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Photocatalytic removal of Malachite green dye from aqueous solutions by nano-composites containing titanium dioxide: A systematic review

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Abstract

Background: Malachite green (MG) is widely used as a fungicide, Bactericide parasiticide in the aquaculture industry, as a food additive, medical disinfectant, and also, as a dye for materials such as silk, leather, paper, etc. In this study, the photocatalytic removal of MG from aqueous solutions using TiO2-containing nanocomposites was reviewed.

Methods: In this study, four databases (PubMed, Web of Science, ScienceDirect, and Scopus) were systematically searched to collect studies on the decomposition of MG using nanocomposites containing TiO_2 under UV light radiation.

Results: In total, 10 related and eligible studies were selected. Based on the results, TiO_2 was doped with iron, Sn, Ag, Si, and Ni. The highest percentage of photocatalytic decomposition for MG was observed in Sn > Ni > Ag > Fe > Si. The removal efficiency of MG in the studied papers was between 75%-100%.

Conclusion: Recombinant nanocomposites had a higher dye removal percentage than uncombined ones because they play an important role in the photocatalytic process of dye, by producing free radicals.

Keywords: Photocatalytic, Malachite green, Nanocomposite, TiO_2, Titanium Dioxide

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Introduction

Organic pollutants in industrial water and wastewater are considered as a significant problem for people around the world. The textile and wastewater industries containing dyes are one of the main sources of pollutants, which are sometimes discharged directly as water effluent into the environment (1). Organic dyes as chemicals are commonly used in many industries such as food, textile, cosmetics, etc. If these dyes enter the environment as wastewater without any treatment, they can be very harmful to humans, aquatic microorganisms, and the environment (2, 3). Among the industries, the textile industry is considered as one of the largest industries consuming water with the production of colored wastewater (4). The textile industry contains organic dyes that are biodegradable and stable and have a high resistance to biodegradation, which is considered as a problem of surface water pollution (5-7). Dyes are divided into different types based on their chemical composition and application. Based on the dyes' chemical structure, they are categorized into 20 to 30 groups, the most significant of which are azo, anthraquinone, and phthalocyanine (8,9). Malachite green (MG) with the chemical formula $C_{52}H_{54}N_4O_{12}$ is one of the cationic organic dyes that have a high solubility in water (2). MG is applied in many industries such as dyeing silk, plastic, hemp, linen, pharmaceuticals, and printing, and due to its easy preparation and low manufacturing cost, its use is very high (10-12). It is used in aquaculture industries for disease control and fish parasites as an antifungal and antiseptic agent, antimicrobial in food and aquaculture industries. MG toxicity is naturally high and its toxicity increases with increasing temperature, concentration, and pH (2,11). When MG enters the food chain, it causes carcinogenic, teratogenic, and mutagenesis effects, respiratory toxicity, reduced human and chromosomal fertility, and chromosome adhesion (13,14). In humans, the ingestion of MG may irritate the gastrointestinal tract. Skin contact with MG causes skin irritation, redness and pain (15,16). Therefore, the removal of MG from the output of fish farming systems or the sewage of textile industries, paper making, etc. is necessary to prevent its adverse effects on aquatic organisms (17). Because dyes are non-degradable molecules, treatment of colored wastewater is difficult. For this reason, various techniques including coagulation, flocculation, advanced oxidation, precipitation, ozonation, aerobic digestion, anaerobic, adsorption, membrane purification, membrane filtration, ion exchange, and optical decomposition are used. The above-mentioned techniques have advantages and limitations. But today, researchers are increasingly using efficient methods, which are economically sustainable technologies for treating colored effluents (18-20). Today, the photocatalyst process is used as a simple and efficient method to remove organic pollutants and dyes from industrial effluents and has been shown to play a significant role in environmental control by decomposing organic pollutants (21-23). The photocatalytic technique is superior to traditional purification techniques. Its characteristics include stability, cost-effectiveness, highly photoactive, fast oxidation, high oxidation of pollutants even at low concentrations, no formation of polycyclic products, etc. This process generates free radicals such as hydroxyl radicals (OH°), which is a very efficient oxidant for organic matter pollutants (5,24). The photocatalytic process with nanocomposites as methods for removing organic dyes from industrial effluents has helped researchers to produce new nanocomposite particles with different composite samples such as organic biopolymers and inorganic salts. Ion exchangers, photocatalysts, etc., operate (24). Titanium dioxide (TiO_2) itself is one of the most extensively used metal oxides with high photocatalytic activity without the formation of secondary pollutants (25,26). Three well-known crystal structures for TiO_2 are known as anatase, tarantula, and brookite. The anatase phase has more photocatalytic activity than rutile and brookite due to having the highest level of activity (27,28). There is a controversial debate about the effectiveness of nanocomposites containing TiO_2 in removal of MG from aqueous environments. Hence, to evaluate the effectiveness of the nanocomposites, this study aimed to systematically review all experimental studies related to this subject.

