological processes are considered the most promising treatment methods for textile wastewater from the environmental and economic perspective [4, 6, 11]. Despite many advantages of biological processes, there are still shortcomings, including the non-degradability of biomass-bound dyes and the difficult adsorption of some types of dyes such as azo and reactive dyes [6, 11].

2 Photocatalysis as AOP for synthetic dye degradation

Photocatalysis is a promising AOP that takes place in the presence of a photocatalyst, which is activated by light [16]. Due to its environmental friendliness and high efficiency, this process has attracted much attention in various scientific fields, including environmental remediation, where various organic and inorganic pollutants can be photocatalytically degraded. This also applies to dyes contained in textile wastewater. Various photocatalysts can be used in photocatalysis, including metal semiconductors such as TiO_2 and ZnO nanoparticles, which are very promising due to their excellent morphological, chemical and optical properties [26]. The efficiency of photocatalysis is directly influenced by the design of the photocatalyst, where the surface-to-volume ratio of the particles, their crystallinity, surface modifications and light absorption capacity play an important role.

2.1 Mechanism of semiconductor photocatalysis

The mechanism of semiconductor photocatalysis is shown in Figure 2 and can be explained as follows [27–29]: when a semiconductor absorbs a photon

with the energy equal to or higher than the bandgap energy (E_g) under irradiation with UV or visible light, the electrons in the valence band (VB) are excited into the vacant conduction band (CB), leaving holes in VB. The resulting free electrons and holes can migrate to the surface of the semiconductor, where they participate in the redox reactions. The electrons react with atmospheric oxygen to form $\bullet O_2^-$ in the reduction reaction and the holes react with absorbed water to form •OH in the oxidation reaction. Both reduction and oxidation take place when the edge of the semiconductor's conduction band is more negative and the edge of its valence band is more positive than the standard redox potential of the reactions. The formation of $\bullet O_2^-$ and •OH, which are the main ROS formed at the semiconductor surface, is crucial for the photocatalytic activity of the semiconductor since ROS can subsequently react with organic pollutants in the oxidation reaction and degrade them to carbon dioxide and water via intermediate compounds. At the same time, holes with a high oxidation potential can directly cause the oxidation of pollutants [25, 29–38]. Nevertheless, the recombination of electrons and holes that can occur during their migration to the semiconductor surface is an undesirable process as it reduces the photocatalytic efficiency of the semiconductor [38].

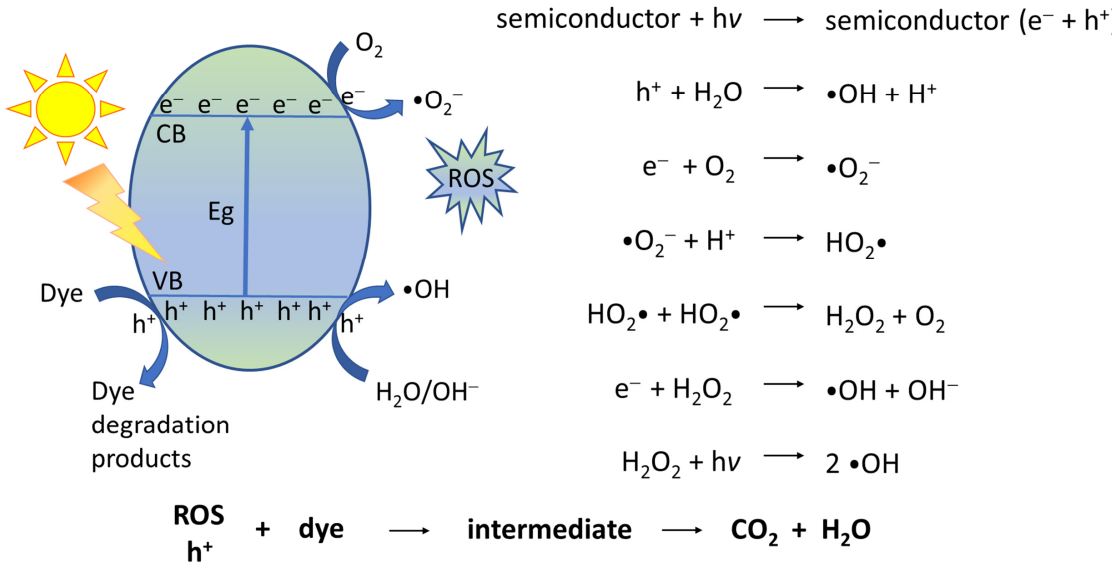

Figure 2: Schematic representation of fundamental mechanism of photocatalytic activity of semiconductors and proposed surface reactions; e^- is electron, h^+ is hole

To improve the separation of electrons and holes and thus the photocatalytic efficiency, semiconductors are doped with different metal and nonmetal ions, loaded with noble metals and coupled with other semiconductors to form heterojunctions [38, 39]. Doping with metal and nonmetal ions is based on the incorporation of host materials into the semiconductor crystal lattice to change the geometric and electronic structure and modulate the charge carrier density in the doped semiconductor. The doped ions introduce additional localised energy levels to trap electrons or holes that immobilise the charge carriers, hence reducing the recombination rate. As the dopant energy levels are formed above the VB or below the CB edge positions in the semiconductor, they decrease the bang gap energy and consequently increase the visible light absorption [40–42]. The loading of semiconductors with noble metals enables the formation of the Schottky-based heterojunction, typical of the semiconductor-metal system, where electrons are easily transferred from the CB of the semiconductor to the metal, which acts

as an electron trapper. By creating a Schottky barrier, the separation of photoinduced charge carriers is maximised and their recombination is prevented [38]. At the same time, visible light excites electrons in the metal, leading to surface plasmon resonance that further enhances photocatalytic activity [43]. The fabrication of semiconductor-semiconductor heterojunctions is one of the most effective strategies to enhance the photocatalytic performance under visible light. The mechanism of photogenerated charge transfer is very complex and depends on the design of the heterojunction. However, the most photocatalytically active heterojunctions are those in which the electrons and holes located in the CB and VB with lower redox power, respectively, are recombined, while ROS are formed in the more energetically favourable CB and VB of semiconductors [44].

2.2 Determination of photocatalytic degradation efficiency

The efficiency of the photocatalytic degradation of dyes can be determined from the degradation rate of the dye [20, 45–57], where the concentration ratio is calculated as follows:

$$Dye\ concentration\ ratio = \frac{c_t}{c_0} \quad (1)$$

In Equation 1, c_t is the dye concentration at a given time of irradiation and c_0 is the initial dye concentration. The lower the dye concentration ratio at a given time, the higher the dye degradation.

