

REMOVAL OF MICRO-POLLUTANTS USING GREEN SYNTHESIZED NANO IRON PARTICLES BY THE ADVANCED OXIDATION PROCESS

RASHMISHREE K.N.*, S. SHRIHARI AND ARUN KUMAR THALLA

Department of Civil Engineering, National Institute of Technology Karnataka, Surathkal, Karnataka, India

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ABSTRACT

Advanced oxidation is a process of removal of pollutants and leads to the combustion of organic and inorganic pollutants or chemical components in the environment especially in water sources. Even though there are different effective processes, many studies have indicated that advanced oxidation process (AOPs) is a more reliable and sustainable method. Therefore, this paper explored the efficacy in the treatment and degradation of micro-pollutants especially using green synthesised iron nanoparticles. Micro-pollutants are mainly found in water bodies as a result of the anthropogenic activities, however, the chemical oxidation methods of AOPs has been found to be effective. The use of green synthesised nanoparticles are sustainable and more efficient than traditional AOPs. Therefore, based on the current findings the study has recommended the use of hybrid green synthesised Iron (Fe) nanoparticles for future applications in mass degradations of micro-pollutants. Another important finding was that green synthesized nanoparticles degrade pollutants that cannot be done by traditional methods of AOPs. Evidently, there is a need to conduct further research on hybrid green synthesised Iron (Fe) nanoparticles and AOPs towards degradations of micro-pollutants. Future scope of the current study has also been presented at the end of the study.

KEY WORDS : Advanced oxidation process, Iron nanoparticles, Micro-pollutants, Green synthesis

INTRODUCTION

The issue of micro-pollutants in surfaces like air, water and solid has been a growing concern for many environmentalists and majority of these micro-pollutants are sourced from industrial effluents like pharmaceutical companies, chemical manufacturing companies, or leaching from dumps and spillage or runoffs from agricultural lands and others (Warner *et al.*, 2019). These results in multiple issues to the environment causing pollution, diseases and contaminations in animals as well as humans and contamination of agricultural produces and may even infect aquatic organisms (Khan *et al.*, 2018). Researches have termed them as “anthropogenic in nature” or caused by human activities usually have no natural background because most of these micro-pollutants are synthetic

chemicals in nature. Numerous organic and inorganic chemicals such as chloride, tritium, nitrate, chlorine, bromide, coprostanol, artificial sweeteners like cyclamate and acesulfame, and others have been discovered from pesticides, pharmaceuticals and personal care products caused by human actions (Khazaei *et al.*, 2017; Katz *et al.*, 2011; Murtaugh and Bunch 1967; Zirlewagen *et al.*, 2016).

The main issue with respect to treating these micro-pollutants are that they are unavailable in the nature. As a result, it is very different for environmentalists and researchers to use effective detecting technologies or methods to treat them. However, over the years various processes has been developed and one of the most common methods used in removal of micro-pollutants is Wastewater Treatment Plants (WWTPs) (Pomies *et al.*, 2013).

Similarly, there are methods like coagulation–flocculation (Reungoat *et al.*, 2010), advanced oxidation processes (AOPs) (Reungoat *et al.*, 2010), membrane processes and membrane bioreactor (Hai *et al.*, 2011), activated carbon adsorption (Zietzschmann *et al.*, 2014), different nano-particles (Hou *et al.*, 2014; Plakas *et al.*, 2016) and more recently use of green synthesised nanoparticles and methods (Hassan *et al.*, 2018; Devatha *et al.*, 2016). Green methods of micro-pollutant treatment are adopted as they are easier to extract from natural sources and are more effective than traditional methods of treatment. Green methods are nothing but the materials or components used in the treatment are sourced from natural extracts like leaves, bio-enzymes, secondary metabolites and others.