Materials and Methods

Search strategy

Systematically searches have been done in databases including PubMed, Web of Science, ScienceDirect, and Scopus between January 2007 and September 2020 to investigate the photocatalytic removal of MG by nanocomposites containing TiO_2 according to the PRISMA guidelines. For this purpose, searches were performed according to Medical Subject Headings (MeSH) with the keywords of "Malachite green" AND ("Photocatalytical" OR "decomposition") AND ("Aqueous" OR "wastewater" OR "water") AND ("Nanocomposites" OR "halloysite" OR "TiO_2").

Inclusion criteria and data extraction

Articles were selected given they provided original data on the subject. Review papers, conference papers, book chapters, protocols, dissertations, and data with photocatalysts based on various types of nanocomposites other than TiO_2 were excluded. The inclusion criteria were English full-text of articles, focusing on the photocatalytic removal of MG using nanocomposite synthesized with TiO_2.

Extracted information available for each study include the name of the first author, place of the study, year of the publication, and information on other variables. The information including pH, reaction contact time, nanocomposite dose, initial concentration of MG dye, if available, was noted and recorded.

Results

The systematic search identified 91 articles in four databases. In the first step, 12 papers out of 91 obtained papers were excluded due to duplication via EndNote X7® software (Thomson Reuters, Canada). Also, 22 articles were excluded due to the lack of entry criteria in the title and abstract screening. Moreover, 47 articles were removed based on the full-text screening. So, 10 articles were eligible and used in the present systematic review, as illustrated in Figure 1.

Table 1 illustrates the main results of the included articles. Among the selected articles, six articles used metal elements along with TiO_2. One article used Fe (29), two articles used tin (Sn) in two different ways (30,31), one article used Ag (29), and the remaining article used nickel (Ni) (32,33). The highest percentage of photocatalytic decomposition for MG was observed in Sn > Ni > Ag > Fe > Si. The remaining 5 articles out of 10 articles, comparing other nanocomposites that used commercial compounds with TiO_2 (34-38). The highest MG removal efficiency (100%) was found in the study of Tayade et al that examined anatase nanocrystalline combined with TiO_2 (the initial MG concentration of 50 $mg.L^{-1}$, and reaction time of 40 minutes) (36). The lowest MG removal efficiency (75%) was found in the study of Yang et al that examined $SiO_2@TiO_2$ composite nanosheets (the initial MG concentration of 50 $mg.L^{-1}$, and reaction time of 90 minutes) (35).

Discussion

The role of iron metal in the performance of TiO_2 nanocomposites

In a study on the removal of MG dye (the initial concentration of 2.5 $mg.L^{-1}$), with the help of TiO_2 and iron metal with different amounts of metal under UV irradiation, it was concluded that undoped TiO_2 ($UTiO_2$) under UV irradiation had 75% removal efficiency. While $0.3FeTiO_2$ and $7FeTiO_2$ had 81% and 73% removal efficiency, respectively (irradiation time was 110 minutes). All Fe^{3+} in the $0.3FeTiO_2$ catalyst is trapped in the TiO_2 crystal lattice, while in the case of the $7FeTiO_2$ catalyst,