The dye degradation efficiency can also be calculated as the percentage of dye degradation as follows [45–47, 49–51, 57, 58]:

$$Dye\ degradation\ percentage = \frac{c_0 - c_t}{c_0} \times 100\ (\%) \quad (2)$$

The higher the dye degradation percentage, the higher the degradation efficiency.

The apparent rate constant, K_{app}, of the photocatalytic reaction can also be a measure of the efficiency of the photocatalytic degradation of dyes, where pseudo first-order kinetics is used as follows [46, 48, 50, 51, 58]:

$$ln\ \frac{c_t}{c_0} = -\ K_{app} \cdot t\ (\mathrm{min}^{-1}) \quad (3)$$

In the treatment of real textile industry wastewater, the efficiency of dye removal/degradation is usually discussed based on the measurements of total organic carbon (TOC) and chemical oxygen demand (COD) measurements before and after wastewater treatment. In this case, the dye concentrations c_0 and c_t in Equation 2 are replaced with TOC_0 and TOC_t or COD_0 and COD_t, and the percentage of TOC or COD removal is calculated as a measure of the mineralisation efficiency of textile wastewater [12, 49, 52].

3 Titanium dioxide and zinc oxide as photocatalysts for dye degradation in real textile wastewater

In the field of textiles, titanium dioxide (TiO_2) and zinc oxide (ZnO) have emerged as the most important semiconductor nanomaterials with a variety of applications for the functionalisation of textile substrates as well as for the effective photocatalytic degradation of various dyes in an aqueous solution [3, 31, 32, 59–61]. The main advantages of TiO_2 and ZnO are their thermal, chemical and photochemical stability, non-toxicity, biocompatibility and low price [2, 32, 62–64].

TiO_2 and ZnO are n-type semiconductors with E_g of about 3.2 eV, which limits their photocatalytic activity to irradiation with UV light [65, 66]. Accordingly, surface modification of TiO_2 and ZnO by doping with metal and non-metal ions, loading with noble metals, such as Ag, coupling with other semiconductors, and dye sensitisation is of great importance to lower E_g and thus increase the photocatalytic activity in visible light [40, 67].

In the process of photocatalytic degradation of dyes in an aqueous solution, TiO_2- and ZnO-based nanomaterials were mostly used as photocatalysts in powder form, which were mixed into the dye solution under the study [22, 49, 50, 54, 68–75] and removed after the photocatalytic treatment usually with centrifugation [22, 49, 50, 71, 74, 75] or filtration [68–70, 72, 73]. In addition to powder form, TiO_2 was applied to various substrates such as transparent glass, glazed ceramic tile and stainless steel by doctor blade technique and used in photocatalytic reactors [45]. In another study, TiO_2 nanotubes were prepared on titanium foil by anodization at 48 V for 2 hours followed by iron doping with hydrothermal treatment at 150 °C for 3 hours and annealing at 550 °C for 1.5 hours [52]. In addition, TiO_2 and ZnO were incorporated into glass-ceramic materials with a conventional melting technique of glass batch followed by heat treatment at 450 °C for 10 hours and used in a batch reactor [76]. Ultra long nanofibers, including the $Bi_2Ti_4O_{11}/TiO_2$ heterojunction, were also produced via electrospinning and used as photocatalyst [77].

It should be noted that the efficiency of photocatalytic degradation of dye solutions is influenced not only by the structure of the photocatalyst, but also by the composition and quality of the wastewater [52]. A model dye solution containing a single synthetic dye at an appropriate concentration cannot simulate the real textile wastewater, which consists of a mixture of synthetic dyes of different chemical structure and several other organic and inorganic substances that can strongly influence the pH, TOC and COD of the wastewater; moreover, the parameters are highly variable [78]. In addition, these pollutants can significantly reduce the degradation rate of dyes by hindering the photocatalytic efficiency of semiconductors. Therefore, the study of photocatalysis as an AOP for the treatment of real textile wastewater from the textile industry is of great importance and represents a challenging research topic. The performance of TiO_2 and ZnO as photocatalysts in single AOP or in combination with other chemical, physical and biological processes for dye removal in real textile wastewater is summarised in Table 1.

Table 1: Treatment systems, photocatalysts, pollutants and experimental performance

Treatment system	Photocatalysts	Pollutant	Experimental performance	Ref.
Single photocatalysis	TiO_2, Al, F co-doped TiO_2 nanoparticles	Wastewater of textile factory, Erode, Tamilnadu, India	0.0125 mM catalyst in 10 ml wastewater, irradiation with visible light for 120 minutes	79
	Fe-doped TiO_2 nanotubes on titanium foil	Artificially compounded textile wastewater	2.5 × 5 cm^2 foil as photocatalyst in 5 mg/L Congo red dye in wastewater, irradiation with visible light for 180 minutes	52
	ZnO quantum dots of different size	Wastewater of dyehouse with pH in range of 6.9, Egypt	0.1 g catalyst in 100 ml wastewater, direct sunlight for 6 hours per day (9 am to 3 pm) for 6 months	81
Photocatalysis in combination with another AOP	TiO_2 nanoparticles	Wastewater from different textile industries in Ghaziabad and Gautam Buddha Nagar districts, Uttar Pradesh, India	TiO_2 at various concentrations (1.5 g/L to 20.0 g/L) in 100 mg/L Remazol Red in wastewater without and in presence of H_2O_2 of different concentrations, irradiation with UV light for 60 minutes	20
	Cd-doped ZnO nanoparticles	Wastewater from dyehouse near Erode, Tamilnadu, India	Cd-doped ZnO at different concentrations (0 to 1 g/L) and pH values (3 to 9) in 500 ml of wastewater irradiation with UV light for 240 minutes in presence of O_3 of different dose	18