Amongst the most commonly used treatment methods AOPs and nano-particles are the most effective techniques (Plakas *et al.*, 2016; Silva *et al.*, 2017; Jinet al., 2012). Activated oxidation processes have mostly used chemicals where the chemicals react with hydroxyl radicals and thereby remove all organic and inorganic pollutants in water and waste water mostly (Deng *et al.*, 2015). Similarly, a few studies have included iron nano-particles or other types of nanoparticles in the treatment of micro-pollutants along with AOPs, usually termed as hybrid AOP's, in the detection and removal of micro-pollutants and in some cases these nano-particles are green synthesised (Bethi *et al.*, 2016; Mansur *et al.*, 2019). Therefore, the current study explores the micro-pollutant removal with the help of hybrid AOP method whereby nano-particles are used and the nano-particles are green synthesised. The objectives of the study are to explore different green sources or extracts for iron nanoparticle in removal of micro-pollutants, the process of removal of micro-pollutants using AOPs and nanoparticles, and the efficacy of iron nanoparticles in removal of micro-pollutants.

What are micro-pollutants?

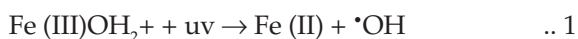
Micro-pollutants are basically pollutants with traces of sources from toxic effluents of industries, chemical effluents from agricultural lands like pesticides, insecticides and others and none the less pollutants from waste burial grounds (Warner *et al.*, 2019). Stamm *et al.*, stated that micro-pollutants as “anthropogenic chemicals that occur in the (aquatic) environment well above a (potential) natural background level due to human activities but with

concentrations remaining at trace levels” (Stamm *et al.*, 2016). The main sources of micro-pollutants are from human activities like agriculture, industrial manufacturing chemical spillage in supply water or sewage water, landfill leachate, pharmaceutical company effluents, and many other human created sources or anthropogenic sources. Micro-pollutants are usually inorganic or organic and even biological components like chromium oxide, zinc, cadmium, copper oxides, gram-positive and gram-negative bacteria, hexavalent chromium, acid dyes, chlorophenols, and other metallic ions (Bethi *et al.*, 2016; Alvarez-Ayuso *et al.*, 2003; Cui *et al.*, 2013). These micro-pollutants have much harmful and even life threatening impact on all living organisms as well as the environment and therefore, their treatment is very important (Warner *et al.*, 2019; Bethi *et al.*, 2016). The contamination of micro-pollutants will not only impact the biotic components but has a strong impact on the entire ecosystem. For instance, micro-pollutants are found to impact the productivity and yield of agriculture and mutations organisms including humans and death of aquatic organisms (Stamm *et al.*, 2016).

Advanced oxidation processes and its effectiveness

Advanced oxidation process (AOPs) is a technique whereby hydroxyl radicals are used because they have high reduction potential that can combust or oxidise many organic and inorganic pollutants or chemical components in water (Siréset *et al.*, 2014). The hydroxyl radicals are basically secondary oxidants produced by hydrogen peroxide or ozone and very low rest concentrations that causes very high reaction against organic compounds. This method helps to accelerate the oxidation and degradation of numerous inorganics as well as organic elements by the combustion process and even degrades elements and chemicals that cannot be treated with conventional treatment methods (Wang *et al.*, 2003; Karimi *et al.*, 2013). The main process that involves in the technique is that hydroxyl radicals convert these chemical compounds into mineral acids or H₂O and/or CO₂ (Joseph *et al.*, 2009). There are different methods that are used in AOPs like the use of sonophotocatalysis (Joseph *et al.*, 2009) or nanoparticles (Kamat *et al.*, 2002) and these methods have been found to be very effective than traditional chemical methods of oxidation-based water treatments (Wang *et al.*, 2003). In sonophotocatalysis the oxidation process is supported by ultraviolet radiations, and ultrasonic sound waves resulting in

the formation of free radicals and degradation of pollutants. On the other hand, semiconductor nanoparticles are reactive in nature and cause the catalysis of the pollutants by activating oxidation process. However, traditional AOPs are chemical processes that help in aromatic micro-pollutant removal and some of these chemical processes like Fenton and Photo-Fenton are still considered to be very effective. In this chemical reaction, the ferrous and hydrogen peroxide reacts with each other that lead to the formation of hydroxyl radical and the oxidation of the radicals reacts on the pollutant by catalysis of H_2O_2 (Hydrogen peroxide) with the help of an iron ion (Atharizade *et al.*, 2015; Du *et al.*, 2011).



