Recent Progress in Doped TiO$_2$ Photocatalysis and Hybrid Advanced Oxidation Processes for Organic Pollutant Removal from Wastewater

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Abstract
Hybrid advanced oxidation processes (HAPOs) for the removal of non-biodegradable organics from wastewater have been studied in recent literature. With the increase in industrial development, the quantity of wastewater generated from these industries also organic wastewater produced by industrial manufacturing has posed threats to the environment. AOP’s are one of the promising advanced technologies for mineralization of organics present in wastewater. Hybrid advanced oxidation process based on the ozonation, sonolysis, Photo-Fenton reagents and electrochemical method, has greater potential for complete mineralization of recalcitrant organics. This review article includes recent progress in the research and application of TiO$_2$ photocatalysis for the removal of non biodegradable organic pollutants present in water. It will provide a quick reference for various hybrid AOPs systems and their effectiveness. This review article provides quick insights into (1) hybrid AOP for treatment of various industrial effluents or model effluents, (2) work done on doped/co-doped photo catalyst as heterogeneous catalysts (3) study of parameters affecting the photocatalysis to enhance complete oxidation of organics present in wastewater. A mechanistic investigation of hybrid advanced oxidation processes with combinations of sonolysis and Fenton process coupled with UV, adsorption and addition of biochar has been discussed.

Introduction
Innovations and productions of new medicines increased number of pharmaceutical industries with accumulation of waste in rivers and on land. Environmental management part always found non-focused and lead to degradation of nature.

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Researchers are working on these issues to resolve these problems. This situation enforced research towards zero effluent discharge, green technology and cleaner development mechanism. Semiconductor photocatalysis has been extensively studied by many researchers for the complete oxidation of refractory organics present in effluent,\textsuperscript{1–3} water splitting for hydrogen production\textsuperscript{4} and solar cells.\textsuperscript{5} The application of TiO\textsubscript{2} as a photocatalyst is limited by UV radiations and recombination of the hole and electron pairs.\textsuperscript{6,7} Rapid industrialization has vastly increased water and air pollution problems as the current generation are interested more in profit and less concerned about waste generation. This situation demands fruitful research be done on waste minimization to avoid such situations and to achieve sustainable development. Objective of this review is to search for efficient and cost-effective AOP for wastewater treatment. Solar light-driven effluent treatment methods have been focused and developed for research.\textsuperscript{8} Titanium dioxide is an N-type semiconductor having an oxygen deficit in its structure. TiO\textsubscript{2} is a superior, nontoxic stable and economical photocatalyst that provides a non-selective and efficient oxidizing agent, Hydroxyl radical (OH\textsuperscript{•}).\textsuperscript{9,10} TiO\textsubscript{2} has shown certain limitations as a photocatalyst: 1) it has a large band gap and works only under UV radiations; 2) its low quantum yield of OH\textsuperscript{•} due to recombination of holes.\textsuperscript{11}

Metal doping in TiO\textsubscript{2}\textsuperscript{1) improves its absorbance in the visible region, e.g. a Ag: 300–800 nm, Co: 400–650 nm and Fe: 300–800 nm,\textsuperscript{12–14} and allow it to work under solar radiation to make cost-effective treatment; 2) provides the excellent trap of electrons prevents recombination of e- and holes results in superior photocactivity;\textsuperscript{15} 3) the Bandgap reduces from pure TiO\textsubscript{2} (3.1 eV) to doped TiO\textsubscript{2} (2.8 eV).\textsuperscript{16,17} Silver and iron are extensively investigated as a dopant for TiO\textsubscript{2} and proved superior photocatalysts for mineralization of active pharmaceutical ingredients(API).\textsuperscript{18–20} Co-doping of TiO\textsubscript{2} using metal dopants is a promising technology for solar mineralization of refractory organics in wastewater. Doping of TiO\textsubscript{2} with Fe and Ag metals enhances the photocatalytic activity due to large reactive sites for photocatalysis.\textsuperscript{21–26} Nanomaterials have magical physical and ocular characteristics due to their size and in carceration e to initiate quantum properties. Nanopowder absorbs much more solar radiation compared to nanofilms. Size, morphology and optical properties can be controlled during solar photocatalysis and photovoltaics results in better absorption of solar irradiations.\textsuperscript{27,28} Several studies on the photo activity of Ag-doped TiO\textsubscript{2} and Ag-Fe co-doped TiO\textsubscript{2} (Ag-Fe CT) catalyst proved co-doped catalyst superior over undoped TiO\textsubscript{2}.\textsuperscript{25,29,30} Anisotropic structure of Ag dopant improved solar radiation absorbance.\textsuperscript{31} In this review, we have described recent progress in advanced oxidation processes with metal dopants, co-doped photocatalysts with their properties and bandgap. Synthesis of nano-doped TiO\textsubscript{2} mechanism of degradation by photocatalysis, operating variables and their effects on degradation and different techniques to modify optical properties of TiO\textsubscript{2} such as the use of metal and non-metal dopants, nanofilms, nanotubes and nanowires are discussed. The feasibility and the effectiveness of recycled photocatalyst have been studied. Hybrid AOPs is proved efficient compared to conventional AOP for complete mineralization of complex organics. Hybrid AOP using Fe doped TiO\textsubscript{2} has shown dual characteristics of photocatalysis and Fenton reaction, which has improved decolorization of wastewater.\textsuperscript{32} Photocatalytic treatment work under normal ambient conditions.\textsuperscript{33} Efficient methylene blue degradation using combining AOP with Fenton reagents, results in production of more OH radicals.\textsuperscript{34} Diclofenac and ibuprofen were converted efficiently in to biodegradable intermediates using planar falling film reactor and Coated TiO\textsubscript{2} on a Pilkington Active glass under UV radiations.\textsuperscript{35,36} This review will be useful to select efficient hybrid AOP for specific industrial wastewater treatment.

**Advanced Oxidation Processes**

AOPs are effluent treatment technology that produces a hydroxyl radical (OH) with highest oxidation potential and performs oxidation of organics to produce carbon dioxide and water as end products. These processes use ozone, photo Fenton reagents, hydrogen peroxide, or semiconductor photocatalysis to generate OH. TiO\textsubscript{2} was focused on photocatalysis by many researchers. It is available in three forms anatase, brookit and rutile. Amongst all these, the tetragonal anatase structure performs efficient photocatalysis.\textsuperscript{37,38} Various advanced oxidation processes consist of pollutant removal technologies
in which hydrogen radicals serve as an active medium. The methods are separated according to the source of the formation of hydroxyl radicals as shown in Fig. 1.  