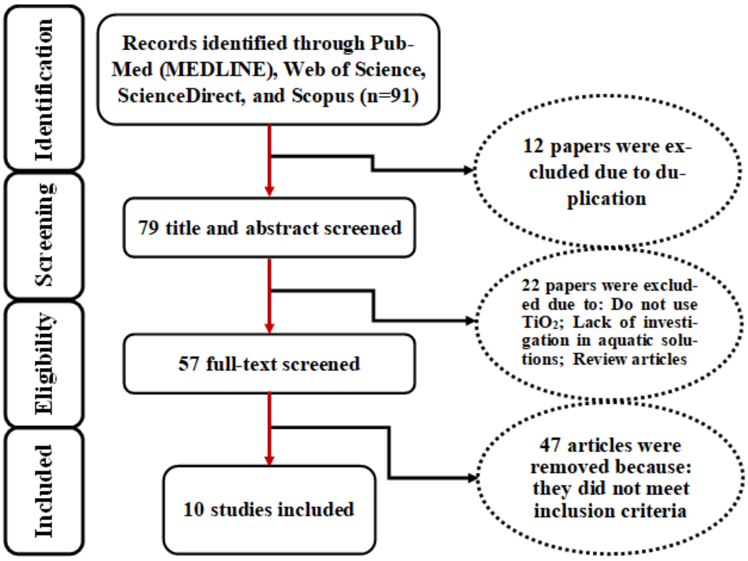

Figure 1. Preferred reporting items for systematic reviews and meta-analysis (PRISMA) flow diagram of database search evidence and inclusion criteria.

it contained iron oxide in addition to Fe^{3+} ions and that doping with Fe^{3+} ions reduced particle size, which decreases the surface area (29). If the dye concentration increases to 5 mg.L^{-1}, the removal efficiency increases slightly. In this situation, it was found that $UTiO_2$ is less effective because it has the smallest surface area. The higher the level of surface area, the higher the photocatalytic performance because it absorbs more photons and dye molecules, and the electrons oxidize the O^{2-} anions by reducing Ti(IV) to Ti(III). The oxygen atoms return and in one place, it creates a void, then, the dye molecules occupy the oxygen void and form hydroxyl groups that tend to be adsorbed on the hydrophilic surface. Because the irradiated surface is almost super-hydrophobic, it absorbs hydroxyl groups and forms active hydroxyl radicals, which play an important role in photocatalytic activity. Another reason for the increase in the removal of $0.3FeTiO_2$ compared to $7FeTiO_2$ is that the first catalyst shows the highest peak value with the help of the XRD test in the titanium anatase phase, but in the $7FeTiO_2$ catalyst, it is shown that the anatase phase peak is reduced or eliminated. The crystalline phase of anatase itself increases the contact surface by reducing the particle size. Fe^{3+} acts as a mediator in doping and causes the transfer of produced electrons and increases the production of free radicals (29). Because the irradiated surface is almost superhydrophobic, it absorbs hydroxyl groups and forms active hydroxyl radicals, which play an important role in the photocatalytic activity, according to the following reactions:

$$TiO_2 + h\upsilon \rightarrow e^- + h^+ \quad (1)$$

$$Fe^{3+} + h^+ \rightarrow Fe^{4+} \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

$$Fe^{2+} + O_2(ads) \rightarrow Fe^{3+} + O^{2-} \quad (4)$$

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+} \quad (5)$$

$$Ti^{3+} O_2(ads) \rightarrow Ti^{4+} + O^-_2 \quad (6)$$

$$Fe^{4+} + OH^-(ads) \rightarrow Fe^{3+} + OH^0(ads) \quad (7)$$

The role of tungstophosphoric acid in the performance of TiO_2 nanocomposites

Rengifo-Herrera et al examined the TiO_2–tungstophosphoric acid (TPA) at different ratios (20% and 30% w/w) (34). The results revealed that under UV-A, the MG solutions were well bleached through the oxidative procedure of N-demethylation being the TiO_2 powder containing 30% (w/w) of TPA (100% of bleaching in 60 minutes). Experiments performed using blue-light irradiation under N_2 atmosphere displayed that TiO_2 powders containing TPA were not able to bleach the MG solutions.

TPA plays an important role in this process because this unchanged compound is known as a heteropoly compound that is an efficient electron trap, and other reasons for the increase in TiO_2–TPA–30% photocatalytic activity compared to TiO_2–TPA–20% and TiO_2–TPA–0% is that the dye molecules on its surface are closer to the titanium surface and simply allow oxidative degradation hydroxyl radicals attached to the surface (34).