Continuation of Table 1

Treatment system	Photocatalysts	Pollutant	Experimental performance	Ref.
Photocatalysis in combination with membrane filtration	Polyethylene glycol capped ZnO nanoparticles	Wastewater from textile factory performing dyeing, printing and finishing in Johor, Malaysia	Photocatalysis (0.08–0.30 g/L photocatalyst and pH of 4–13) for 240 minutes under UV irradiation followed by membrane ultrafiltration	83
Photocatalysis in combination with biological treatment	TiO_2, ZnO nanoparticles	Wastewater from dyehouse in Santa Catarina, Brazil	Photocatalysis under UV light irradiation for 120 minutes (150 mg of catalyst in 250 ml of wastewater) followed by aerobic bioprocess for 48 hours	22
	ZnO/polypyrrole nanocomposite	Wastewater from Gama S. A., textile industry in Mar del Plata, Argentina	Biological treatment for 96 hours followed by photocatalysis (0.5–2.0 g/L catalyst in 200 ml of wastewater) for 60 minutes	84

Table 1 shows that there are very few studies dealing with the photocatalysis of real textile wastewater. In these studies, TiO_2 and ZnO are used in a single AOP or in combination with other chemical, physical and biological processes. These processes are very complex and therefore difficult to compare as they differ in terms of chemical structure, morphology and concentration of the photocatalyst, the composition of the industrial wastewater and the experimental performances and conditions. They are presented in the following sections.

3.1 Photocatalysis as single AOP

Photocatalysis in the presence of TiO_2 and ZnO as semiconductor photocatalysts has already shown promise for photodegradation and mineralisation of real textile wastewater. The efficiency of photocatalysis is influenced by several factors, of which the structure of the photocatalyst and the composition of wastewater have been studied in detail.

3.1.1 TiO_2 versus Al and F co-doped TiO_2

Recently, the photocatalytic degradation of real textile wastewater (TEWW) compared to the dye methyl orange (MO) was studied using TiO_2 and aluminium (Al) and fluorine (F) co-doped TiO_2 (TAF10) nanoparticles under visible light irradiation (Figure 3) [79].

The results show that the absorbance of both the MO solution and TEWW decreased with increasing irradiation time, indicating an efficient decolourisation of the dye by both photocatalysts. It is also evident that the degradation efficiency is affected by both the dye solution and the structure of the photocatalyst. A comparison of the spectra in Figure 3a and Figure 3b shows that, as expected, the photocatalytic activity of TAF10 was higher than that of TiO_2 due to the co-doping of Al and F in TiO_2, resulting in an almost complete decolourisation of MO after 120 minutes of irradiation. This result was also confirmed by the calculated apparent rate constant of MO,

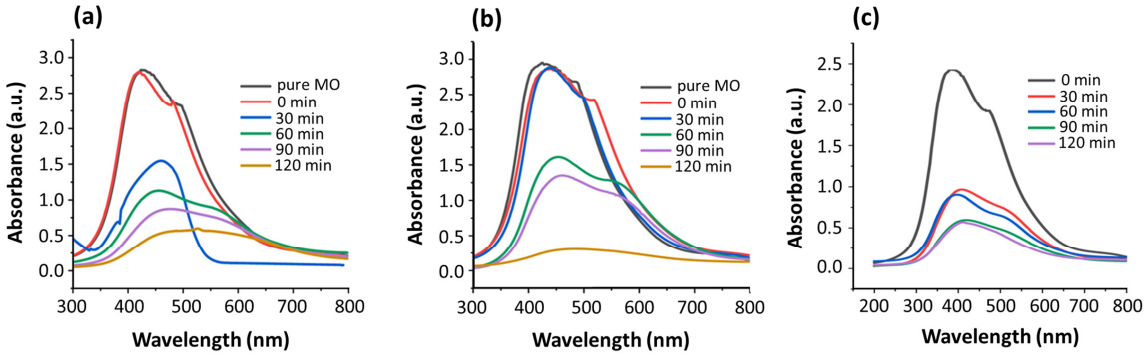

Figure 3: Photocatalytic degradation of MO dye with TiO_2 (a) and TAF10 (b) and of TEWW (c) with TAF10 (reprinted with permission from [79]; Copyright 2022, Elsevier)

which was higher for TAF10 (K_{app} = 0.0174 min^{-1}) than for TiO_2 (K_{app} = 0.0126 min^{-1}). Moreover, the efficiency of the TEWW degradation with TAF10 during the first hour of irradiation was much higher than that of MO; however, the efficiency decreased significantly during the second hour of irradiation (Figure 3c), resulting in the Kapp value of TEWW of 0.0134 min^{-1}, which is lower compared to the K_{app} value of MO obtained with the same photocatalyst.

3.1.2 Fe-doped TiO_2

To investigate the effect of chemical additives used in different steps of textile chemical processes on the photocatalytic removal and mineralisation efficiency of the dye Congo Red (CR), the real textile wastewater was imitated by adding glucose as a desizing and reducing agent, sodium carbonate as a scouring agent, ferric chloride as a colouring agent, magnesium sulphate as a printing agent and ammonium chloride as a finishing agent to the CR solution (Figure 4) [52]. For this purpose, iron-doped titanium dioxide nanotubes (Fe–TiO_2) were used as the photocatalyst and the batch experiments were carried out in the laboratory photoreactor under visible light irradiation for 180 minutes after the adsorption-desorption equilibrium was reached in the dark. The