Applications of AOPs

AOP's are mostly used in waste water treatment, drinking water filtration processes, and treatment of landfill leachate water or running water from meeting the water bodies. These processes included the use of "ozonation (O3)" (Rosenfeldt *et al.*, 2006), "ozone combined with hydrogen peroxide (O3/H₂O₂)" (Arslan *et al.*, 1999) and "UV irradiation (O3/UV)" or both "(O3/H₂O₂/UV)" (Lucas *et al.*, 2010), "ozone combined with catalysts (O3/catalysts)" (Choi *et al.*, 2012), "UV/H₂O₂" (Lucas *et al.*, 2010), "Fenton" (Atharizade *et al.*, 2015), "photo-Fenton processes (Fe²⁺/H₂O₂ and Fe²⁺/H₂O₂/UV)" (Atharizade *et al.*, 2015), "the ultrasonic cavitation process" (Torres *et al.*, 2007) and "photo catalysis" (Joseph *et al.*, 2009) have been effective in treatment of pollutants from waste waters from running into water bodies and filtration units for drinking water. Many studies have reported over 80% treatment for contaminants in waste water like diclofenac using AOP and ozonation (Huber *et al.*, 2005), estradiol and ethinylestradiol using UV/chlorine and Chlorine dioxide (ClO₂) (Sichel *et al.*, 2011; Jiang *et al.*, 2005), ketoprofen using UV lamp (Szabó *et al.*, 2011) and carbamazepine using UV lamp (Avisar *et al.*, 2010). However, studies have indicated that ozonation process along with AOPs are the most effective methods because they treat almost 100% of all organic and inorganic pollutants in the waste water (Huber *et al.*, 2005; Liu *et al.*, 2019; Renge *et al.*, 2012). Apart from this the use of nanoparticles in AOPs has been widely used because of its cost effectiveness than other methods as well as the efficacy of the treatment process is far effective and advanced than ozonation or UV methods (Hou

et al., 2014; Nasirian *et al.*, 2017; Moussavi *et al.*, 2014). However, with the rise in green products and sustainability, green synthesized nano-particles have been gaining popularity in treatment of micro-pollutants (Devatha *et al.*, 2016; Mansur *et al.*, 2014).

Green synthesis of nano-particles

Green production or green synthesis to be more specific is the process where nano-particles are extracted from natural sources like leaves, plant extracts, microbial metabolites and others (Devatha *et al.*, 2016). Various researches have been conducted until now whereby plant extracts as well as microbial extracts has been used in development of nano-particles like iron based or titanium dioxide based, that has the ability to oxidise pollutants. The main reason for using green synthesized nano-particles is because of its sustainability, being cost effective, higher level of efficiency in pollutant degradation and reduces time for reaction (Devatha *et al.*, 2016; Shahwan *et al.*, 2011). Different sources of green nanoparticles for AOPs have been presented in Table 1.

In most cases, the use of green synthesis nanoparticles helps to efficiently degrade micro-pollutants in waste water treatment or running water to water bodies (Shahwan *et al.*, 201; Wang *et al.*, 2014; Machado *et al.*, 2013; Kumar *et al.*, 2013; Huang *et al.*, 2014; Njagi *et al.*, 2011; Thakur *et al.*, 2014; Senthil *et al.*, 2012; Smuleac *et al.*, 2011; Ehrampoush *et al.*, 2015; Pattanayak *et al.*, 2013; Goutam *et al.*, 2018; Rao *et al.*, 2015; Khade *et al.*, 2015; Shen *et al.*, 2017; Sood *et al.*, 2015; Joseph *et al.*, 2015; Das *et al.*, 2018; Kataria *et al.*, 2018; Bhattacharjee *et al.*, 2014; Pandian *et al.*, 2015). However, in one case, the study of Rao *et al.*, used orange waste in synthesis of TiO₂ nanoparticles (Rao *et al.*, 2015). Different forms of nano-particles found to be used in micro-pollutant treatment were iron nanoparticles, TiO₂NPs, Ce-doped TiO₂NPs (Titanium dioxide), Strontium or Sr-doped TiO₂NPs, silver nano-particles, cupric oxide NPs, Silver/Silver Chloride nano-particles, Iron (II,III) Oxide nanoparticles, Tin-oxide nanoparticles and nickel nanoparticles (Shahwan *et al.*, 2011; Pattanayak *et al.*, 2013; Goutam *et al.*, 2018; Rao *et al.*, 2015; Khade *et al.*, 2015; Shen *et al.*, 2017; Sood *et al.*, 2015; Joseph *et al.*, 2015; Das *et al.*, 2018; Kataria *et al.*, 2018; Bhattacharjee *et al.*, 2014; Pandian *et al.*, 2015).

