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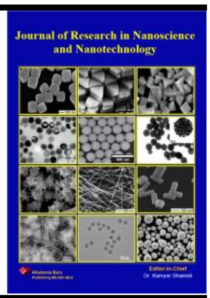

Photocatalytic Degradation with Green Synthesized Metal Oxide Nanoparticles – A Mini Review

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ABSTRACT

Water pollution is one of the major problems faced by mankind worldwide. With the increase of populations and urbanization, the natural water resources are under great threat due to the release of untreated effluent. An alternative treatment method, photocatalysis, emerged as a promising solution. Photocatalysis process utilizes photosensitive catalyst to degrade the pollutant and one of the most common catalyst being used is metal oxide. To increase the photocatalytic activity, nanosized metal oxide being used instead of its bulk form. In these recent years, metal oxide nanoparticles production has been shifted towards a more environmentally friendly process which is also commonly known as green synthesis. In this review, we discussed on the photocatalytic process and production via green synthesis of common metal oxide nanoparticles being used as photocatalyst.

Keywords: Metal oxide, nanoparticles, green synthesis, photocatalysis

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1. Introduction

Water pollution is one of the major issues faced by mankind worldwide. Natural resources are under great threat with the increase of populations and urbanization. Statistic show that about 1.2 billion people unable to access safe drinking water and millions died due to diseases cause by unsafe water [1]. Major contributor to the pollution of natural waters is the effluent from various industries. According to the World Bank's estimation, textile dyeing and treatment effluent cause about 20 % of water pollution [2]. The industries wastewater being released contained various toxic compounds which can cause harmful effect to both human and aquatic life [3, 4].

In a conventional wastewater treatment, biological process followed by chemical coagulation is employed Although this treatment unit's processes are effective in various pollutants, it is high in cost as it requires specific equipment and high energy. Furthermore, generation of large amount of by-product lead to problem of safe disposal [4, 5]. Due to these issues, the focus of textile wastewater treatment has been shifted to advanced oxidation processes (AOPs). This process involves the generation and the use of the hydroxyl radical as strong oxidant to destroy the compounds until all the constituents degraded or mineralized to carbon dioxide and water [5, 6]. The most common AOPs process being research is photocatalysis. Photocatalysis utilizes semiconductor materials such as titanium dioxide (TiO_2), zinc oxide (ZnO) and iron oxide gain much interest in treatment of wastewater due to its safe and detoxification nature to the environment [7].

Nanotechnology has garnered a lot of attention around the world across many fields. It is defined as a field of research that involved in the development of very small materials which is within nanometer range [8]. Nanomaterials are unique as they display different properties compared to their bulk counterpart. Due to their small size, they have a greater relative surface area which resulted to enhance properties [9, 10]. To obtain nanomaterials, there are two main approaches which are "top-down" and "bottom-up" approach. In "top-down" approach, it involves breakage of large material to nanomaterials. However, this method generate particles with wide size distribution and variation of morphologies [11]. "Bottom-up" approach is much more common in nanomaterials synthesis and it involves the growing of nanoparticles from single atom [8]. This approach resulted in better nanomaterials in terms of shape and size which is useful in targeted applications. In these recent years, the synthesis process has been more focus towards green synthesis [12]. In general, green synthesis makes use of environmentally friendly, non-toxic and safe reagent. The overall cost of synthesis process reduced because no additional chemical is needed. Furthermore, the overall experimental process is relatively mild which can save the energy. Hence this mini review focused on the photocatalytic degradation of pollutants using green synthesized metal oxide nanoparticles.

2. Photocatalytic process

Advanced oxidation processes (AOPs) is one of the emerging techniques in wastewater treatment and this is due to previous reports of the success of almost complete pollutants' degradation [13, 14]. AOPs able to degrade the pollutants through the production of reactive oxygen species such as hydroxyl (·OH) and superoxide ($\cdot O_2^-$) radicals and generation of these radical species can proceed to several pathways. The four most common and well-known pathways are photolysis, ozonation, Fenton process and photocatalysis. Photolysis and ozonation defined as methods that use hydrogen peroxide together with ultraviolet and ozone to generate radical species respectively. Fenton process is currently being used as part of wastewater treatment and this process involve the usage of hydrogen peroxide with ferrous ion as catalyst. The last pathway is photocatalysis and generation of radical species is through utilization of light absorbing materials such as semiconductor materials [15, 16]. Among these four methods, photocatalysis method has been gaining preference over the other method due to the nature of photocatalysis which utilizes renewable solar energy and does not rely on the usage of chemical. Therefore, photocatalysis is considered as green and sustainable process.