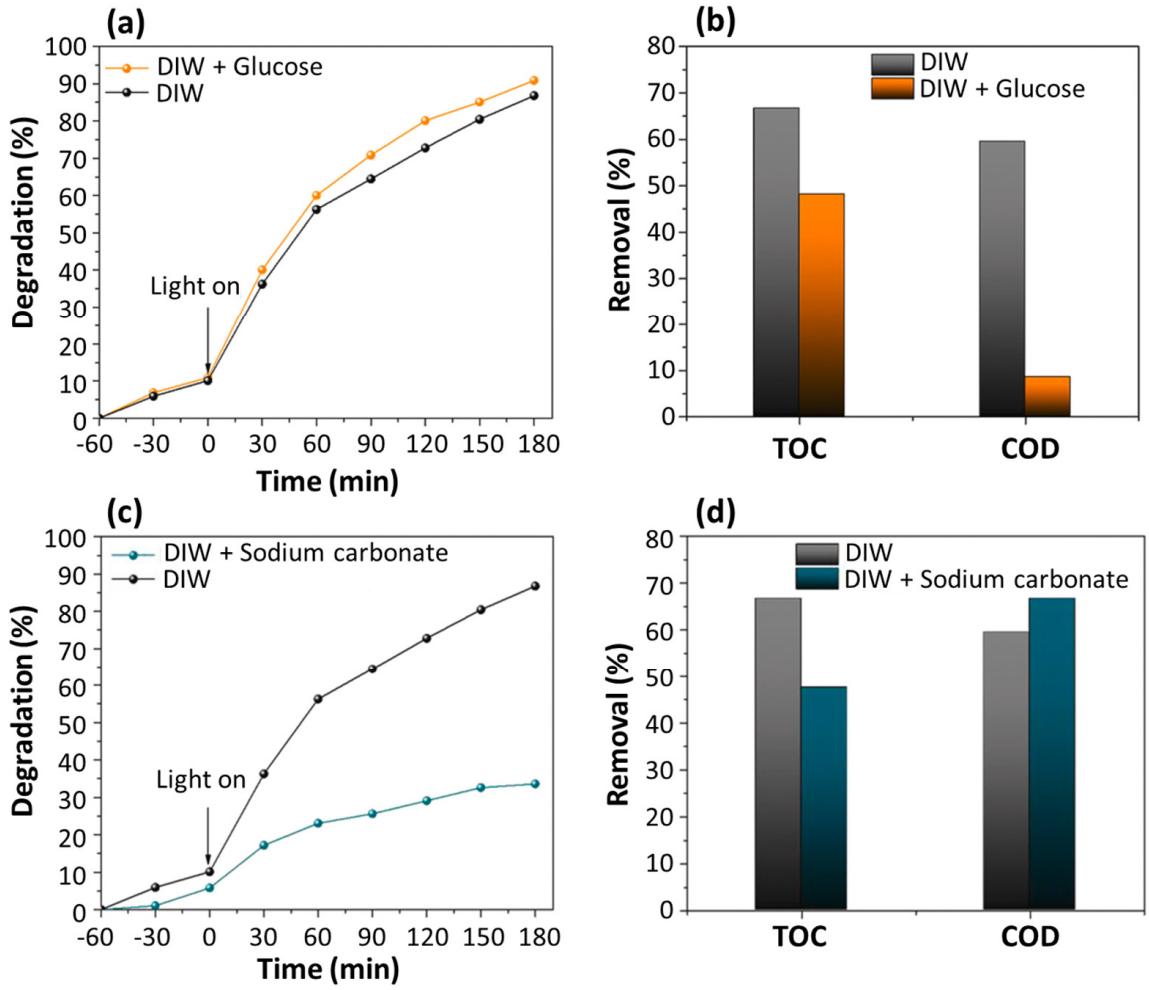

Figure 4: Impacts of glucose on dye degradation efficiency of CR (a) and removal efficiency of TOC and COD (b); impacts of sodium carbonate on degradation efficiency of CR (c) and removal efficiency of TOC and COD (d) (concentrations: CR = 5 mg/L, Glucose = 500 mg/L Sodium carbonate = 500 mg/L); DIW stands for deionised water (reprinted with permission from [52]; Copyright 2021, Elsevier)

results show that the degree of the CR photodegradation increased with the irradiation time and that the structure of the additives directly affected the photodegradation efficiency.

For example, the addition of a small amount of glucose to the CR solution did not hinder the efficiency of the photocatalytic degradation of CR, it even improved it (Figure 4a). The most reasonable explanation for this phenomenon was that glucose acts as a co-substrate that undergoes the oxidation reaction and thus affects the degradation of CR. It is believed that glucose acts as a scavenger of the photoinduced holes during the photocatalytic reaction and prevents the recombination of electron-hole pairs on the Fe–TiO_2 nanotubes. At the same time, the oxidation of glucose by holes did not hinder the photodegradation of CR, since the main ROS for the oxidation of CR was •OH, as shown by the results of the degradation mechanism. In contrast, the addition of glucose to the CR solution did not positively affect the removal of TOC and COD, as the presence of glucose decreased TOC removal by 19% and COD removal by 50% (Figure 4b).

The presence of sodium carbonate in the CR solution significantly delayed the photodegradation of CR, which dropped from 86% to 34% after 180 minutes of irradiation (Figure 4c). The reason for this phenomenon was attributed to the combination of the ability of carbonate ions to scavenge •OH and the competitive adsorption of carbonate ions on the catalyst surface and blocking of the active sites [52, 80]. The effect of sodium carbonate on TOC and COD removal efficiency was opposite. While TOC removal decreased with the addition of sodium carbonate, COD removal increased (Figure 4d). The decrease in the TOC removal efficiency was related to the lower CR degradation in the presence of sodium carbonate. However, the concomitant increase in COD removal suggests that sodium carbonate triggered the decomposition of inorganic compounds in the solution, resulting in a decrease in COD, but not TOC [52].

3.1.3 ZnO of different morphologies

To investigate the photodegradation efficiency of a real industrial wastewater from an Egyptian dye factory under sunlight irradiation, four ZnO samples of different morphologies and sizes were used for the experiment, including two ZnO quantum dots (QD) with the average sizes of 7.1 nm and 9.8 nm, and two ZnO nanoparticles (Nano) with the average sizes of 13.5 nm and 34 nm (Figure 5) [81]. Commercial ZnO powder was used as a reference. The experiments were conducted for 6 hours (from 9 am to 3 pm) on different study days from May to October 2018, and the solar photocatalytic activity of the ZnO samples was investigated by determining COD before and after the degradation experiment.

The results show that the COD values of real industrial wastewater before the photocatalytic experiments ranged from 4985 mg/L to 6867 mg/L, regardless of the study date, and that the COD values decreased in the presence of ZnO samples after 6 hours of irradiation (Figure 5a). It is also evident that the COD removal increased with the decrease of the ZnO particle size, indicating the effectiveness of the size effect of ZnO QDs on the photodegradation processes. The reusability of ZnO QDs and Nano ZnO for 8 times in the photodegradation process of wastewater resulted in a decrease in the photodegradation rate, and only the mineralisation efficiency achieved by ZnO QDs with the particle size of 7.1 nm stayed below the COD limit after the 8th recycling process (Figure 5b). It is assumed that the size of the photocatalyst increases during the recycling process, which is a consequence of the accumulation of photocatalysts with repeated use.

Research shows that doping TiO_2 with metal and non-metal ions and reducing ZnO particle size significantly increase the efficiency of the wastewater photodegradation process. It is also obvious that the photocatalytic degradation of wastewater is directly affected by the chemical additives present. If the additive ions can scavenge ROS, the photocatalytic process will be significantly hindered.