Table 1 shows the oxidation potentials of various oxidizing agents. OH• Radical is nontoxic, nonselective and has the highest oxidation potential hence it is capable to mineralize a major category of organic materials from wastewater during photocatalysis.

### Table 1: Oxidation potential of different oxidants

| Oxidizing Agent | Potential of oxidation (V) |
|-----------------|---------------------------|
| OH•             | 2.8                       |
| O₂⁻             | 2.4                       |
| O₃             | 2.1                       |
| H₂O₂           | 1.8                       |
| HOCl           | 1.5                       |
| O₂             | 1.2                       |

Some benefits of research of AOPs are as follows:
1. Newer technology to produce strong and non-specific hydroxyl radical oxidizing agent;
2. To set up the highest standards for effluent treatment;
3. To develop an advanced mode of operation and competitiveness.

Table 2 summarizes different AOPs used for the degradation of various organics.

### Table 2: Different Advanced Oxidation Processes for component degradation

| Sr. No. | AOPs                        | Component for degradation | Experimental conditions | Results | Ref. |
|---------|-----------------------------|---------------------------|-------------------------|---------|------|
| 1       | TiO₂-photocatalytic         | Tetracycline (TC)         | Total Carbon 5–20 mg/L, TiO₂ 0.5-2 g/L for degradation, TiO₂ 1 g/L, 12 W halogen lamp Total Carbon 10 mg/L | Optimum TiO₂ conc. 1 g/L Toxicity removal 84% in 240 min | 19 |
| 2       | aerobic, anaerobic          | Ciprofloxacin (CIP)       | Aerobic/anaerobic reactor, sonication, photolysis | COD removal and CIP yields were 95% and 83%, 95% and 81% after 45 min, 98% and 88% | 41 |
| 3       | TiO₂-assisted ozonation in  | cyanotoxin                | pH 7, O30.25-2 mg/L, TiO₂·500 mg/L, CYN 5 mg/L | Pseudo first order, ozonation increased degradation from 75.7% to 98.9% | 42 |
4 hybrid ozonation
- nano filtration-
continuous process

COD inlet 1300 mg/L
COD outlet 50 mg/L (96.15%) ozone
treatment increase permeate flux
and decreased fouling index due to less flocculation so pores are not clogged.

5 Ozonation,
$\text{H}_2\text{O}_2$/UV and
$\text{TiO}_2$ Photocatalysis

- Carbamazepine,
propranolol,
clofibric acid,
diclofenac, oflo-
xacin, sulfamet-
hoxazole, blue-
green algae

- Hydrogen peroxide
(30% w/w), pH 7.6,
time: 20 min, ozone
13.875 mg/L, 0.3 gm/L
$\text{TiO}_2$, UV 300 W, 48 hr
TiO$_2$, -poliensis, rotifer),
80% removal
of each organic
toxicity (% survival
of blue-green algae
Synechococcusleo

6 Combined
GAC adsorption
and
$\text{UV254/H}_2\text{O}_2$ wastewater

2.12 to 6.37 mg
$\text{H}_2\text{O}_2$/mgCOD,
time 3 hr, pH 3.4
20-60 min GAC,
pH 3.4

Highest TOC removal 88%

Major merits of AOP includes the faster rate of mineralization, non biodegradable organics are completely oxidized into $\text{CO}_2$ and $\text{H}_2\text{O}$, treated effluent can be directly reused without further purification, avoid sludge generation and its handling problems, it can be easily clubbed with existing ETP with little modification, and economic operation and maintenance compared to incineration. Demerits of AOPs are higher capital costs, complex and unknown reaction chemistry may sometimes lead to more hazardous intermediates formation and photochemical reactor design and operation are difficult. Challenges of AOPs are photocatalyst deactivation and unknown routes for different reactions, development of proper doped catalysts to enhance the absorption of solar radiation, the selectivity of photocatalyst may sometimes pose a problem in treatment when a mixture of different organics is present, electron and hole recombine to result in lower net generation of OH radicals, scale-up and commercialization of process and UV radiations may sometimes degrade ozone, chlorine and hydrogen peroxide which are useful oxidizing agents in the process.

Titanium Dioxide Photocatalysis

Semiconductor oxides have a greater number of surface atoms on a surface which enables photon absorption and performs various oxidation and reduction reactions for complete removal of a variety of organics from aqueous solutions. Titanium dioxide is widely preferred for photocatalysis due to its stability, reusability, nontoxicity, anti-corrosiveness and low cost. Different other oxides that can also be used for photocatalysis are zinc, tin, zirconium, cadmium and iron. Hydroxyl radicals react with organics to produce carbon dioxide and water.

The main reactions involved in photocatalysis are shown below (equation (1) to equation (8)).

**Photon absorption:**

$$\text{MO} + h\nu \rightarrow \text{MO} + e^-_{\text{CB}} + h^+_{\text{VB}} \quad \ldots(1)$$

**Oxidation:**

$$h^+ + \text{OH}^-_{\text{surface}} \rightarrow \text{OH} \cdot \quad \ldots(2)$$

$$\text{H}_2\text{O} + h^+ \rightarrow \text{OH} + \text{H}^+ \quad \ldots(3)$$

$$\text{H}_2\text{O} + h^+ \rightarrow \text{H}^+ + \frac{1}{2} \text{H}_2\text{O}_2 \quad \ldots(4)$$

$$\text{H}_2\text{O}_2 \rightarrow 2 \text{OH}^+ \quad \ldots(5)$$

**Reduction:**

$$\text{O}_2 + e^- \rightarrow \text{O}_2^- \quad \ldots(6)$$
H₂O + O₂ → H₂O₂ + O₂ \(\ldots(7)\)

**Electron and hole combination:**
\[ h^+ + e^- \rightarrow \text{energy} \] \(\ldots(8)\)

where MO is a metal oxide, hv are photons, h⁺ are holes. When photons bombard on TiO₂ surface it enables electron movement and reactions on an interface where large numbers of organic substances are absorbed from the effluent. Semiconductor TiO₂ absorbs photons and transfer electron from the valance band (vb) to the conduction band (cb). On the valence band, holes are generated which reacts with H₂O or OH- to produce hydroxyl radicals. TiO₂ is N-type semiconductor material. Hole performs oxidation reactions and electron performs reduction reactions as shown in equations (1) to (9) on the surface along with complete oxidation of organics to produce CO₂ and H₂O.