The role of Sn metal in the performance of TiO_2 nanocomposites

Sayılkan et al, reported that where TiO_2 was prepared in single and double layers on a glass surface and Sn metal was doped on it, the experiments showed that the higher the number of layers, the higher the percentage of removal

Table 1. The main extracted information of the 10 articles selected in the present study

First Author	Country	Catalyst Type	C_0[a] (mg.L^{-1})	Optimal Condition					The main finding	Ref.
				Best NC*	NC dose	Time[b] (min)	pH	R[c] (%)		
Asiltürk M	Turkey	TiO_2+UV TiO_2+0.3Fe+UV TiO_2+7Fe+UV	2.5	0.3FeTiO_2 (film)	6-8 µm	110	NR**	85	Fe^{3+}-doped TiO_2 enhanced the photodegradation performance as compared to the UTiO_2 coated surface.	(29)
Rengifo-Herrera JA	Argentina	TiO_2–TPA–0%+UV TiO_2–TPA–20%+UV TiO_2–TPA–30%+UV	3.56	TiO_2–TPA–30%+UV	1 g/L	240	pH=2	88	TiO_2–TPA–30% has a higher photocatalytic activity; anatase TiO_2 particles are excited under UV irradiation, making charge separation; the TPA or WOx types can perform as traps for the photo-induced electrons, diminishing the recombination; photo-induced holes on WOx can oxidize the adsorbed MG molecules.	(34)
SayilkanF	Turkey	Sn_4+TiO_2+UV Sn_4+TiO_2+Vis mono layer and double layer (first uses second use)	5.2	Sn_4+TiO_2+UV (double layer)	15 µm	250	NR	90	Double layer coated surfaces have high photocatalytic activity; TEOS is a greater barrier for Na ions under UV irradiation.	(30)
Sayilkan F	Turkey	Sn_4+TiO_2+UV Sn_4+TiO_2+Vis with solid ratios of 50%, 60% for doped TiO_2, and 53% in un-doped TiO2	5	Sn_4+TiO_2+UV (ratios of 60%, film)	10-12 µm	200	NR	87	The coated surfaces have excellent super-hydrophilic properties; the metal ion doping effectively improved the photocatalytic activity of the TiO_2 film; the kinetics of the MG removal reaction follows the pseudo-first-order equation.	(31)
Yang J	China	CNS-SiO_2@TiO_2	20	CNS-SiO_2@ TiO_2	0.5 g/L	90	NR	75	The good catalytic activity of the CNS-SiO_2@TiO_2; it is reusable for degradation of MG in the aqueous solution; it has a larger reactive area, greater degradation rate (96%), and a shorter irradiation time (90 min); the NC worked as an emulsifier and a photocatalyst simultaneously at emulsion interface.	(35)
Saha S	India	Commercial TiO_2 P25TiO_2, nano grade 1 mol% $AgNO_3$+TiO_2 2 mol% $AgNO_3$+TiO_2 1 mol% $AgNO_3$+P25TiO_2 combusted TiO_2	70	1 mol% $AgNO_3$+TiO_2	1 g/L	60	pH=7	85.71	P25 TiO_2 ~ combusted TiO_2 > Silver impregnated (1 mol%) TiO_2 > Silver impregnated (2 mol%) TiO_2 > Silver impregnated P25 TiO_2; the presence of Ag in TiO_2 improves the mineralization of MG but decreases the decolorization effectiveness; 1% Ag-impregnated TiO_2 was found the best; the MG (25 mg.L^{-1}) is bleached totally upon 1 h of UV irradiation.	(32)
Tayade RJ	India	Anatase nanocrystalline+TiO_2 Rutile nanocrystalline+TiO_2	75	Anatase phase	0.2 g/L	40	NR	100	Anatase phase TiO_2 had the higher photocatalytic performance due to parameters like band-gap, number of hydroxyl groups, surface area, and porosity of the catalyst.	(36)
Du F	China	E-spun PANCMA RGO/PANCMA RGO/PANCMA TiO_2/PANCMA GO/TiO_2/PANCMA RGO/TiO_2/PANCMA E-spun TiO_2/PANCMA E-spun RGO/TiO_2/ PANCMA	0.1	RGO/TiO_2/ PANCMA NFs	11.56 µg/ mg	60	pH=7	91.4	The E-spun RGO/TiO_2/PANCMA NFs displayed higher adsorption capacity; under improved situations, 90.6% of MG in 50 mL solution was removed on the NFs in 2 min.	(37)
Jo WK	Korea	TiO_2-coated mosquito net+UV	4.75	TiO_2-coated mosquito net+UV	NR	240	NR	88	The photocatalytic degradation of MG was obtained 88% for 4 h; the addition of H_2O_2 can improve the photocatalytic degradation.	(38)
Purkayastha MD	India	NiO-TiO_2 (TN)	5	NiO-TiO_2 (TN)	0.01 g/L	50	NR	87	87% efficiency is observed at the concentration of 5 ppm dye with 10 ppm catalyst; the existence of inorganic ions and organic matter affected the aggregate size of TN but caused a decline in photoactivity; the nanocomposite appears suitable for energy preservation and environmental applications.	(33)