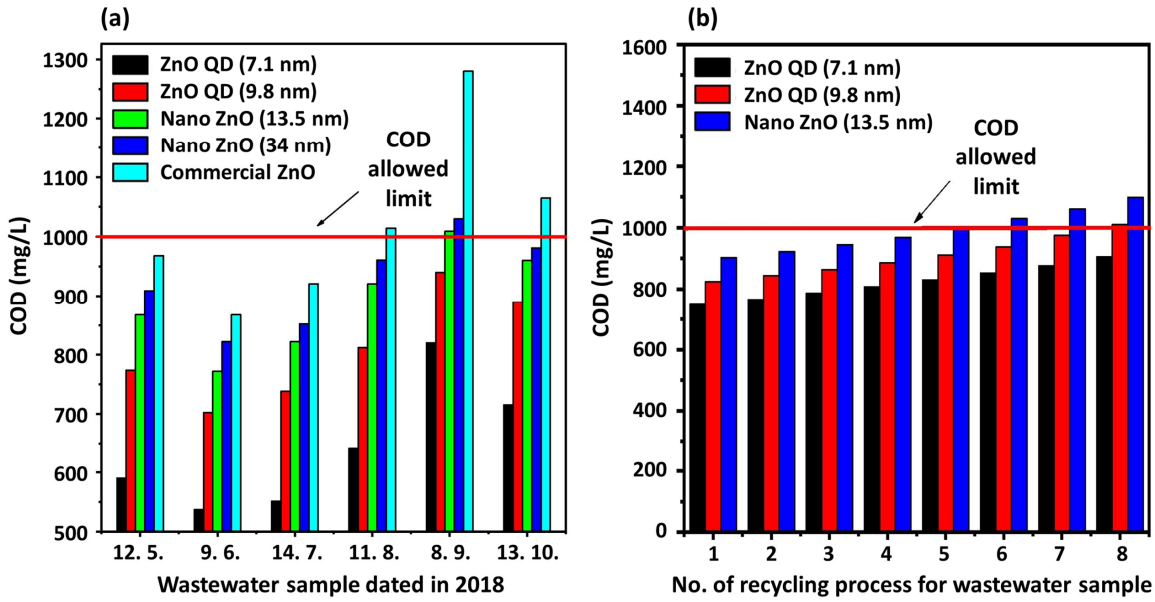

Figure 5: COD limits and situation of real industrial wastewater for six months using ZnO QDs, Nano ZnO and commercial ZnO during photocatalysis by sunlight (a); COD limits for recycling process of real industrial wastewater in October 2019 in presence of ZnO NDs and Nano ZnO during photocatalysis by sunlight (b) (reprinted with permission from [81]; Copyright 2020, Elsevier)

3.2 Photocatalysis in combination with other chemical, physical and biological processes

To increase the efficiency of wastewater treatment, photocatalysis has already been advantageously combined with other chemical, physical and biological processes. A combination of different processes for wastewater treatment offers several advantages over single treatments, as certain process combinations, their proper integration and optimisation can create the synergistic effect in their performance that is critical for efficient, versatile, scalable, cost-effective and environmentally sound wastewater treatment.

3.2.1 TiO_2 in combination with H_2O_2 versus photo-Fenton

To study the photodegradation activity of the dye Remazol Red (RR) in textile industry wastewater, a nanosized TiO_2 photocatalyst was used in combination with H_2O_2 under UV irradiation, and the results were compared with the photo-Fenton process as a rapid and cost-effective AOP [20]. The degree of dye degradation was calculated based on the initial and final TOC values and presented as TOC removal (Figure 6).

The results show that the presence of 5 mM H_2O_2 increased the photocatalytic activity of TiO_2 compared with that obtained in the absence of H_2O_2 and that the photocatalytic activity also increased when the concentration of TiO_2 increased from 0.20 g/L to 0.50 g/L (Figure 6a). This resulted in an RR dye degradation efficiency of 90% in 210 minutes in the presence of 0.5 g/L TiO_2 and 5 mM H_2O_2. UV irradiation is thought to cause photolysis of H_2O_2, generating additional •OH radicals that have a synergistic effect on the photocatalytic activity of TiO_2 and consequently on the photodegradation of the RR dye. A further increase in the TiO_2 concentration to 1.0 g/L increased the rate of dye degradation and resulted in an almost complete degradation (≈ 98%) in 60 minutes. However, a comparison of these results with the RR dye degradation in the photo-Fenton treatment revealed that a complete dye degradation (100%)

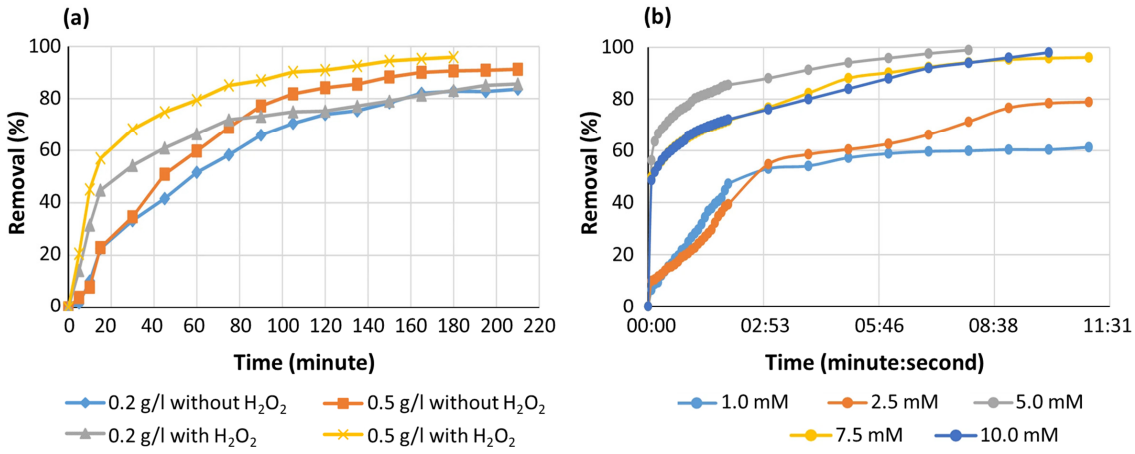

Figure 6: Photocatalytic degradation of RR dye with TiO_2 in presence and absence of H_2O_2 (a); photo-Fenton treatment of RR dye at Fe^{2+} concentration varying H_2O_2 concentration (mM) and pH 3.0 (b) (reprinted with permission from [20]; Copyright 2021, Springer)

was achieved in the experiment with 0.5 mM Fe^{2+} and 5.0 mM H_2O_2 at pH 3 in only 8 minutes (Figure 6b). An economic comparison of the two processes also shows that the photo-Fenton process is not only faster, but also less expensive.