For efficient photocatalysis, the bandgap should be lower which promotes the transfer of e⁻ and holes. This will also influence the redox potential of photogenerated electrons and the oxidation potential of holes. The handling of TiO₂ powder form is difficult and the cost of UV radiation makes the treatment energy-intensive and uneconomical. These issues limit the commercialization of AOPs for industrial effluent treatment. These limitations can be overcome by surface modification of TiO₂ with transition metal doping which reduces the bandgap and greater absorption of visible light is possible, also the dopant metals trap e⁻ and prevent its recombination with holes, hence, the photocatalysis can be performed under solar radiation to make system economical for removal of refractory organics compared to incineration treatment. Various metal dopants are Chromium, manganese, cobalt, copper, iron Nickel, Zinc, cerium, Neodymium, Eurotium, Lanthanum, etc. and various non-metal dopants are Palladium chloride, carbon, nitrogen, and Flouride.

**Recyclability of Photocatalyst**

TiO₂ doped with 33% Fe₂O₃ core-shell photocatalyst has enhanced paracetamol removal by photocatalysis from water and the photocatalyst could be easily separated and reused for four recycle runs. Ag decorated Fe₂O₃/TiO₂ coated cenosphere prepared via Modified sol-gel and wet impregnation can be recycled for 8 cycles with a slight reduction in Methylene blue degradation efficiency. The novel engineered photocomposite core-shell structure Fe₂O₃@SiO₂@TiO₂ showed greater photoactivity.
compared to commercial TiO$_2$. The catalyst provided easy separability using a magnet and was recycled for 10 numbers of recycling runs without a decrease in efficiency.\textsuperscript{22} When the Ag-Fe CT with Ti/Ag mole ratio 30 photocatalysts were reused for six numbers of runs, 63.25\% COD was removed in 5 hr solar light irradiation, indicating more deactivation of the catalyst during photocatalysis; which represented that the Ag-Fe CT 30 could be recyclable effectively for 4 cycles. The reduction in % COD removal was only less than 5\% after three runs of recycling for Ag-Fe CT 30. Ag-Fe CT 30 catalyst has proved its stability even after 4 recycle runs and it can perform photocatalysis under solar radiation effectively for the photocatalysis of drug intermediates.\textsuperscript{16}

Dye degradation efficiency by Fe$^{3+}$ doped TiO$_2$ has been found to decrease by 9\% at the end of six recycle runs.\textsuperscript{55} Ag-Fe CT and Fe$_2$O$_3$/SiO$_2$ co-doped TiO$_2$ and Ag-Fe CT supported on graphene oxide has shown good stability for 5 recycle runs.\textsuperscript{58} Table 4 summarizes the literature review done for the recyclability of photocatalysts. The photocatalysts can be recovered after treatment and efficiently used for several runs without loss in efficiency of treatment or component degradation. The result showed a decrease in photocatalytic activity with an increase in the number of recycling runs as the poisoning of the catalyst increases due to surface blockage, less adsorption and low rate of oxidation reaction.\textsuperscript{7}

Table 3: Feasibility and effectiveness of photocatalyst for recyclability

| Sr. No. | Catalyst | Synthesis method | Model pollutant and exptry. Conditions | Recyclability runs | Result | Ref. |
|---------|----------|------------------|----------------------------------------|-------------------|--------|-----|
| 1       | Fe$_3$O$_4$–TiO$_2$ | Solvothermal and micro-thermal method | Phenol, UV light, 100-300 min, 0.5 g/L | 2 | Degradation was 100\%, 70\%, 32\% for P25 and Fe$_3$O$_4$–TiO$_2$ (3 ml titanium butoxide), Fe$3O4$–TiO$_2$ (10 ml Titanium butoxide) respectively | 2 |
| 2       | Fe$_3$O$_4$@SiO$_2$/β-NaY F$_4$:Yb$^{3+}$, Tm$^{3+}$/TiO$_2$ | sol–gel process and solvol-thema | methyl blue, methyl orange, rhodamine B, and phenol under 1-10 ppm, 144 min, Laser light, 10 g/L | 4 | 76.62\%, 68.48\%, 30.05\% and 27.16\% | 57 |
| 3       | Ag-doped TiO$_2$, Ag:Ti molar ratio: 0.02-0.12 | solgel | Acetamiprid- 20 mg/L-insecticide, UV light, 60 min, 0.4 g/L | 6 | Ag/Ti = 0.06 opti, as Ag increase rutile phase increase | 58 |
| 4       | Fe$^{3+}$-doped TiO$_2$-1-4 wt % | modified sol-gel | azo dye acid orange 7-50 mg/L, solar, UV and visible light, 18 min, 0.3 g/L | 4 | 100 % UV, 100 % visible, 90 % solar in 2 hr, 3 wt % opt-98.9 % | 55 |
| 5       | N-TiO$_2$/Fe$_3$O$_4$ @SiO$_2$ and Ag-Fe | coprec pitation | bisphenol A: 2 mg/L, visible light, 90 min | 3 | 100 % and 88\% using Ag-Fe and N-TiO$_2$/Fe$_3$O$_4$ @SiO$_2$, respectively | 56 |
| 6       | Ag-doped TiO$_2$-P25 | surface impreg | Drug: pentoxifylline | 10 | Ag-TiO$_2$-P25: Opt.: 0.75 g/L cat | 30 |
Ammonical nitrogen removal using photocatalysis

NH\textsubscript{4}-N removal is higher in alkaline pH during photocatalysis. At lower pH, the surface of photocatalyst has a positive charge whereas ammoniacal nitrogen compounds can be adsorbed only on the surface which has a negative charge.\textsuperscript{93} NH\textsubscript{4}-N removal is more when pH is greater than 10. Researchers have reported that it is not possible to oxidize NH\textsubscript{4}-N OH by radicals.\textsuperscript{94}