One of the best advantages of using green nanoparticles is that the pH level is about 4-5 and makes it safe for the environment and with lower

pH the reaction between iron bearing minerals and hydrogen peroxide is much higher and effective (Shahwana *et al.*, 2011). The efficiency of the decomposition of dyes and others organic matter is reduced when the pH level is above 4 and mostly in cases of use of Iron or Fenton oxidation reaction. Lower the formation of ferric hydroxide precipitation in case of Iron based oxidation process higher is the efficiency of degradation of dyes. During Fenton reaction sludge and anions are formed in higher concentrations which causes the conversion of hydrogen peroxide to reduce or inefficient and thereby the pH also reduces (Shahwana *et al.*, 2011). The advantage of using plant-based Iron particles in the degradation of dyes is that the plant-based cell cultures are easier to control and are more stable plus the reaction time does not degrade with time but in traditional or synthetically produced nanoparticles the degradation is faster (Ajitha *et al.*, 2015). In addition, the use of plant or green based nanoparticles for AOPs can be easily scaled up for large scale synthesis in the degradation of organic elements. Furthermore, they are also economic and can function in optimal temperatures and reduce the concerns of eco-friendly water treatment processes. The use of plant-based components as nanoparticles for the degradation process is stable and also improves the biocompatible functionalities enhancing the action of the nanoparticles to be used in antibacterial activity in water treatment process (Njagi *et al.*, 2015).

In addition, most of the treatment procedures using green synthesised nanoparticles showed an efficacy of more than 80% on an average indicating the feasibility and sustainability of using green synthesized nanoparticles for micro-pollutant treatment (Sood *et al.*, 2015). Use of green products are more stable during the reaction process and the reaction does not easily degrade thereby, increasing the potency of degradation process to a maximum of 80% (Ajitha *et al.*, 2015). The most advantageous point of using Titanium dioxide has been a proven method of highly efficient method in the degradation of methyl orange (MO) and are economic as well as environmental friendly (Khade *et al.*, 2015). The use of surfactants that helps to maintain the "shape-controlled synthesis" of nanoparticles because of presence of both hydrophobic and hydrophilic components and thereby does not allow the agglomeration of the chemical or the particles being used with

nanoparticles to ensure that the toxic dye is effectively degraded (Bhattacharjee *et al.*, 2014). Also, the advantage of using these surfactants is that they act as capping agents and therefore, improves the processes like flocculation in the treatment of waste water or dye degradation. However, using this method was found to be effective in degradation of methyl violet 6B dye.

Efficacy of different green synthesised iron nanoparticles (FeNP) in micro-pollutant treatment

Green synthesis of FeNPs has been categorised into three main sourcing methods; one being direct plant extracts, secondly plant biomasses, and lastly, use of plant biomass as template (Herlekar *et al.*, 2014). Furthermore, FeNP variants nZVI (Zerovalent iron nanoparticles) and iron oxide have been mostly used because they are the only compounds that can be extracted with ease and reduced efforts and efficiently. One of the most commonly used plant extracts is from tea plants or green tea variants like *Camellia sinensis* or tea plant (Hoag *et al.*, 2009), Oolong and black tea (Huang *et al.*, 2014). Tea plant extracts are mainly used because they are easy to extract, can be extracted in normal room temperatures, reduced extraction time and effort and effective tea polyphenols acted as the reducing and capping agent (Herlekar *et al.*, 2014). Polyphenols from tea usually comprise of theaflavins or flavonoids and others and are usually and are good capping agents because of their ability to reduce nanoparticle overgrowth as well as aggregation of the particles used in degradation process (Herlekar *et al.*, 2014). Furthermore, these polyphenols also act as stabilising agents thereby increasing the efficacy of the reaction process of the nanoparticles and thereby improves the degradation of toxic elements. As it is known the capping agents comprises of polar head and non-polar tail and therefore, it helps to keep the nanoparticles from overreaction when in contact with organic elements and the polar head keeps the nanoparticle stable in their activity. In other words, these capping agents act in colloidal synthesis of nanoparticles which is an important process in green synthesis of nanoparticles in waste water treatment processes (Khade *et al.*, 2015; Herlekar *et al.*, 2014). Surfactants also acts as capping agents and their processes are the same and their main function is to ensure that the agglomeration of the nanoparticles with high surface energy is maintained (Bhattacharjee *et al.*, 2014). By providing colloidal stability the costs of