3.2.2 Cd-doped ZnO in combination with O_3

In another study, photocatalytic ozonation (PCO), which integrates photocatalysis in the presence of ozonation, was described as an effective approach for the degradation of real textile wastewater under UV irradiation (Figure 7) [18]. For this purpose, ZnO nanocatalyst doped with cadmium (Cd–ZnO) was synthesised and used in a photoreactor connected to an ozone (O_3) generator. The operating parameters such as O_3 dose, pH, and Cd–ZnO amount were studied to achieve the optimal conditions for PCO, i.e. O_3 dose of 0.44 g/h, pH of 7 and 0.2 g/L Cd–ZnO. The efficiency of the mineralisation of textile wastewater with PCO (Cd–ZnO/UV/O_3) was determined based on COD determination at different times of wastewater treatment and compared with that of separate photocatalysis (Cd–ZnO/UV) and ozonation (O_3/UV) processes (Figure 7a).

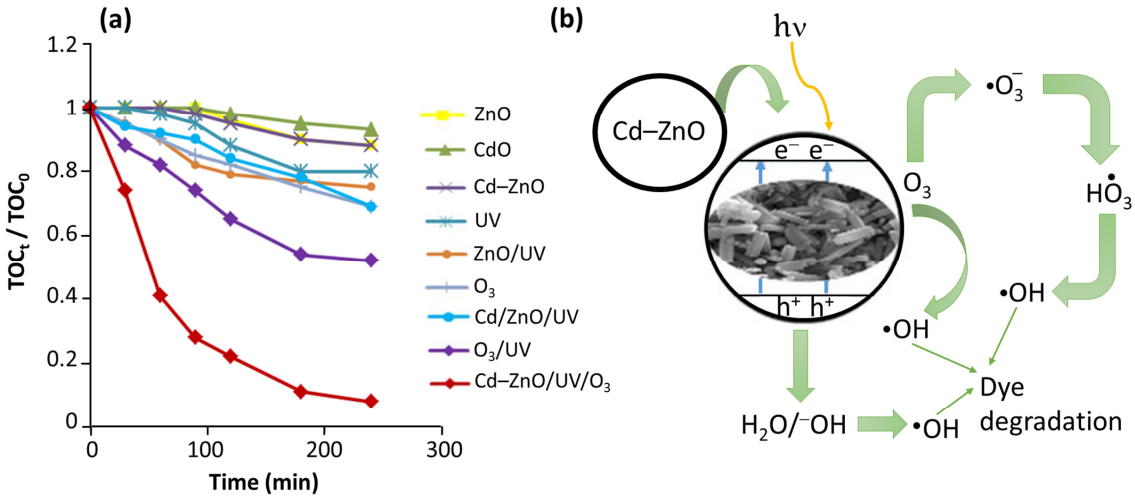

Figure 7: Mineralisation of textile wastewater with different processes (a); mechanism of Cd–ZnO/UV/O_3 for degradation of textile wastewater (b) (reprinted with permission from [18]; Copyright 2019, OIP Publishing)

The results show that the mineralisation rate observed with Cd–ZnO/UV/O_3 was by 4.2 times and 3.5 times higher than that of Cd–ZnO/UV and O_3/UV, respectively, indicating a synergistic effect between O_3 and Cd–ZnO/UV in PCO. This was due to the efficient trapping of generated electrons with O_3, resulting in the formation of ozonide radical anions ($\bullet O_3^-$). The radicals react rapidly with protons in the solution to form perhydroxyl radicals ($HO_3\bullet$), which then contribute to the formation of •OH (Figure 7b). Due to the more efficient trapping of photogenerated electrons with O_3, a recombination between holes and electrons is minimised, leading to the formation of a larger number of •OH, which accelerates the photocatalytic reaction [82].

3.2.3 Polyethylene glycol capped ZnO in combination with membrane filtration

A membrane photocatalytic reactor (MPR) (Figure 8a), which is a hybrid system of photocatalysis process and membrane filtration system, was used as an environmentally friendly approach for industrial textile wastewater treatment [83]. In MPR, the photocatalytic degradation of the wastewater was performed under UV-C irradiation in the photocatalytic reactor in the presence of polyethylene glycol capped ZnO (ZnO-PEG) nanoparticles as the initial treatment, followed by filtration through the polypiperazine-amide (PPA) tight ultrafiltration membrane (UF-PPA). The photocatalytic efficiency of the ZnO-PEG nanoparticles was estimated by analysing the flux decline during membrane filtration, where the normalised flux was calculated as the ratio between wastewater flux and pure water flux.

The results show that a photocatalytic degradation of wastewater with ZnO-PEG significantly reduced the pollutants filtered by the UF-PPA membrane, which prevented pore plugging of the