| Supported on | Method | Conc. | Degradation | TOC | COD | Res. | pH |
|-------------|--------|------|-------------|-----|-----|------|----|
| Clay beads, Fe-Ag-TiO\textsubscript{2} composite (1.5 wt %) | Supported Ag | (PEN) 50 mg/L, methylene blue | 68% | 90% | 30 min | 50 | 29 |
| 7 | Clay supp. Fe doped TiO\textsubscript{2} (1-4 %: 2% opt) | Surface impregnation | Pesticide-Carbendazim: 4-10 gm/L, methyl blue | 70% | UV | 30 | 59 |
| 8 | Fe\textsuperscript{3+} doped TiO\textsubscript{2} film with Fe\textsuperscript{3+} =0, 1, 3, 5, 7 and 10 | Spin coating | methyl blue, 10-5 mg/L visible, 150 min, 0.5 g/L | 96.7% | 10th | 10 | 60 |
| 9 | Fe doped TiO\textsubscript{2}-3% | Sol gel | methyl blue, 10-4 mol/L visible, 150 min, 0.5 g/L | 59, 97, 79% for TiO\textsubscript{2}, 3% Fe and 7% Fe-TiO\textsubscript{2} | 7 |
| 10 | Cu\textsuperscript{2+}, Ag\textsuperscript{+}, Zn\textsuperscript{2+}, Fe\textsuperscript{3+}, and Al\textsuperscript{3+} ion and Pt metallic | Sol gel, 0.5 mol % dopant metal | Para nitrophenol: 10-4 mol/L, 480 min, 1 g/L | 50% -TiO\textsubscript{2}, 55: Fe 0.5, Fe 2: 35, Fe 5: 15, Ag 0.5: 58, Ag 2: 60, Pt 0.1: 79% | 61 |
| 11 | Ag-doped TiO\textsubscript{2} pillars-2.8 % | Wet impregnation and high temp thermal reduction | 2,4-dichlorophenol: 5 mg/L, 30 ml, visible, 120 min 1.67 g/L | 99% | 10 |
| 12 | Au-Ag NPs -decorated TiO\textsubscript{2} -modified Fe\textsubscript{3}O\textsubscript{4} | Solvo thermal | Textile waste water-Rh6G dye 30 ppm, xenon lamp, 60 min 2.67 g/L | 95% removal. 8% efficiency decreased after 5 runs | 38 |

\*NA: data not available
When pH is above 9, NH$_4^+$-N can be converted into NH$_3$.

Hence acidic or neutral condition does not favor NH$_3$–N removal simultaneously with organics. Table 5 summaries research done for ammonical nitrogen removal by photocatalysis.

### Table 4: Ammonical nitrogen removal during photocatalysis

| Sr. No. | Catalyst | Synthesis method | Model | light pollutant | Opt pH | Catalyst | Time, dose | Result hr | Ref. |
|---------|----------|------------------|-------|----------------|-------|----------|------------|----------|------|
| 1       | TiO$_2$ film on glass beads: to 10 layers of TiO$_2$ thin film. | Coating with sol-gel method | NH$_4$Cl solution 300 ml, ammonia conc. 700 mg/L | UV light | 7 | film | 2 hr | 6 coating opt, 70 % removal efficiency | 66 |
| 2       | Cu/ZnO/rGO Nanocomposite | Sol-gel | Domestic wastewater NH$_4$+:N: 10, 30, 50, 70, and 100 mg/L | Visible-Xenon lamp | 10 | 0.2-2 g/L, opt 2 | 2 hr | Optimum: NH$_4$+ conc. = 50 mg/L, catalyst conc. = 2 g/L, pH 10, 83% removal efficiency | 67 |
| 3       | La/Fe/TiO$_2$ composite | Sol-gel | NA | 500 W mercury lamp | 10 | 1 g/L, | 3 hr | 64.6% removal efficiency | 68 |
| 4       | TiO$_2$ | Sol-gel | Secondary treated effluent: Ammonia conc. 26 – 214 mg/l | UV light | 10.7 | 2.1 g/L | 3.5 hr | 50 % removal efficiency | 65 |
| 5       | Ag/Fe co-doped TiO$_2$ Sol-gel | Industrial effluent, COD: 88660 mg/L, NH$_3$-N:3287 mg/L | Solar | | 5 | 1g/L | 5 hr | 64.69% COD removal, 16.05% NH$_3$-N removal | 16 |

*NA: data not available

**Hybrid Advanced Oxidation processes**

COD removal using three methods, combining electrochemical process with AOP, Fenton reagent and flotation HAOP technology has been proved effective in the treatment of pharmaceutical wastewater for COD removal$^{64}$. An ultrasound when used in combination with photocatalysis, Fenton Reagent and the Photolysis process, proved efficient for non-biodegradable toxic organics removal. This combination of AOP will overcome problems of repelling photocatalyst and pollutants due to similar charges. A sonophotocatalysis has been found effective for the removal of variety of organics present in wastewater.$^{70}$ Hybrid AOPs with sonolysis, Fenton and photo- ferrioxalate system with sonolysis has been studied for degradation of two dyes: Acid Red B and Methylene Blue. Sonolysis alone has shown the lowest efficiency. Coupling of sonolysis with either Fenton or photo- ferrioxalate system has shown the greater ability of decolorization. Ternary coupling of all these three systems has shown a negative effect of dyes degradation due to the interaction of individual mechanisms$^{71}$. Table 5 summaries research done on hybrid advanced oxidation processes.
Table 5: Hybrid advanced oxidation processes

