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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 electro chemical 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.

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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,[1–3] water splitting for hydrogen production[4] and solar cells.[5] The application of TiO_2 as a photocatalyst is limited by UV radiations and recombination of the hole and electron pairs.[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.[8] Titanium dioxide is an N-type semiconductor having an oxygen deficit in its structure. TiO_2 is a superior, nontoxic stable and economical photocatalyst that provides a non-selective and efficient oxidizing agent, Hydroxyl radical (OH*).[9,10.] TiO_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* due to recombination of holes.[11]

Metal doping in $TiO_2$1) improves its absorbance in the visible region, e.g. a Ag: 300-800 nm, Co: 400-650 nm and Fe: 300-800 nm,[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 photoactivity;[15] 3) the Bandgap reduces from pure TiO_2 (3.1 eV) to doped TiO_2 (2.8 eV),[16, 17] Silver and iron are extensively investigated as a dopant for TiO_2 and proved superior photocatalysts for mineralization of active pharmaceutical ingredients(API).[18–20] Co-doping of TiO_2 using metal dopants is a promising technology for solar mineralization of refractory organics in wastewater. Doping of TiO_2 with Fe and Ag metals enhances the photocatalytic activity due to large reactive sites for photocatalysis.[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.[27,28] Several studies on the photo activity of Ag-doped TiO_2 and Ag-Fe co-doped TiO_2 (Ag-Fe CT) catalyst proved co-doped catalyst superior over undoped TiO_2.[25,29,30] Anisotropic structure of Ag dopant improved solar radiation absorbance.[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_2, mechanism of degradation by photocatalysis, operating variables and their effects on degradation and different techniques to modify optical properties of TiO_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_2 has shown dual characteristics of photocatalysis and Fenton reaction, which has improved decolorization of wastewater.[32] Photocatalytic treatment work under normal ambient conditions.[33] Efficient methylene blue degradation using combining AOP with Fenton reagents, results in production of more OH radicals.[34] Diclofenac and ibuprofen were converted efficiently in to biodegradable intermediates using planar falling film reactor andCoated TiO_2 on a Pilkington Active glass under UV radiations.[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_2 was focused on photocatalysis by many researchers. It is available in three forms anatase, brookite and rutile. Amongst all these, the tetragonal anatase structure performs efficient photocatalysis.[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.[39]

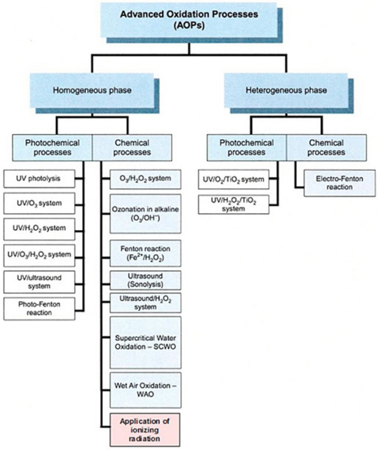

Fig.1: Types of Advanced Oxidation Processes

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[40]

Oxidizing Agent	Potential of oxidation (V)
OH•	2.8
O_2-	2.4
O_3	2.1
H_2O_2	1.8
HOCl	1.5
O_2	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	TiO_2-photocatalytic degradation	Tetracycline (TC)	Total Carbon 5–20 mg/L, TiO_2- 0.5-2 g/L 30 min in dark, 2 hr for photocatalytic degradation, TiO_2- 1 g/L, 12 W halogen lamp Total Carbon 10 mg/L	Optimum TiO_2 conc.1 g/L Toxicity removal 84 % in 240 min	19
2	aerobic, anaerobic, aerobic/anaerobic reactor, sonication, photocatalysis reactor	Ciprofloxacin (CIP)	Aerobic/anaerobic seque -ntial reactor system – Hydraulic retention time=10 days Organic loading rate= 0.2 g COD/L, Sonication at a power of 640 W and 35 kHz 45°C,pH 7, 45 min irradi-ation time, 210 W UV lamp, 0.5 g/L TiO_2 25°C	COD removal and CIP yields were 95% and 83%, 95% and 81% after 45 min, 98% and 88%	41
3	TiO_2-assisted ozonation in water	cyanotoxin cylindrospe -rmopsin (CYN)	pH 7, O30.25-2 mg/L, TiO_2=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		ozone – 1.17-4.85 mg/lit, NF module.- (AFC30) Polyamide film membrane with 75% CaCl2 retention, Flow rate: 8 L/min, 30 bar, 25°C	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.	43
5	Ozonation, H_2O_2/UV and TiO_2 Photo-catalysis	Carbamazep -ine, 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 TiO_2, UV 300 W, 48hr	Complete removal of toxicity (% survival of blue-green algae Synechococcusleo -poliensis, rotifer), 80 % removal of each organic	44
6	Combined GAC adsorption and UV254/H_2O_2	pharmaceutical wastewater	2.12 to 6.37 mg H_2O_2/mgCOD, time 3hr, pH 3.4 20-60 min GAC, pH 3.4	Highest TOC removal 88%	45