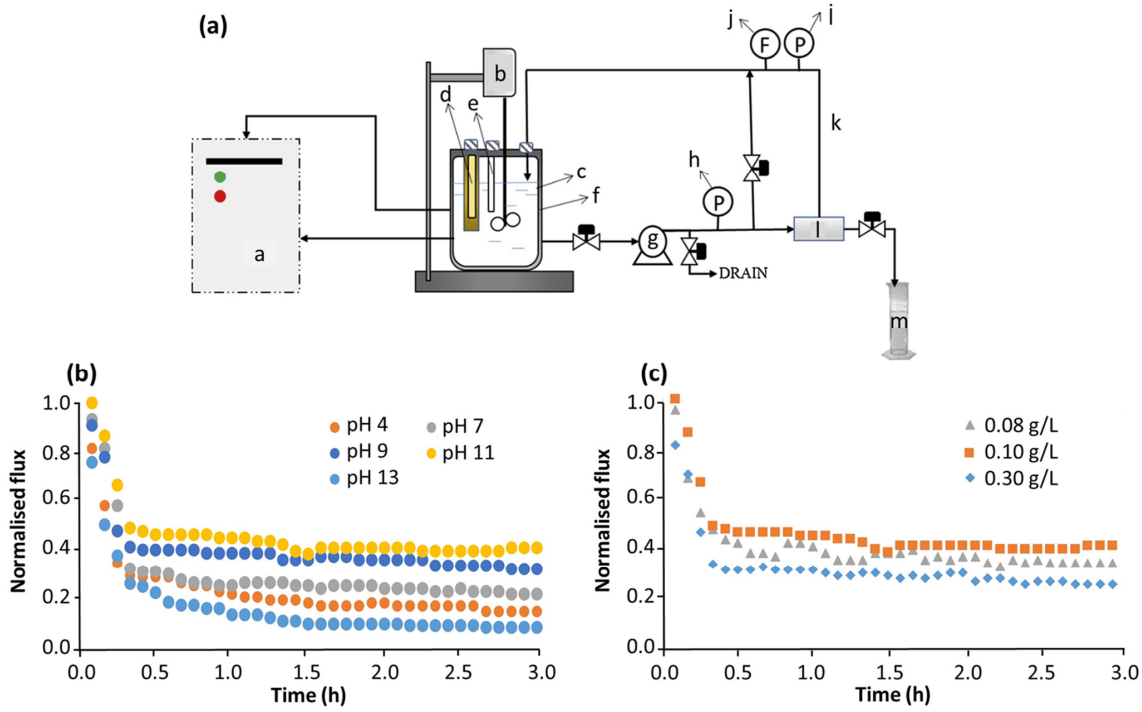

Figure 8: Schematic diagram of MPR (a) (Legend: a – water chiller, b – overhead stirrer with stand, c – photocatalytic reactor, d – UV lamp, e – feed, f – cooling jacket, g – pump, h, i – pressure gauge, j – flow meter, k – recycle flow, l – membrane filtration system, m – measuring cylinder); normalised flux of UF-PPA membrane against time under different pH of industrial wastewater at loading of ZnO-PEG = 0.10 g/L (b); normalised flux of UF-PPA membrane against time under different loading of ZnO-PEG nanoparticles at pH = 11 (c); reaction conditions: dilution of wastewater = 75%, pressure = 6 bars (reprinted with permission from [83]; Copyright 2019, Elsevier)

membrane for its permeability to be maintained and permeate flux through it sustained. The influence of the initial wastewater pH and the ZnO-PEG loading on the process performance was investigated, and the optimal operating conditions of ZnO-PEG in the MPR system were determined at pH 11 (Figure 8b), 0.10 g/L ZnO-PEG nanoparticles (Figure 8c), and 75% dilution of the textile wastewater. Under these conditions, the presence of ZnO-PEG nanoparticles as a photocatalyst significantly improved the effectiveness of the MPR system, resulting in maximal photocatalytic degradation efficiency and minimal membrane fouling.

3.2.4 TiO_2 and ZnO in combination with biological system

The coupled photocatalytic and biological process was applied to the treatment of industrial textile wastewater, including photocatalytic degradation of wastewater in the presence of ZnO or TiO_2 as photocatalysts under UV irradiation, followed by an aerobic bioprocess using sludge microorganisms acclimated to textile wastewater (Figure 9) [22]. The photocatalytic process was performed in the reactor for 2 hours and the biological test was performed in the incubator under suitable conditions for 12, 24 and 28 hours.

The results show that the absorption peak of the wastewater decreased significantly during the UV-assisted photocatalysis in the presence of TiO_2, resulting in a 44% decolourisation of the wastewater and that the subsequent bioprocess additionally contributed to the decolourisation of the wastewater, resulting in an 88% colour removal after 12 hours and a nearly complete decolourisation of 97% within 48 hours of biological treatment (Figure 9a). These results indicate that the combined TiO_2/UV and biological system is suitable for the decolourisation of real textile wastewater. In contrast to TiO_2, photocatalysis with ZnO was much less effective and caused virtually no changes in the absorption spectrum after 2 hours of photocatalysis (Figure 9b). The lower photocatalytic efficiency of ZnO compared to TiO_2 was attributed to the lower surface area of ZnO particles. The subsequent biological process did not contribute to the efficiency of the combined process; hance, only 48% of the colour was removed after 48 hours of treatment. These results demonstrate the importance of photocatalysis for the decolourisation efficiency of the combined photocatalytic-biological process.

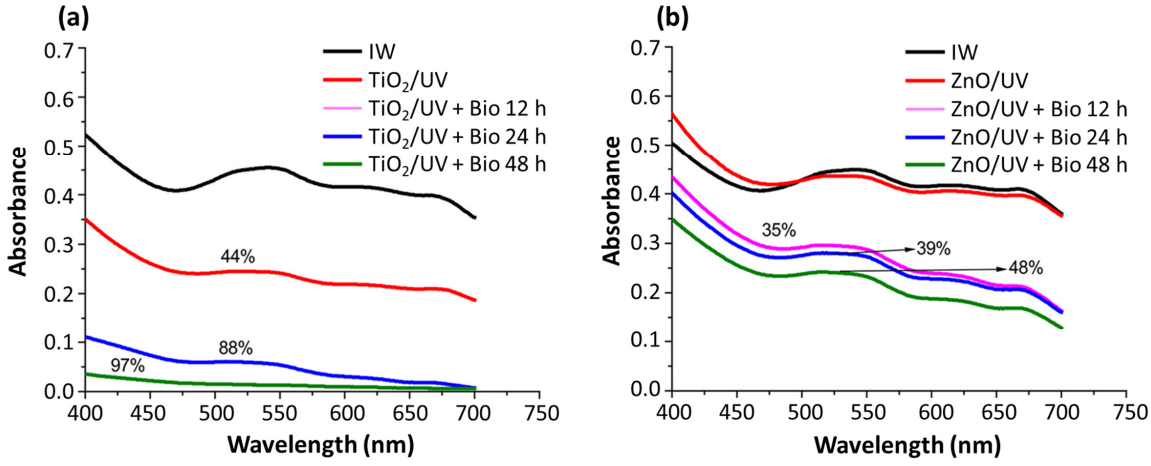

Figure 9: Absorption spectra of industrial wastewater before (IW) and after photocatalytic treatment (TiO_2/UV and ZnO/UV) and combined photocatalytic-biological treatment (TiO_2/UV + Bio and ZnO/UV + Bio), including percentage of colour removal after each treatment step; photocatalysis with TiO_2 (a), and ZnO (b) (reprinted with permission from [22]; Copyright 2019, John Wiley and Sons