Note: a = Initial concentration of MG; b = Reaction time; c = Nanocomposite efficiency; *NC = Nanocomposite; **NR = Not reported.

due to the higher amount of Sn (30). Controlling particle size and increasing the contact surface, and improving electron transfer efficiency enhances photocatalytic efficiency. Sn ions may be substituted for titanium to form the solid compound $Ti_{1-x}Sn_xO_2$, which due to its high photocatalytic performance, tends to degrade MG more.

Sayılkan et al (31) used Sn-doped and un-doped TiO_2 nanoparticles at three solid ratios 50%, 60% in doped TiO_2, and 53% in un-doped TiO_2. The highest removal percentage was observed at solid ratio of 60%. By increasing the solid ratio, the electrons oxidize the O^{2-} anion holes by reducing the Ti(IV) to Ti(III) and the oxygen atoms return and create a void. The dye molecules then occupy the oxygen void, forming hydroxyl groups that tend to be adsorbed on the hydrophilic surface. As the irradiated surface is almost super-hydrophilic, it absorbs hydroxyl groups and forms active hydroxyl radicals, which play an important role in photocatalytic activity. Another reason was the high reaction rate, which has led to an increase in its photocatalytic activity. Reasons for increasing the percentage of decomposed TiO_2 doped with Sn compared to non-doped TiO_2 are high micropore surface area, crystal size, and micropore volume, but for non-doped TiO_2, the surface area and average diameter of adsorption pores are smaller. Doped with Sn, Sn^{4+} is present in the reaction medium, which by controlling the particle size (by reducing it increases the surface area) and the crystal size of the oxides and reducing the size of the powder, causes the powder to take a spherical shape. Interestingly, in Sn-doped TiO_2, the crystal size and particle size are smaller than those in non-doped TiO_2. Doped Sn^{4+} also improves the transfer efficiency of electrons from the LUMO Malachite band to the conduction band of Sn doped with TiO_2. These electrons oxidize O^{2-} anionic holes and oxygen atoms by reducing Ti(IV) to Ti(III). It returns and creates a void. Then, the dye molecules occupy the oxygen void and form hydroxyl groups that tend to be adsorbed on the hydrophilic surface. And form active hydroxyl radicals that play an important role in photocatalytic activity. It was revealed that Sn doped with TiO_2 is capable of absorbing UV light and can be used for irradiated photocatalytic applications.

The role of SiO_2@TiO_2 nanosheets in the performance of TiO_2 nanocomposites

Yang et al (35) used CNS-SiO_2@TiO_2 composite nanosheets for photocatalytic decomposition of MG dye. This study revealed that the nanosheet has effective catalytic performance and reusability in photocatalytic degradation of MG in aqueous solution, decomposition rate higher than 96% in less than 90 minutes. The reason for its high efficiency is its high contact surface, which can have good potential in wastewater treatment. The rate of decomposition of MG increased with exposure to UV radiation, but without the addition of CNS-SiO_2@TiO_2, the amount of decomposition was very low and only 8% after 80 minutes of irradiation. The decomposition rate was enhanced by increasing the decomposition time due to N-demethylation and emulsification process, which caused the effective contact surface between the substrate and the catalyst, but as experiments show, with increasing time and the MG concentration from a certain value, the efficiency of MG photocatalytic analysis by CNS-SiO_2@TiO_2 decreases because the MG molecules adsorbed on the surface of the catalyst cause less oxygen to reach the catalyst and this reduces the decomposition efficiency (35).