| Sr. No. | Hybrid AOP                                                                 | Compound for degradation/ treatment | Experimental condition                                                                 | Result                                                                 | Ref. |
|---------|-----------------------------------------------------------------------------|--------------------------------------|---------------------------------------------------------------------------------------|------------------------------------------------------------------------|------|
| 1       | Advanced oxidation with O₃ addition, adsorption by activated charcoal       | Pharmaceutical effluent              | pH 5-11, time – AOP- 3 hr, adsorption with charcoal - 2.5 hr                           | H₂O₂ addition with AOP: COD removal: 75-88%. Further continuation of treatment with adsorption by activated charcoal- COD removal reached up to 93% | 72   |
| 2       | hydrodynamic cavitation with Fe₃O₄ nanophoto-catalyst                    | P-nitrophenol (PNP)                 | 8 atm -pressure, 3-pH, 20 mg/L-PNP, Fe₃O₄ to H₂O₂ ratio= 1:1, H₂O₂:0.6 mol/L, H₂O₂:0.6 mol/L | PNP degradation 78%                                                  | 73   |
| 3       | hydrodynamic cavitation (HC) with ZnO/ZnFe₂O₄ and persulfate system+ Magnetic separation for recycle | Carbamazepine (CBZ)                | 9 atm-pressure, 4-pH, 15 mg/L-CRB, 18 W UV, 500mg/L-Na₂S₂O₈, 500 mg/L-ZnO/ZnFe₂O₄ | 98% CBZ degradation                                                  | 74   |
| 4       | electrocatalytic process                                                   | Industrial raw effluent (antibiotics) | Cathod: carbon, anode: Ti/PtIr plate                                                | 100% COD removal                                                      | 75   |
| 5       | UV/ZnO nps/O₂                                                              | 4-Nitro aniline (4-NA)              | catalyst dose: 3 g/L, pH:5, 4-NA: 10 mg/L, time: 60 min                           | Degradation of 4-NA: 92%                                               | 76   |
| 6       | MOFs@COFs hybrid materials with C₃N₄· sulfate radical-based advanced oxidation processes | bisphenol A (BPA)                 | Visible light                                                                        | BPA degradation 99%                                                   |      |
| 7       | UV-C or hydrogen peroxide                                                  | Boscalid, pyra -clostralin, fenbuconazole and glyphosate-Pesticides- Pesticides removal on apple dyes | H₂O₂, UV-C                                                              | glyphosate -99% removal, boscalid, pyraclostrolin and fenbuconazole degradation 88 %, 100 % and 70 % respectively dyes removal-90%, 0.75 wt.% CuO adsorbed 38% higher and degraded 26% more methylene blue than WO₃ nanofibers | 77   |
| 8       | CuO particle-WO₃ nanofiber hybrids-(adsorb -ent/photocatalyst)             | WO₃ nanofibers and CuO nps, visible light |                                                                                     |                                                                        | 78   |
Conclusion
This review described various advanced oxidation processes with their merits, demerits, benefits and challenges. Various dopants have been compared for their enhanced photoactivity. The mechanism TiO$_2$ semiconductor doped with Ag and Fe has been discussed. The degradation of various chemical compounds using TiO$_2$-based photocatalysts, including mechanisms and factors affecting the process have been summarized. Hybrid AOP with photocatalyst is proved an effective method for treatment of wastewater. Addition of different oxidizing agents and materials such as H$_2$O$_2$, Fenton reagents and biochar have increased organic removal efficiency from wastewater. Electro Fenton and electrolysis, cavitation was used effectively for wastewater treatment. Advanced oxidation with O$_3$ addition, adsorption by activated charcoal for pharmaceutical wastewater treatment was also effective. This paper concludes that proper selection of Hybrid AOP can provide efficient mineralization of organics present in wastewater at low cost. Recyclability studies showed that photocatalyst can be separated after treatment and reused up to several runs efficiently without much decline in treatment efficiency.

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References
1. Makeswari M, Saraswathi P. Photo catalytic degradation of methylene blue and methyl orange from aqueous solution using solar light onto chitosan bi-metal oxide composite. *SM Appl Sci*. 2020;2(3). doi:10.1007/s42452-020-1980-4
2. Lendzion-Bieluń Z, Wojciechowska A, Grzechulska-Damszel J, Narkiewicz U, Śniadecki Z, Idzikowski B. Effective processes of phenol degradation on Fe3O4–TiO2 nanostructured magnetic photocatalyst. *J Phys Chem Solids*. 2020;136. doi:10.1016/j.jpcs.2019.109178
3. Dubey RS, Krishnamurthy KV, Singh S. Experimental studies of TiO2 nanoparticles synthesized by sol-gel and solvothermal routes for DSSCs application. *Results Phys*. 2019;14:102390. doi:10.1016/j.rinp.2019.102390
4. Cao S, Chan T-S, Lu Y-R, et al. Photocatalytic pure water splitting with high efficiency and value by Pt/porous brookite TiO2 nanoflutes. *Nano Energy*. Published online November 2019:104287. doi:10.1016/j.nanoen.2019.104287

5. Iqbal M, Ali A, Ahmad KS, et al. Synthesis and characterization of transition metals doped CuO nanostructure and their application in hybrid bulk heterojunction solar cells. *SN Appl Sci*. 2019;1(6):1-8. doi:10.1007/s42452-019-0663-5

6. Basavarajappa PS, Patil SB, Ganganagappa N, Reddy KR, Raghu A V., Reddy CV. Recent progress in metal-doped TiO2, non-metal doped/codoped TiO2 and TiO2 nanostructured hybrids for enhanced photocatalysis. *Int J Hydrogen Energy*. 2020;45(13):7764-7778. doi:10.1016/j.ijhydene.2019.07.241

7. Komaraiah D, Radha E, Kalarikkal N, Sivakumar J, Ramana Reddy M V., Sayanna R. Structural, optical and photoluminescence studies of sol-gel synthesized pure and iron doped TiO2 photocatalysts. *Ceram Int*. 2019;45(18):25060-25068. doi:10.1016/j.ceramint.2019.03.170

8. Khanna A, Shetty VK. Solar light induced photocatalytic degradation of Reactive Blue 220 (RB-220) dye with highly efficient Ag@TiO2 core-shell nanoparticles: A comparison with UV photocatalysis. *Sol Energy*. 2014;99:67-76. doi:10.1016/j.solener.2013.10.032

9. Chen D, Ray AK. *Photocatalytic Kinetics of Phenol and Its Derivatives over UV Irradiated TiO2*. Vol 23.; 1999. doi:10.1016/S0926-3373(99)00068-8

10. Nagaveni KMSHM. Photocatalytic degradation of various dyes by combustion synthesized nano anatase TiO2. *Appl Catal B Environ*. 2003;45(1);23-28. doi:DOI: 10.1016/S0926-3373(03)00124-3

11. Al-Hartomy OA. Synthesis, characterization, photocatalytic and photovoltaic performance of Ag-doped TiO2 loaded on the Pt-carbon spheres *Mater Sci Semicond Process*. 2014;27(1):71-78. doi:10.1016/j.msse.2014.06.025

12. Varadharajan K, Singaram B, Mani R, Jeyaram J. Enhanced Visible Light Photocatalytic Activity of Ag and Zn Doped and Codoped TiO2 Nanoparticles. *J Clust Sci*. 2016;27(5):1815-1829. doi:10.1007/s10876-016-1044-5

13. Birben NC, Uyguner-Demirel CS, Kavurmaci S Sen, et al. Application of Fe-doped TiO2 specimens for the solar photocatalytic degradation of humic acid. *Catal Today*. 2017;281:78-84. doi:10.1016/j.cattod.2016.06.020

14. Çiçan M, Drăgan N, Crişan D, et al. The effects of Fe, Co and Ni dopants on TiO2 structure of sol–gel nanopowders used as photocatalysts for environmental protection: A comparative study. *Ceram Int*. 2016;42(2):3088-3095. doi:10.1016/j.ceramint.2015.10.097

15. Başaran Dindaş G, Çalışkan Y, Çelebi EE, Tekbaş M, Bektas N, Yatmaz HC. Treatment of pharmaceutical wastewater by combination of electrocoagulation, electro-fenton and photocatalytic oxidation processes. *J Environ Chem Eng*. 2020;8(3). doi:10.1016/J.JECE.2020.103777