Photocatalysis mechanism for pollutant degradation can proceed through two pathways which are indirect and direct mechanism with indirect mechanism being the most common. In the indirect reaction process, it begins with photoexcitation. Through irradiation of light, the semiconductor will be activated. The photon energy from light source will excite the electron from valence band (VB) to the conduction band (CB) and this led to generation of hole (h^+) in VB and photogenerated electron (e^-) in CB. The e^- in CB will react with dissolve oxygen to form O_2^- radical and this radical will further react with water to form ·OH radicals. In the VB, the h^+ will react with water to form ·OH radicals. ·OH radicals is the most crucial as it is the main radical that involve in the degradation of pollutantss [16, 17]. The schematic representation of photocatalytic pollutant degradation is shown in Figure 1 and the reaction of pollutant degradation can be expressed as follow:

$$Photocatalyst + hv \longrightarrow h_{VB}^{+} + e_{CB}^{-} \quad (1)$$
$$h_{VB}^{+} + H_2O \longrightarrow H^{+} + \cdot OH \quad (2)$$
$$e_{CB}^{-} + O_2 \longrightarrow \cdot O_2^{-} \quad (3)$$
$$\cdot O_2^{-} + H_2O \longrightarrow 2\ \cdot OH \quad (4)$$
$$Pollutant + \cdot OH \longrightarrow CO_2 + H_2O + intermediate\ product \quad (5)$$
$$h_{VB}^{+} + dye \longrightarrow oxidation\ products \quad (6)$$
$$e_{CB}^{-} + dye \longrightarrow reduction\ products \quad (7)$$

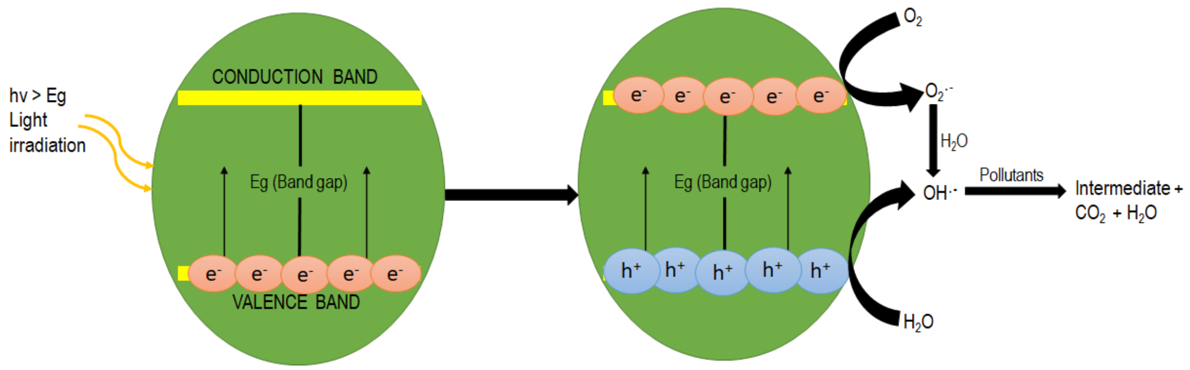

Figure 1. Schematic representation of photocatalytic degradation process.

3. Green synthesis metal oxide nanoparticles

Recent researches on synthesis of nanoparticles have been focusing on green chemistry pathway. This pathway utilizes biological entities such as plants, microorganism and carbohydrate in the production of nanoparticles [18, 19]. Previous researches showed that green synthesized nanomaterials exhibited better size and morphology. Furthermore, green synthesis process poses many advantages such as environmentally friendly, simple, easy, economical and mild synthesis process [20]. In this section, we will be focusing on the green synthesized metal oxide nanoparticles such as titanium dioxide nanoparticles (TiO_2 NPs), zinc oxide nanoparticles (ZnO NPs) and iron oxide nanoparticles (IONPs) for the application of photocatalytic degradation of pollutants. Table 1 shows the green synthesized metal oxide nanoparticles with the respective green agent and their application towards photocatalytic degradation.