The role of $AgNO_3$ in the performance of TiO_2 nanocomposites

Saha et al (32) used TO (Commercial TiO_2), PTO (P25 TiO_2, nano grade), STO(I) (1 mol% $AgNO_3$ + TO), STO(II) (2 mol% $AgNO_3$ + TO), SPTO (1 mol% $AgNO_3$ + PTO), and CTO (combusted TiO_2). The highest removal percentage of MG is related to commercial P25 TiO_2, PTO (92%), and subsequent further decomposition was obtained by the combustion of TiO_2, CTO (90%). STO (I) has a higher percentage of decomposition (85%) than STO (lI) (74%) due to higher UV screening before reaching TiO_2 level if present in STO (II). A comparison of SPTO and PTO showed that the amount of decomposition of the first one (60%) is lower than the second one (92%) and this is due to the presence of silver in SPTO, which causes a catalytic reduction, and the surface may have decreased due to saturation with a silver (32).

The role of anatase and rutile phases in the performance of TiO_2 nanocomposites

Tayade et al (36) examined anatase and rutile phases of titanium to remove MG. Their results revealed that anatase type has a higher photocatalytic activity. The highest decomposition (100%) was obtained in an experiment with the rutile phase for MG for 3 hours under UV irradiation, but the same result was obtained with the help of the anatase phase for 1 hour. One of the reasons for the great photocatalytic performance of the anatase phase is the surface area (124 $m^2.g^{-1}$ and the pores are 7.5 nm) as compared to the rutile phase (2 $m^2.g^{-1}$ and the diameter is 5.4 nm). The photocatalytic activity is extremely dependent on the hydroxyl group on the surface that attacks contaminants in water. High surface area is also useful for accommodating more groups of hydroxyl. Another reason for the superiority of anatase over rutile is the increase in band gap in the pairs of electron holes (36).

The role of graphene oxide in the performance of TiO_2 nanocomposites

Du et al (37) used the composite nanofibers of graphene oxide, TiO_2 for effective adsorption and photocatalytic removal of MG. Decomposition percent of MG by E-spun

RGO/TiO_2/PANCMA NFs was obtained 90.6%. However, by adsorption on NFs for 60 minutes under UV irradiation, the amount of dye decomposition for 2 minutes was 91.4%. The reason for the increased performance of E-spun RGO/TiO_2/PANCMA NFs compared to E-spun TiO_2/PANCMA and GO/TiO_2/PANCMA NFs was its high current density, which was itself a factor in separating pairs of electron holes. Another reason is that the charge transfer rate between the surfaces of the E-spun RGO/TiO_2/PANCMA NFs was faster and produced more electrons, resulting in better photocatalytic activity; spun is RGO/TiO_2/PANCMA NFs because the effects of pH through protonation in solution affect the form of malachite and have a clear effect on dye adsorption. Because under acidic conditions it produced protons (H^+) that combined with O_2 in solution to produce H_2O_2 and irradiated with the same hydrogen peroxide, producing hydroxyl radicals that acted as a powerful oxidant in photocatalytic action (37).

The role of mosquito net in the performance of TiO_2 nanocomposites

Jo and Tayade (38) experimented TiO_2 on a mosquito net to decompose MG under UV light. For 4 hours, the decomposition percentage of 88% was achieved. Factors affecting high photocatalytic efficiency with the help of TiO_2 include the release of photocatalytic nanoparticles in the refined solution, electronic properties and photocatalytic structure, phase composition, band gap, the surface area play an effective role in the ability of the photocatalyst. When the TiO_2 photocatalyst is irradiated, light with energy equal to or higher than the energy of the band gap is excited by absorbing the light of the electron band. Water or organic contaminants absorbed on the TiO_2 surface react with the charge transfer. The reaction of $H^+$with OH^- or H_2O results in the formation of hydroxyl-OH radicals, each of which are strong oxidants that attack the desired undesirable organic pollutants. The production of oxygen peroxide during the reaction is a powerful oxidant that plays an important role in the photocatalytic degradation of dyes, and this oxygen peroxide increases the concentration of hydroxyl radicals (38).