16. Bhatti DT, Parikh SP. Solar Light Induced Photocatalysis for Treatment of High COD Pharmaceutical Effluent with Recyclable Ag-Fe Codoped TiO2: Kinetics of COD Removal. *Curr World Environ*. 2020;15(1):137-150. doi:10.12944/cwe.15.1.17

17. Carbuloni CF, Savoia JE, Santos JSP, et al. Degradation of metformin in water by TiO2–ZrO2 photocatalysis. *J Environ Manage*. 2020;262:110347. doi:10.1016/j.jenvman.2020.110347

18. Darshana B, Parikh S, Shah M. Potential of Ag–Fe co-doped TiO2 nanocomposite for solar photocatalysis of high COD pharmaceutical effluent and influencing factors. *Energy, Ecol Environ*. 2020;5(5):344-358. doi:10.1007/s40974-020-00162-6

19. Watkinson AJ, Murby EJ, Costanzo SD. Removal of antibiotics in conventional and advanced wastewater treatment: Implications for environmental discharge and wastewater recycling. *Water Res*. 2007;41(18):4164-4176. doi:10.1016/j.watres.2007.04.005

20. Zhu XD, Wang YJ, Sun RJ, Zhou DM. Photocatalytic degradation of tetracycline
in aqueous solution by nanosized TiO2. *Chemosphere*. 2013;92(8):925-932. doi:10.1016/j.chemosphere.2013.02.066

21. Wang W, Zhang J, Chen F, He D, Anpo M. Preparation and photocatalytic properties of Fe3+-doped Ag@TiO2 core-shell nanoparticles. *J Colloid Interface Sci*. 2008;323(1):182-186. doi:10.1016/j.jcis.2008.03.043

22. Chi Y, Yuan Q, Li Y, et al. Magnetically separable Fe3O4@SiO2@TiO2-Ag microspheres with well-designed nanostructure and enhanced photocatalytic activity. *J Hazard Mater*. 2013;262:404-411. doi:10.1016/j.jhazmat.2013.08.077

23. Harifi T, Montazer M. Fe 3+ :Ag/TiO2 nanocomposite: Synthesis, characterization and photocatalytic activity under UV and visible light irradiation. *Appl Catal A Gen*. 2014;473:104-115. doi:10.1016/j.apcata.2014.01.005

24. Tedsree K, Temnuch N, Sriplai N, et al. Ag modified Fe3O4@TiO2 magnetic core-shell nanocomposites for photocatalytic degradation of methylene blue. In: *Materials Today: Proceedings*. Vol 4. Elsevier Ltd; 2017:6576-6584. doi:10.1016/j.matpr.2017.06.170

25. Petronella F, Truppi A, Sibillano T, et al. Multifunctional TiO2/FexOy/Ag based nanocrystalline heterostructures for photocatalytic degradation of a recalcitrant pollutant. *Catal Today*. 2017;284:100-106. doi:10.1016/j.cattod.2016.11.025

26. Zhan J, Zhang H, Zhu G. Magnetic photocatalysts of cenospheres coated with Fe3O4/4TiO2 core/shell nanoparticles decorated with Ag nanoparticles. *Ceram Int*. 2014;40(6):8547-8559. doi:10.1016/j.ceramint.2014.01.069

27. Qian LL, Wang ZX, Zhu LM, Li K, Li BL, Wu B. Synthesis, structure, spectral characteristic and photocatalytic degradation of organic dyes of a copper metal-organic framework based on tr(triazole) and pimelate. *Spectrochim Acta - Part A Mol Biomol Spectrosc*. 2019;214:372-377. doi:10.1016/j.saa.2019.02.059

28. Nasralla N, Yeganeh M, Astuti Y, et al. Structural and spectroscopic study of Fe-doped TiO2 nanoparticles prepared by sol-gel method. *Sci Iran*. 2013;20(3):1018-1022. doi:10.1016/j.scient.2013.05.017

29. Jaihindh DP, Chen CC, Fu YP. Reduced graphene oxide-supported Ag-loaded Fe-doped TiO2 for the degradation mechanism of methylene blue and its electrochemical properties. *RSC Adv.* 2018;8(12):6488-6501. doi:10.1039/c7ra13418e

30. Bansal P, Verma A. Applications of sunlight responsive Fe-Ag-TiO2 composite incorporating in-situ dual effect for the degradation of pentoxifylline. *Mater Sci Eng B Solid-State Mater Adv Technol*. 2018;236-237:197-207. doi:10.1016/j.mseb.2018.11.016

31. Miller OD, Hsu CW, Reid MTH, et al. Fundamental limits to extinction by metallic nanoparticles. *Phys Rev Lett*. 2013;112(12). doi:10.1103/PhysRevLett.112.123903

32. Bethi B, Sonawane SH, Rohit GS, et al. Investigation of TiO2 photocatalyst performance for decolorization in the presence of hydrodynamic cavitation as hybrid AOP. *Ultrason Sonochem*. 2016;28:150-160. doi:10.1016/j.ultsonch.2015.07.008

33. Mukim A, Vistanty H, Zen N. Hybrid advanced oxidation process (HAOP) as highly efficient and powerful treatment for complete demineralization of antibiotics. *Sep Purif Technol*. 2020;241:116728. doi:10.1016/j.seppur.2020.116728

34. Karim MAH, Aziz KHH, Omer KM, et al. Degradation of aqueous organic dye pollutants by heterogeneous photo-assisted Fenton-like process using natural mineral activator: Parameter optimization and degradation kinetics. *IOP Conf Ser Earth Environ Sci*. 2021;958(1):012011. doi:10.1088/1755-1315/958/1/012011

35. Hama Aziz KH. Application of different advanced oxidation processes for the removal of chloroacetic acids using a planar falling film reactor. *undefined*. 2019;228:377-383. doi:10.1016/J.CHEMOSPHERE.2019.04.160

36. Aziz KHH, Omer KM, Mahyar A, Miessner H, Mueller S, Moeller D. Application of Photocatalytic Falling Film Reactor to Elucidate the Degradation Pathways of Pharmaceutical Diclofenac and Ibuprofen
37. Giampiccolo A, Tobaldi DM, Leonardi SG, et al. Sol gel graphene/TiO2 nanoparticles for the photocatalytic-assisted sensing and abatement of NO2. *Appl Catal B Environ.* 2019;243:183-194. doi:10.1016/j.apcata.2018.10.032

38. Amoli-Diva M, Anvari A, Sadighi-Bonabi R. Synthesis of magneto-plasmonic Au-Ag NPs-decorated TiO2-modified Fe3O4 nanocomposite with enhanced laser/solar-driven photocatalytic activity for degradation of dye pollutant in textile wastewater. *Ceram Int.* 2019;45(14):17837-17846. doi:10.1016/j.ceramint.2019.05.355

39. Trojanowicz M, Bojanowska-Czajka A, Bartosiewicz I, Kulisa K. Advanced Oxidation/Reduction Processes for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) – A review of recent advances. *Chem Eng J.* 2018;336:170-199. doi:10.1016/j.cej.2017.10.153

40. Sharma Sandip jayesh ruparelia. A general review on Advanced Oxidation Processes for waste water treatment. *Chemistry (Easton).* Published online 2011.