Major merits of AOP includes the faster rate of mineralization, non biodegradable organics are completely oxidized into CO_2 and H_2O, 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 arePhotocatalyst deactivation and unknown routes for different reactions,[46] 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[47] and UV radiations may sometimes degrade ozone, chlorine and hydrogen peroxide which are useful oxidizing agents in the process.[39]

Titanium Dioxide Photocatalysis

Semiconductor oxides have a greater number of surface atoms ona 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 photocatalys is are zinc, tin, zirconium, cadmium and iron.Hydroxyl radicals react with organics to produce carbon dioxide and water.[6,48] The main reactions involved in photocatalys is are shown below (equation (1) to equation (8)):[49]

Photon absorption:

$$MO + hv^{\cdot} \rightarrow MO + {}_{e}{}^{-}{}_{CB} + h+_{VB} \quad ...(1)$$

Oxidation:

$$h^{+} + OH-_{(Surface)} \rightarrow OH \bullet \quad ...(2)$$

$$H_2O + h^{+} \rightarrow OH \bullet + H+ \quad ...(3)$$

$$H_2O + h^{+} \rightarrow H^{+} + \tfrac{1}{2} H_2O_2 \quad ...(4)$$

$$H_2O_2 \rightarrow 2\ OH\bullet \quad ...(5)$$

Reduction:

$$O_2 + e- \rightarrow O_2- \quad ...(6)$$

$H_2O + O_2^- + H^+ \rightarrow H_2O_2 + O_2$ ...(7)

Electron and hole combination:
$h^+ + {}_e{-}\rightarrow$ energy ...(8)

where MO is a metal oxide, hv are photons, h^+ are holes. When photons bombard on TiO_2 surface it enables electron movement and reactions on an interface where large numbers of organic substances are absorbed from the effluent. Semiconductor TiO_2 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 H_2O or OH- to produce hydroxyl radicals. TiO_2 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 CO_2 and H_2O.

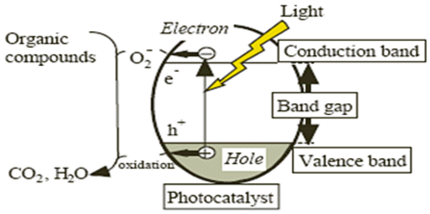

Fig. 2: Mechanism of photocatalysis[50]

When semiconductors such as TiO_2 absorb light e- jumps from the vb to the cb. Nanoparticles have a large surface to volume ratio and also contain more atoms on their surface which substantially absorb photons. Nanoparticles can perform photocatalys is rapidly before e- and hole recombine.[17,51] Parameters affecting photocatalysis are Organic load, catalyst concentration, reactor design (batch, continuous, immobilized/suspended catalyst etc.), adsorption and UV irradiation time (optimum), temperature, pH, light intensity and presence of ionic species.[81]

Doping in Nano-Structured TiO_2 for enhanced photocatalytic activity

Doping is one of the methods to improve optical properties, reduce bandgap and overcome e-/hole recombination as metals trap e- result in enhanced photocatalytic activity of semi conductor oxides. Doping will provide efficient and economical photocatalysis as it can replace UV photocatalysis with solar or visible irradiations. Loading of TiO_2 surface with dopant will engineer the photocatalyst with improved trapping of charge carriers. Thus Doping increases organics degradation efficiency.[52] Dopant will create oxygen defects and shifts light absorption from UV to the visible region by improving absorption bandwidth. The efficiency of photocatalysis may differ based on the position of the dopant on the TiO_2 structure. Based on synthesis methods, the dopant can take a position on the surface or it can be included in lattice structure or as core and thus these positions may lead to different photocatalytic activity and degradation efficiency. Metals and non-metals both can work as dopants but major research concludes that metal dopants possess strong surface plasmon resonance (SPR), work efficiently under solar radiations during photocatalysis.[53]

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.[53] The handling of TiO_2 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 TiO_2 with transition metal doping which reduces the bandgap and greater absorption of visible light is possible, also the dopant metals trape 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 Nickle, Zinc, cerium, Neodymium, Eurotium, Lanthanum, etc. and various non-mental dopants are Palladium chloride, carbon, nitrogen, and Flouride.