nanoparticle stabilisation reduce and there is no need for external stabilising agents and by stabilising the uncontrolled growth in the initial stages also improves the costs of degradation processes and therefore, effective as a cost reducing agent as well as a capping agent and thereby effective in degradation of bromothymol blue. The extracted FeNP from *Camellia sinensis* tea plant was seen to have above 70% of effectiveness in the degradation of micro-pollutant like bromothymol blue, borohydride and a few other organic chemicals. Similarly, green synthesis of Fenton-like catalyst was found to be effective in the degradation or oxidation of cationic dyes and anionic dyes (pollutants) like methylene blue and methyl orange respectively (Shahwan *et al.*, 2011). The efficacy in case of methylene blue was found to be between 96.3% and 86.6% for different concentrations, whereas, methyl orange (pollutant) was found to degrade between 61.6% and 47.1% for different concentrations.

The use of other forms of plant extracts has been termed as “plant extract derived from agrowaste” (Herlekar *et al.*, 2014), like the use of *Sorghum sp.* (Njagi *et al.*, 2011) or the use of leaf extract from *Eucalyptus sp.* (Wang *et al.*, 2014) or the use of plantain peel extract (Venkateswarlu *et al.*, 2013). In

case of using *Sorghum sp.* it was used to extract Fe and silver nanoparticles to degrade bromothymol blue in waste water and drinking water. The extracted Fe and silver nanoparticles were found to be very effective by approximately 80% degradation or oxidation of bromothymol blue. Besides, the reduction of COD was also achieved by 80% in comparison to the studies reported. (Nasirian *et al.*, 2017; Avisar *et al.*, 2010; Moussavi *et al.*, 2014; Shahwan *et al.*, 2011; Jiang *et al.*, 2005; Senthil *et al.*, 2012; Kumar *et al.*, 2013; Machado *et al.*, 2013), which may be because the reducing agent was combined with UV treatment of the ground water. Wang’s study found that using Iron nanoparticles helped in achieving 80% of oxygen usage for chemical reaction to degrade the chemicals or organic materials in the water (Wang *et al.*, 2014). This level was even higher than Jiang and colleague whereby the oxygen usage for chemical reaction was around 30% and therefore, it may be stated that ferrate (VI) oxidation has less COD demand than FeNPs. However, the effectiveness of removal of organic and toxic components from water surfaces using green synthesised nanoparticles show an estimated degradation between 30% and 80%. By reduction of the COD by nanoparticles, it helps in better removal of the pollutants in the water, because higher COD

Table 1. List showing the types of green synthesised nano-particles for micro-pollutant treatment

Type of nanoparticle	Source of green synthesis	Reference
Fe or iron nanoparticles (NPs)	Green tea leaf	Shahwan <i>et al.</i> , (2011)
	Eucalyptus leaf extracts	Wang <i>et al.</i> , (2014)
	Tree extract	Machado <i>et al.</i> , (2013)
	Terminalia chebula fruit extract	Kumar <i>et al.</i> , (2013)
	Oolong and black tea leaf extract	Huang <i>et al.</i> , (2014)
	Sorghum bran extract	Njagi <i>et al.</i> , (2011)
	Colocasia esculenta leaves extract	Thakur <i>et al.</i> , (2014)
	Tridax procumbens	Senthil <i>et al.</i> , (2012)
	Green tea extract	Smuleac <i>et al.</i> , (2011)
	Tangerine peel extract	Ehrampoush <i>et al.</i> , (2015)
	<i>Azadirachta indica</i> extract	Pattanayak <i>et al.</i> , (2013)
	Titanium dioxide or TiO ₂	<i>Jatropha curcas</i> L. leaf extract
Orange fruit waste extract		Rao <i>et al.</i> , (2015)
Plant leaf-based extract		Khade <i>et al.</i> , (2015)
Cerium or Ce-doped TiO ₂	Plant based extract	Shen <i>et al.</i> , (2017)
Strontium or Sr-doped TiO ₂	Plant based extract	Sood <i>et al.</i> , (2015)
Silver Nano-particles	Mukiamaderaspatna plant extract	Joseph <i>et al.</i> , (2015)
Cupric oxide	Madhucalongifolia plant extract	Das <i>et al.</i> , (2018)
Silver/Silver Chloride or Ag/Ag	Momordica charantia plant extract	Devi <i>et al.</i> , (2016)
Carbon nano-particles		
Iron (II, III) Oxide or Fe ₃ O ₄ nanoparticles	Plant based extract	Kataria <i>et al.</i> , (2018)
Tin-oxide nanoparticles or SnO ₂	Plant based extract	Bhattacharjee <i>et al.</i> , (2014)
Nickel nanoparticles (NPs)	Ocimum sanctum extract	Pandian <i>et al.</i> , (2015)