41. Angela, Szabolcs, Zsuzsanna, Gábor C. Advanced Treatment of Pharmaceutical Wastewater by Nano Filtration and Ozonation. In: *FASCICUIE* 2012.; 2012.

42. Wu CC, Huang WJ, Ji BH. Degradation of cyanotoxin cylindrospermopsin by TiO2-assisted ozonation in water. *J Environ Sci Heal - Part A Toxic/Hazardous Subst Environ Eng.* 2015;50(11):1116-1126. doi:10.1080/10934529.2015.1047664

43. Chittala G, Mogadati PS. PERFORMANCE STUDIES ON A PHARMACEUTICAL WASTEWATER TREATMENT PLANT WITH A SPECIAL REFERENCE TO TOTAL DISSOLVED SOLIDS REMOVAL. *Int J life Sci Biotechnol pharma Res.* 2012;1(1).

44. Andreozzi R, Campanella L, Frayssé B, et al. Effects of advanced oxidation processes (AOPs) on the toxicity of a mixture of pharmaceuticals. *Water Sci Technol.* 2004;50(5):23-28. doi:10.2166/wst.2004.0304

45. Ghafoori S, Shah KK, Mehrvar M, Chan PK. Pharmaceutical wastewater treatment using granular activated carbon and UV/H2O2 processes: Experimental analysis and modelling. *Can J Chem Eng.* 2014;92(7):1163-1173. doi:10.1002/cjce.21981

46. Chen Q, Yu Z, Pan Y, et al. Enhancing the photocatalytic and antibacterial property of polyvinylidene fluoride membrane by blending Ag–TiO2 nanocomposites. *J Mater Sci Mater Electron.* 2017;28(4):3865-3874. doi:10.1007/s10854-016-5999-7

47. Xiu Z, Guo M, Zhao T, et al. Recent advances in Ti3+ self-doped nanostructured TiO2 visible light photocatalysts for environmental and energy applications. *Chem Eng J.* Published online February 2019. doi:10.1016/j.cej.2019.123011

48. Huang M, Li J, Huang Y, et al. Construction of g-C3N4 based heterojunction photocatalyst by coupling TiO2-SnO2 solid solution for efficient multipurpose photocatalysis. *J Alloys Compd.* Published online November 2020:158132. doi:10.1016/j.jallcom.2020.158132

49. Khanna A, Shetty K V. Solar light-driven photocatalytic degradation of Anthraquinone dye-contaminated water by engineered Ag@TiO2 core–shell nanoparticles. *Desalin Water Treat.* 2014;10(3):376-385. doi:10.1080/19443994.2014.888681

50. Yang H, Zhang K, Shi R, Li X, Dong X, Yu Y. Sol-gel synthesis of TiO2 nanoparticles and photocatalytic degradation of methyl orange in aqueous TiO2 suspensions. *J Alloys Compd.* 2006;413(1-2):302-306. doi:10.1016/j.jallcom.2005.06.061

51. Rabbani M, Safalou moghaddam S, Rahimi R. Photocatalytic degradation of 4-nitrophenol in aqueous N, S-codoped TiO2 suspensions. In: *International Electronic Conference on Synthetic Organic Chemistry.* MDPI AG; 2019:1-30. doi:10.3390/ecsoc-15-00791

52. Stasinakis 66. A.S. (PDF) Use of Selected Advanced Oxidation Processes (AOPs) for Wastewater Treatment – a Mini Review. *Glob Nest.* 2008;10(3):376-385.

53. Banerjee AN. The design, fabrication, and photocatalytic utility of nanostructured semiconductors: Focus on TiO2-based nanostructures. *Nanotechnol Sci Appl.* 2011;4(1):35-65. doi:10.2147/NSA.S9040
54. Gupta SM, Tripathi M. A review of TiO2 nanoparticles. *Chinese Sci Bull.* 2011;56(16):1639-1657. doi:10.1007/s11434-011-4476-1

55. Han F, Kambala VSR, Dharmarajan R, Liu Y, Naidu R. Photocatalytic degradation of azo dye acid orange 7 using different light sources over Fe3+-doped TiO2 nanocatalysts. *Environ Technol Innov.* 2018;12:27-42. doi:10.1016/j.eti.2018.07.004

56. He J, Zeng X, Lan S, Lo IMC. Reusable magnetic Ag/Fe, N-TiO2/Fe3O4@SiO2 composite for simultaneous photocatalytic disinfection of E. coli and degradation of bisphenol A in sewage under visible light. *Chemosphere.* 2019;217:869-878. doi:10.1016/j.chemosphere.2018.11.072

57. Chen Z, Fu ML. Recyclable magnetic Fe3O4@SiO2/β-NaYF4:Yb3+,Tm3+/TiO2 composites with NIR enhanced photocatalytic activity. *Mater Res Bull.* 2018;107:194-203. doi:10.1016/j.materresbull.2018.07.016

58. Cao Y, Tan H, Shi T, Tang T, Li J. Preparation of Ag-doped TiO2 nanoparticles for photocatalytic degradation of acetamiprid in water. *J Chem Technol Biotechnol.* 2008;83(4):546-552. doi:10.1002/jctb.1831

59. Kaur T, Sraw A, Wanchoo RK, Toor AP. Solar assisted degradation of carbendazim in water using clay beads immobilized with TiO2 & Fe doped TiO2. *Sol Energy.* 2018;162:45-56. doi:10.1016/j.solener.2017.11.033

60. R. Renugadevi1 TV, R. Narayanasamy SP, P.Krishnamurthi. Structural, optical properties and photocatalytic activity of Fe3C doped TiO2 thin films deposited by sol-gel spin coating - Google Search. *Rasayan J Chem.* 2016;9(2):125-132.