Recyclability of Photocatalyst

TiO_2 doped with 33% Fe_2O_3 core-shell photocatalyst has enhanced paracetamol removal by photocatalysis from water and the photocatalyst could be easily separated and reused for four recycle runs.[28] Ag decorated Fe_3O_4/TiO_2 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.[26] The novel engineered photocomposite core-shell structure $Fe_3O_4@SiO_2@TiO_2$ 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.[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.[16] Dye degradation efficiency by Fe^{3+} doped TiO_2 has been found to decrease by 9% at the end of six recycle runs.[55] Ag-Fe CT and Fe_2O_3/SiO_2 co-doped TiO_2 and Ag-Fe CT supported on graphene oxide has shown good stability for 5 recycle runs.[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.[7]

Table 3: Feasibility and effectiveness of photocatalyst for recyclability

Sr. No.	Catalyst	Synthesis method	Model pollutant and expt. Conditions	Recycla-bility runs	Result	Ref.
1	Fe_3O_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_3O_4 –TiO2 (3 ml titanium butoxide), Fe3O4–TiO_2 (10 ml Titanium butoxide) respectively	2
2	Fe_3O_4@ SiO_2/β-NaY F4:Yb^{3}+, Tm^{3}+/TiO_2	sol–gel process and solvol-therma	methylene 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_3O_4 @SiO_2 and Ag-Fe	copreci pitation	bisphenol A: 2 mg/L, visible light, 90 min	3	100 % and 88% using Ag-Fe and N-TiO_2/Fe_3O_4 @SiO_2 respectively	56
6	Ag-doped TiO_2-P25	surface impreg	Drug: pentoxi fylline	10	Ag-TiO2-P25: Opt.: 0.75 g/L cat	30

	supported on Clay beads, Fe-Ag-TiO_2 composite (1.5 wt %)	-nation method	(PEN) 50 mg/L, 40 ml solution, solar, 1.5 g/L, 30 min		conc., 75% and 68% degradation in TOC and COD resp. 90% degradation of PEN in 30 min	
7	graphene oxide supported Ag -Fe TiO_2 -1 wt% of Ag	chemical reduction and the hydro thermal	methylene blue 20 mg/L and 4-NP, visible, 150 min, 0.2 g/L	3	rGO supported Ag-Fe CT, rGO supported Fe -TiO_2, Fe -TiO_2 and undoped TiO_2-95 and 89%, 82%, and 74.6%, respectively	29
8	Clay suppo. Fe doped TiO_2 (1-4 %: 2% opt)	surface impregnation method	Pesticide-Carbendazim: 4-10 gm/L, UV and solar, 4 g/50 clay beads, 300 min	40	70 % degrade-UV. TiO_2: 82 UV+63 sun light, Fe TiO_2 - 93 % sun light and 67 % UV	59
9	Fe^{3+} doped TiO_2 film- with Fe^{3+} =0, 1, 3, 5, 7 and 10	spin coating	methylene blue, 5 mg/L, 25 mL, visible, 240 min	10	96.7 % at 7% opt. 83.5 % at 10th round end	60
10	Fe doped TiO_2-3%	Sol gel	methylene blue: 10-5 mg/L visible, 150 min, 0.5 g/L		59, 97, 79 % for TiO_2, 3% Fe and 7% Fe-TiO_2	7
11	Cu^{2+}, Ag^{+}, Zn^{2+}, Fe^{3+}, and Al^{3+} ion and Pt metallic +effect of doping, Cr^{3+}, Mn^{2+} and Co^{2+}: -ve effect of doping	Sol gel, 0.5 mol % dopant metal	Para nitrophenol: 10-4 mol/L, 480 min, 1 g/L	3	50 % -TiO_2, 55: Fe 0.5, Fe 2 : 35, Fe 5: 15, Ag 0.5: 58, Ag 2: 60, Pt 0.1: 79 %	61
12	Ag-doped TiO_2 pillars-2.8 %	Wet impre gnation and high temp thermal reduction	2,4-dichlorophenol -5 mg/L-30 ml, visible, 120 min 1.67 g/L	10	99 %	62
13	Au-Ag NPs -decorated TiO_2 -modified Fe_3O_4	Solvo thermal	Textile waste water-Rh6G dye 30 ppm, xenon lamp, 60 min 2.67 g/L	5	95 % removal. 8% efficiency decreased after 5 runs	38