3.2.5 ZnO/polypyrrole in combination with biological system

In another proposed coupled photocatalytic-biological process, biological treatment of textile wastewater was conducted as a pretreatment and photocatalysis as a subsequent process using a ZnO/polypyrrole (ZnO/PPy) composite [84]. Previously, the bacterial consortium was collected from the inspection chamber of the factory sewer and enriched for the biological treatment, and the optimal amount of ZnO/PPy photocatalyst and its recyclability were determined for photocatalysis. In the combined process, real textile wastewater containing the azo dye Direct Black 22 was pretreated with a bacterial consortium for 96 hours and then photodegraded in the presence of ZnO/PPy for one hour under UV irradiation (Figure 10a). The time dependence of Direct Black 22 was observed in both treatments. The results show that when the two process steps were applied separately, the biological treatment resulted in 71.3% decolourisation of the dye and 80.0% removal of TOC, while the photocatalysis resulted in 83.6% decolourisation of the dye and 88.4% removal of TOC (Figure 10b). Coupling the two treatment processes resulted in a much higher decolourisation efficiency of 95.7%, while the final TOC removal reached remarkable 99.9% (Figure 10b).

The presented combined processes have proved the importance of their performance for wastewater treatment. It is obvious that the efficiency of photocatalysis is significantly increased in the presence of oxidants such as H_2O_2 and O_3. In fact, the addition of H_2O_2 was found to have a synergistic effect on the photocatalytic activity of nanosized TiO_2, as H_2O_2 generates additional •OH radicals under UV irradiation. The synergistic effect between the ZnO-based nanocomposite and O_3 was attributed to the efficient capture of the generated electrons by O_3, leading to the formation of $•O_3^-$ and $HO_3•$, which then contribute to the formation of •OH. In a hybrid system of photocatalysis and membrane filtration, the initial photocatalytic treatment of wastewater with ZnO under UV-C irradiation significantly improved the efficiency of the ultrafiltration membrane system, resulting in maximum photocatalytic degradation efficiency and minimal membrane fouling. The coupled photocatalytic and biological processes also proved to be promising treatment methods, with photocatalysis performed as a pretreatment or as a subsequent process. The coupling of the two processes resulted in significantly higher decolourisation efficiency and TOC removal compared to the processes performed separately.

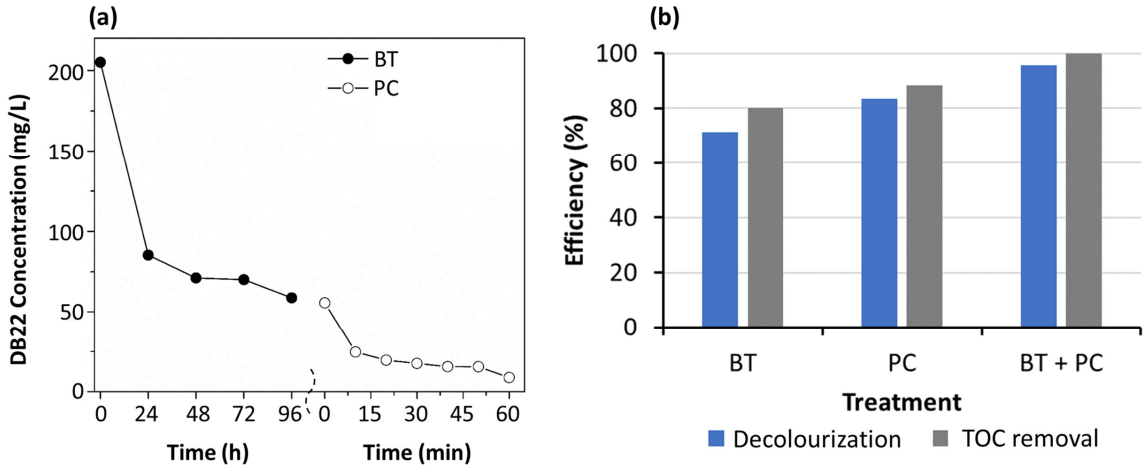

Figure 10: Sequential biological treatment and photocatalysis of real textile wastewater containing azo dye Direct Black 22 (a); decolorisation and TOC removal efficiencies of individual steps of separately applied treatments and coupled treatment (b); DB22 stands for Direct Black 22, BT stands for biological treatment, PC stands for photocatalytic treatment (reprinted with permission from [84]; Copyright 2020, Elsevier)

4 Conclusion

The treatment of real textile wastewater to remove synthetic dyes prior to disposal to the municipal wastewater treatment plant or the environment remains a major challenge. Various physical, chemical and biological processes have been used for this purpose, among which photocatalysis has already established itself as one of the most challenging ones.

Both TiO_2- and ZnO-based photocatalysis have unique advantages that make them an important AOP for textile wastewater treatment. One of the key advantages is environmental sustainability, as TiO_2 and ZnO are recognised as biocompatible, non-toxic, and chemically inert nanomaterials on the one hand, and the ability of photocatalysis to degrade the pollutants to water and carbon dioxide without hazardous by-products on the other hand. It should be emphasised that photocatalysis can be used in a variety of environmental remediation processes to convert toxic pollutants into harmless products, which would not be possible with conventional wastewater treatment processes. However, in addition to the advantages, there are also some limitations of photocatalysis. One of them is its narrow spectral response, mostly in the UV range, which limits its ability to utilise a broader spectrum of sunlight. In addition, the introduction of photocatalysis for large-scale applications is still a challenging research topic as it is usually studied under ideal laboratory conditions. To improve the applicability of photosynthesis in real-world scenarios and to ensure the long-term stability of the photocatalysis system, further research and development efforts are needed for a careful construction and design of large-scale photocatalytic reactors.

In addition to single photocatalytic processes, combined processes in which photocatalysis is coupled with other chemical, physical and biological processes have attracted a considerable interest due to their synergistic effects in wastewater treatment. Photocatalysis has been successfully performed in the presence of other oxidants such as H_2O_2 and O_3, and in combination with ultrafiltration and biological processes. In these studies, a proper system design and determination of optimal treatment parameters are of great importance to take advantage of each process and maximise treatment performance. The complementation of the coupled processes and the creation of a synergistic effect resulted in more efficient comprehensive and diverse pollutant removal compared to a single wastewater treatment. When photocatalysis is coupled with membrane filtration as pretreatment, fouling can be reduced, which improves and stabilises filtration performance. By combining photocatalysis as a pretreatment with a biological process, organic load is reduced, which lowers energy consumption and operational costs.

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