61. Mahy JG, Lambert SD, Léonard GLM, et al. Towards a large scale aqueous sol-gel synthesis of doped TiO2: Study of various metallic dopings for the photocatalytic degradation of p-nitrophenol. *J Photochem Photobiol A Chem.* 2016;329:189-202. doi:10.1016/j.jphotochem.2016.06.029

62. Suwarnkar MB, Dhabbe RS, Kadam AN, Garadkar KM. Enhanced photocatalytic activity of Ag doped TiO2 nanoparticles synthesized by a microwave assisted method. *Ceram Int.* 2014;40(4):5489-5496. doi:10.1016/j.ceramint.2013.10.137

63. Sun D, Sun W, Yang W, Li Q, Shang JK. Efficient photocatalytic removal of aqueous NH4+-NH3 by palladium-modified nitrogen-doped titanium oxide nanoparticles under visible light illumination, even in weak alkaline solutions. *Chem Eng J.* 2015;264:728-734. doi:10.1016/j.cej.2014.12.012

64. Lee J, Park H, Choi W. Selective Photocatalytic Oxidation of NH 3 to N 2 on Platinized TiO 2 in Water. *Environ Sci Technol.* 2002;36(24):5462-5468. doi:10.1021/es025930s

65. Xue Gong, Haifeng Wang, Chun Yang, Quan Li XC& JH. Treatment of ammonia nitrogen wastewater from coal gasification process with TiO2 photocatalysts doped with metal ions. *Futur Cities Environ.* 2015;1(12).

66. Gong X, Wang H, Yang C, Li Q, Chen X, Hu J. Photocatalytic degradation of high ammonia concentration wastewater by TiO2. *Futur Cities Environ.* 2017;1(0):12. doi:10.1186/s40984-015-0012-9

67. He S, Hou P, Petropoulos E, et al. High efficient visible-light photocatalytic performance of Cu/ZnO/rGO nanocomposite for decomposing of aqueous ammonia and treatment of domestic wastewater. *Front Chem.* 2018;6(JUN). doi:10.3389/fchem.2018.00219

68. Luo X, Chen C, Yang J, et al. Characterization of La/Fe/TiO2 and its photocatalytic performance in ammonia nitrogen wastewater. *Int J Environ Res Public Health.* 2015;12(11):14626-14639. doi:10.3390/ijerph121114626

69. Mukimin A, Vistanty H. Hybrid advanced oxidation process (HAOP) as an effective pharmaceutical wastewater treatment. *E3S Web Conf.* 2019;125:03007. doi:10.1051/E3SCONF/201912503007

70. Madhavan J, Theerthagiri J, Balaji D, Sunitha S, Choi MY, Ashokkumar M. Hybrid Advanced Oxidation Processes Involving Ultrasound: An Overview. *Molecules.* 2019;24(18). doi:10.3390/MOLECULES24183341

71. Chakma S, Das L, Moholkar VS. Dye decolorization with hybrid advanced oxidation processes comprising sonolysis/Fenton-like/photo-ferricyanide systems: A mechanistic investigation. *Sep Purif Technol.* 2015;156:596-607. doi:10.1016/J.SEPPUR.2015.10.055
72. Patel S, Mondal S, Majumder SK, Das P, Ghosh P. Treatment of a Pharmaceutical Industrial Effluent by a Hybrid Process of Advanced Oxidation and Adsorption. *ACS Omega*. 2020;5(50):32305-32317. doi:10.1021/ACSOMEGA.0C04139

73. Roy K, Moholkar VS. p–nitrophenol degradation by hybrid advanced oxidation process of heterogeneous Fenton assisted hydrodynamic cavitation: Discernment of synergistic interactions and chemical mechanism. *Chemosphere*. 2021;283:131114. doi:10.1016/J.CHEMOSPHERE.2021.131114

74. Roy K, Moholkar VS. Mechanistic analysis of carbamazepine degradation in hybrid advanced oxidation process of hydrodynamic cavitation/UV/persulfate in the presence of ZnO/ZnFe2O4. *Sep Purif Technol*. 2021;270:118764. doi:10.1016/J.SEPPUR.2021.118764

75. Malakootian M, Gharaghani MA, Dehdarirad A, et al. ZnO nanoparticles immobilized on the surface of stones to study the removal efficiency of 4-nitroaniline by the hybrid advanced oxidation process (UV/ZnO/ O3). *J Mol Struct*. 2019;1176:766-776. doi:10.1016/J.MOLSTRUC.2018.09.033

76. Lv SW, Liu JM, Li CY, Zhao N, Wang ZH, Wang S. Two novel MOFs@COFs hybrid-based photocatalytic platforms coupling with sulfate radical-involved advanced oxidation processes for enhanced degradation of bisphenol A. *Chemosphere*. 2020;243:125378. doi:10.1016/J.CHEMOSPHERE.2019.125378

77. Skanes B, Ho J, Warriner K, Prosser RS. Degradation of boscalid, pyraclostrobin, fenbuconazole, and glyphosate residues by an advanced oxidative process utilizing ultraviolet light and hydrogen peroxide. *J Photochem Photobiol A Chem*. 2021;418:113382. doi:10.1016/J.JPHOTOCHEM.2021.113382

78. Dursun S, Koyuncu SN, Kaya IC, Kaya GG, Kalem V, Akyildiz H. Production of CuO–WO3 hybrids and their dye removal capacity/performance from wastewater by adsorption/photocatalysis. *J Water Process Eng*. 2020;36:101390. doi:10.1016/J.JWPE.2020.101390

79. Chen H, Zhang YJ, He PY, Li CJ, Li H. Coupling of self-supporting geopolymer membrane with intercepted Cr(III) for dye wastewater treatment by hybrid photocatalysis and membrane separation. *Appl Surf Sci*. 2020;515:146024. doi:10.1016/J.APSUSC.2020.146024

80. Truong HB, Huy BT, Ray SK, Lee YI, Cho J, Hur J. H2O2-assisted photocatalysis for removal of natural organic matter using nanosheet C3N4-WO3 composite under visible light and the hybrid system with ultrafiltration. *ChemEng J*. 2020;399:125733. doi:10.1016/J.CEJ.2020.125733

81. Fazal T, Razzaq A, Javed F, et al. Integrating adsorption and photocatalysis: A cost effective strategy for textile wastewater treatment using hybrid biochar-TiO2 composite. *J Hazard Mater*. 2020;390:121623. doi:10.1016/J.JHAZMAT.2019.121623