*NA: data not available

Ammonical nitrogen removal using photocatalysis

NH_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.[93] NH_4-N removal is more when pH is greater than 10. Researchers have reported that it is not possible to oxidize NH_4-N OH by radicals.[94]

When pH is above 9, NH_4-N can be converted into NH_3.[95] 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_4Cl 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 Nanocom posite	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+}con. = 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[69]. 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 O_3 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 Fe_3O_4 nanophoto-catalyst	P-nitrophenol (PNP)	8 atm -pressure, 3-pH, 20 mg/L-PNP, Fe_3O_4 to H_2O_2 ratio= 1:1, H_2O_2:0.6 mol/L,	PNP degradation 78%	73
3	hydrodynamic cavitation (HC) with $ZnO/ZnFe_2O_4$ and persulfate system+ Magnetic separation for recycle	Carbamazepine (CBZ)	9 atm-pressure, 4-pH, 15 mg/L-CRZ, 18 W UV, 500mg/L-$Na_2S_2O_8$, 500 mg/L-$ZnO/ZnFe_2O_4$	98 % CBZ degradation	74
4	electrocatalytic process	Industrial raw effluent (antibiotics)	Cathod: carbon, anode: Ti/PtIr plate	100% COD removal	33
5	UV/ZnO nps/O_3	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%	75
6	MOFs@COFs hybrid materials with C_3N_4 : sulfate radical-based advanced oxidation processes	bisphenol A (BPA)	Visible light	BPA degradation 99%	76
7	UV-C or hydrogen peroxide	Boscalid, pyra -clostrobin, fenbuconazole and glyphosate-Pesticides removal on apple	H_2O_2, UV-C	glyphosate -99% removal, boscalid, pyraclostrobin and fenbuconazole degradation 88 %, 100 % and 70 % respectively	77
8	CuO particle-WO_3 nanofiber hybrids-(adsorb -ent/photocatalyst)	dyes	WO_3 nanofibers and CuO nps, visible light	dyes removal-90%, 0.75 wt.% CuO adsorbed 38% higher and degraded 26% more methylene blue than WO_3 nanofibers	78

9	hybrid photoca -talysis and Cr(III) dispersed memb -rane-geo polymer membrane separation	Dyes wastewater	50 min at 0.09 MPa	100% degradation	79
10	nano-sheet C_3N_4-WO_3 composite (nsCW21 with the addition of H_2O_2	Natural organic matter (NOM)	5 hr, visible light photocatalysis	Without the addition of H_2O_2: 71% removal, With the addition of H_2O_2: 91% removal, catalyst was stable up to 5 recycle runs.	80
11	Hybrid biochar-TiO_2	textile wastewater treatment	74.3 mg/g, biochar (30.4 mg/g) and pure TiO_2 (1.50 mg/g)	biochar and TiO_2 alone - 85 % and 43 % degradation efficiencies respectively, coupling both-99% photo degradation efficiency	81

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 aneffective method for treatment of wastewater. Addition of different oxidizing agent and materials such as H_2O_2, Fenton reagents and biochar have increased organics removal efficiency from wastewater. Electro Fenton and electrolysis, cavitation was used effectively for wastewater treatment. Advanced oxidation with O_3 addition, adsorption by activated charcoalfor 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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Conflict of interest

The authors do not have any conflict of interest.

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. *SN 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 TiO 2*. Vol 23.; 1999. doi:10.1016/S0926-3373(99)00068-5
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.mssp.2014.06.025
12. Varadharajan K, Singaram B, Mani R, Jeyaram J. Enhanced Visible Light Photocatalytic Activity of Ag and Zn Doped and Codoped TiO2Nanoparticles. *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. Crişan 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, Çalişkan Y, Çelebi EE, Tekbaş M, Bektaş 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/ TiO 2 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, Pinitsoontorn S. 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 Fe3O 4/TiO2 core/shell nanoparticles decorated with Ag nanopartilces. *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 tri(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. Mukimin 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

in Aqueous Solutions. *Coatings* 2019, Vol 9, Page 465. 2019;9(8):465. doi:10.3390/COATINGS9080465

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.apcatb.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 treatment 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, Fraysse 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-ferrioxalate 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 İC, 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. *Chem Eng 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