1 Table 1: Green synthesized metal oxide nanoparticles and their application towards photocatalytic degradation

Metal oxide nanoparticles	Biomaterial	Size and morphology	Pollutants	Photodegradation	Light irradiation	References
TiO_2	Aloe vera leaves extract	Flake like 96 nm	Rhodamine B	58 % (50 min)	Visible	[21]
	Mangrove extract	Deformed Spherical 40 nm	Reactive blue 19 Red 76	~15 % (120 min) ~15 % (120 min)	Visible	[22]
	Calotropis gigantea leaf extract	Spherical 42 nm	Metformin	97 % (240 min)	Visible	[23]
	Aegle marmelos leaf extract	Spherical 150 nm	Ornidazole	66 % (300 min)	UV	[24]
	Monsonia burkeana plant extract	Spherical 2 – 18 nm	Methylene blue	86 % (180 min)	UV	[25]
	Lagenaria siceraria leaf extract	Irregular sphere 10 – 14 nm	Reactive green 19	99 % (60 min)	UV	[26]
	Citrus aurantium fruit peel extract	Spherical 34 nm	Methylene blue	91 % (150 min)	UV	[27]
	Deinbollia pinnata leaves extract	Semi-spherical 33-48 nm	Methyl orange	99 % (150 min)	UV	[28]
	Acacia catechu extract	Spherical and hexagonal 18 nm	Rhodamine B Rose bengal	99 % (120 min) 97 % (120 min)	Visible	[29]
	Salvia officinalis leaves extract	Spherical 50 – 120 nm	Reactive black 5 Reactive blue 19 Brilliant blue R	69 % (60 min) 74 % (60 min) 79 % (60 min)	UV	[30]

ZnO	*Averrhoe carrambola* fruit extract	Flake like 20 nm	Congo red	93 % (180 min)	UV	[31]
	Abelmoschus esculentus mucilage	Spheres and rod like 29 – 70 nm	Methylene Blue Rhodamine B	95 % (60 min) 100 % (50 min)	UV	[32]
	Eucalyptus leaf extract	Agglomerated particles	Malachite green	90 % (60 min)	UV	[33]
	Cynara scolymus leave extract	Spherical 66 nm	Methyl violet Malachite green	94 % (120 min) 90 % (120 min)	UV	[34]
	Cyanometra ramiflora leaves extract	Nanoflowers	Rhodamine B	98 % (200 min)	Visible	[35]
	Punica granatum leaves extract	Spherical 10 – 30 nm	Coomassie brilliant blue R-250	~89 % (180 min)	Visible	[36]
	Hydnocarpus alpina extract	Spherical 39 nm	Methylene blue	96 % (30 min)	UV	[37]
	Longan seed extract	Hexagonal 10 – 100 nm	Methylene blue Malachite green Methyl orang Orange II	~100 % (180 min) ~85 % (180 min) ~55 % (180 min) ~80 % (180 min)	Visible	[38]

	Leucaena leucocephala leaves extract	Spherical 50 – 200 nm	Crystal violet	~99 % (90 min)	UV	[39]
	Mussaenda frondosa leaves, stems and callus extracts	Spongy, spherical and porous agglomerated nanoparticles	Methylene blue	30 – 90 % (120 min)	UV	[40]
	Ulva lactuca seaweed extract	Agglomerated sponge like 10 – 50 nm	Methylene blue	90 % (120 min)	Visible	[41]
	Pullulan	Spherical and hexagonal 28 – 127 nm	Methyl orange Rhodamine B	~99 % (60 min) ~99 % (60 min)	UV	[42]
IONPs	*Aegle marmelos* extract	Agglomerated particles	Brilliant green	96 % (90 min)	UV	[43]
	Tamarix aphylla extract	Spherical	Methylene blue	100 % (60 min)	Visible	[44]
	Wedelia urticifolia DC. Leaf extract	Nanorod 15 – 70 nm	Methylene blue	98 % (360 min)	Visible	[45]
	Withania coagulans extract	Nanorods 16 nm	Sarafanin dye	~70% (180 min)	Visible	[46]
	Carica papaya leaves extract	Agglomerated particles 22 nm	Remazol yellow RR dye	77 % (360 min)	Visible	[47]
	Ruellia tuberosa leaves extract	Hexagonal nanorods 53 nm	Crystal violet	80 % (150 min)	Visible	[48]
	Psidium guavaja and *Moringa oleifera* leaves extract	Spherical and non-uniformed rod 1 nm	Methylene blue	~20 % (60 min)	Visible	[49]