The role of nickel metal (Ni) in the performance of TiO_2 nanocomposites

In the study of Purkayastha et al (33), nanocomposites containing TiO_2 and nickel metal (Ni) were used. The results showed that the best photocatalytic efficiency (87%) was observed at the optimum concentration of 5 ppm with 10 ppm of catalyst. Separation of charge carriers and their transfer at the nanocomposite junction is where these carriers are produced in the reaction solution and NiO is transferred to the TiO_2 conduction band, and this process causes oxygen uptake and production of superoxide (O^2) radicals, which play an active role in photocatalytic activity. Experiments have shown that increasing the dye concentration reduces the decomposition process but increasing the catalyst causes a significant increase in the dye due to the presence of active sites on the titanium surface to absorb the dye, which reduces the activation energy for dye degradation (33).

The role of environmental factors (pH, reaction time, initial concentration, catalyst dose)

pH can affect the surface charge of photocatalyst and adsorption capacity (3,14-16). Tan et al (20) and Gupta et al (11) discussed the effect of pH on the attractive or repulsive force of nanocomposites. Generally, at high pH, due to the negative surface of the nanocomposite, it favors the absorption of cations and an electrostatic attraction is created. But at acidic pH, the surface of the nanocomposite, due to protonation, becomes positively charged and favors the adsorption of anions. Moreover, the production of hydroxyl radicals is high in the alkaline range. Electrons oxidize oxygen molecules to produce peroxide radicals. This radical, combined with ambient hydrogen, produces hydroxyl radicals that play an important role in photocatalytic activity (23).

The longer the time, the more color molecules are in contact with the nanocomposite and the more interaction between the dye and the nanocomposite is provided and the more production opportunities are provided for free radicals (37).

With increasing catalyst dose in the removal process, a decreasing trend was observed. The reason for this trend is that with increasing the activity level of the catalyst, the bleaching increases to a certain amount because at higher amounts, the suspended particles of the catalyst prevent the passage of ultraviolet light and cause more light scattering. Therefore, a further increase in the amount of catalyst does not affect the efficiency of photocatalytic decomposition (20,25).

With increasing dye concentration, the dye removal efficiency increased to a certain extent and further increase of dye concentration led to a decrease in removal efficiency. The removal rate depends on the formation of free radicals at the catalyst surface and the probability of reaction with the dye molecules. The reason for the decrease in decolorization due to the increase in dye concentration is that the active sites on the catalyst surface are covered by dye molecules and the production of hydroxyl radicals is reduced. Another reason that can be mentioned is that at high concentrations of dye, a large amount of UV is absorbed by the dye molecule instead of being absorbed by the nanocomposite particles, and the catalyst efficiency decreases due to the radical reduction of hydroxyl and peroxide (32,35).

In this review study, the number of articles for each type of nanocomposite was less than two articles, therefore, it was not possible to perform a meta-analysis (39). Because all other synthesis techniques are less transparent and/or are less likely to be valid. There are some gaps in this field of study conducting such research on real samples, and performing the process on the effluent of MG on biological organisms such as Daphnia. Moreover, in this study, only photocatalytic processes that use UV light were analyzed. The effect of this process can be examined with other lights such as visible or sunlight.

Conclusion

There is a notorious debate about the effectiveness of nanocomposites containing TiO_2 in the removal of MG from aqueous environments. Therefore, investigation of the photocatalytic activity of the nanocomposites is of great importance. Hence, in the present systematic review, a total of 10 relevant and suitable studies were collected. According to the findings of the reviewed studies, TiO_2 was doped with iron, Sn, Ag, Si, and Ni. The highest percentage of photocatalytic decomposition for MG was observed in Sn > Ni > Ag > Fe > Si (90, 87, 85.71, 85, and 75%, respectively). Based on these results, it is necessary to take into account some parameters such as initial MG concentration, irradiation time, catalysts dose, pH, etc., to improve photocatalytic efficiency. Increasing the dye concentration reduces the decomposition process, but increasing the catalyst causes a significant increase in the dye due to the presence of active sites on the titanium surface to absorb the dye, which reduces the activation energy to degrade the dye. Finally, it is noteworthy that recombinant nanocomposites had a higher dye removal percentage than uncombined ones because they perform an important role in the photocatalytic process. By producing free radicals, they play a more effective role in the photocatalytic process of dye.

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Ethical issues

The authors hereby certify that all the data collected during the research are expressed in the manuscript, and no data from the study has been or will be published elsewhere separately.

Competing interests

The authors declare that there is no conflict of interests.

Authors' contributions

All authors were involved in the study design, data collection and analysis, and manuscript preparation. The final version of the manuscript was reviewed and confirmed by both authors.

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