Rhizophora mucronata leaves extract	Agglomerated particles	Phenol red Crystal violet	83 % 95 %	Visible	[50]
Spiny amaranth leaves extract	Spherical	Naphthalene	97 % (150 min)	UV	[51]
Pomogranate seeds extract	Semi-spherical 25 – 55 nm	Reactive blue	95 % (56 min)	UV	[52]

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3.1. Titanium dioxide nanoparticles

Titanium dioxide nanoparticles (TiO_2 NPs) is one of the most popular photocatalyst being used. This is due to their favorable properties such as non-toxic, low-cost, good photosensitivity, photocatalytic stability and abundant availability. It has the band gap value of 3.2 eV for anatase and 3.03 eV for rutile phase [53]. Sonker and co-workers reported on fabrication of TiO_2 NPs with nanosheet morphology using aloe vera leaves extract. The synthesized sample was able to degrade 58 % of Rhodamine B dye in 50 minutes under visible light irradiation [21]. In another work, TiO_2 NPs was successfully produced with *Salvia officinalis* leaves extract. The produced sample exhibited spherical morphology with particle size ranging from 50 – 120 nm. This sample managed to degrade 3 azo dyes, Reactive Black 5, Reactive Blue 19 and Brilliant Blue R with degradation percentage of 69, 74 and 79 % respectively [30].

3.2. Zinc oxide nanoparticles

Zinc oxide nanoparticles (ZnO NPs) has emerged as a promising candidate for photocatalytic degradation of dyes. ZnO can be found in nature within the earth crust in the form of mineral zincite but typically ZnO is obtained through synthesis [54]. ZnO is a n-type semiconductor which has a broad direct band gap width (3.37 eV), large excitation binding energy (60 meV) and absorb larger fraction of the UV spectrum. It has three crystal structure which are rocksalt, wurtzite and cubic (zinc blend) and among these three, wurtzite structure has the highest thermodynamic [55, 59]. Varadavenkatesan and colleagues reported on the production of ZnO NPs with nanoflowers morphology using the leaves extract of *Cyanometra ramiflora*. The synthesized sample managed to degrade Rhodamine B dye up to 98 % in 200 minutes [35]. Our previous work reported on the production of ZnO NPs using biopolymer, pullulan. The dyes Rhodamine B and Methyl orange were successfully degraded in 60 minutes under UV irradiation [42]

3.3 Iron oxide nanoparticles

Iron oxide is a transition metal oxide. It has three crystalline structure such as hematite (α-Fe_2O_3), magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). Among all these crystal structures, hematite is most stable and most commonly applied as photocatalyst [53-57]. However, in this review, we referred any form of crystal structure as iron oxide nanoparticles (IONPs). Rather and co-workers reported on the synthesis of IONPs using Wedelia urticifolia DC. Leaf extract with nanorods morphology. The sample managed to degrade methylene blue dye up to 98 % in 360 minutes under visible light irradiation [45]. Another work reported on the production of IONPs using the leaves extract of spinny amaranth [58-59]. The synthesized sample was then tested towards photodegradation of naphthalene where degradation efficiency of 97 % was obtained within 150 minutes under UV irradiation [51].

4. Conclusions

In conclusion, there are various metal oxides nanoparticles that can be used for photocatalytic degradation applications with the most common being TiO_2 NPs, ZnO NPs and IONPs. Furthermore, the type of pollutants that can be degraded is no longer limited to dyes only but also extend to other organic pollutants such as pharmaceutical products and others. This review discovers that even green synthesized metal oxide nanoparticles have the capability to photodegrade the pollutants which is a promising outcome. However, this review only focused three types of metal oxide nanoparticles and only on singular state.

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