in water means more toxic pollutants and low COD the vice versa. Similarly, the use of plantain peel extract was also found to be very effective in the reduction of micro-pollutants like toxic metals and dyes by a minimum of 60% and was termed as potent green synthesised FeNPs for environmental remediation of groundwater toxic elements and dump-fill toxic leachates (Venkateswarlu *et al.*, 2013). The FeNPs were extracted from banana peel ash as well as *Colocasia esculenta* or Taro leaves extract with the aim to oxidize and degrade pharmaceutical elements and toxic micro-pollutants like tetrabromobisphenol and cadmium (Thakur and Karak., 2014). The use of this nanoparticle found that it took a maximum of 30 minutes to bio-remediate the water body with an efficacy level of 70% and more. Similar, high and effective and efficient green synthesis of FeNPs has been informed in many studies where the minimum reductions of micro-pollutants are recorded at 50% and the maximum by 98%.

Summary and Conceptual Protocol

AOPs and nanoparticles are two most commonly used methods in the reduction and degradation of anthropogenic elements commonly termed as micro-pollutants (Bethi *et al.*, 2016; Plakas *et al.*, 2016). Even though synthetically produced nanoparticles have been used till date with AOPs for oxidation of micro-pollutants, but the use of green synthesised nanoparticles have not yet been used along with AOPs for reduction of micro-pollutants. Therefore, following conceptual framework has been formed that shows the process to be used and followed for using a hybrid green synthesised Fe nanoparticle and AOPs. It is conceptualised that ground water or waste water or sewage water can be treated by combination of traditional AOP method whereby hydroxyl radicals from the chemicals will convert these pollutants into mineral acids or H_2O and/or CO_2 (Joseph *et al.*, 2009) and with the help of tea plant extracts (Huang *et al.*, 2014; Hoag *et al.*, 2009) iron nanoparticles can be extracted which reacts with pollutants like toxic elements and dyes by oxidation process. It has already been seen that the combination of AOP to other methods like $UV/O_3/H_2O_2$ and nanoparticles are very effective (Bethi *et al.*, 2016; Lucas *et al.*, 2010) and therefore, the combination of green synthesised nanoparticles and AOP will also be effective as well as sustainable.

Rising levels of micro-pollutants in water bodies

like ground water or riverine and oceans as well as in supply drinking water has been alarming in the past decade and this has led to development of numerous technologies and chemical processes that helps in the treatment of micro-pollutants in water bodies as well as waste water. Different types of reduction methods include coagulation–flocculation, advanced oxidation processes (AOPs), membrane processes and membrane bioreactor, activated carbon adsorption, different nanoparticles, and more recently use of green synthesised nanoparticles. Micro-pollutants in water bodies have been mainly rising from the uncontrolled and reduced measures against anthropogenic activities. In this regard it was found that AOPs are the most effective conventional methods of micro-pollutant reduction and oxidation because they are effective and have higher efficiency. However, there is one issue of using nanoparticles and AOPs as hybrid method in reduction of toxic pollutants, which is the risk of sedimentary chemicals remaining in the water from the AOP process; which means the process of oxidising has to be performed again and is therefore considered to be less effective. However, the use of plant extracts and natural extract called green synthesis of nanoparticles are sustainable and reduces the mentioned threat. The use of green synthesised nanoparticle in reduction and degradation of micro-pollutants has been mainly researched with respect to iron nanoparticles and are very effective, even more effective than AOPs. The main gaps found from this review paper are that there is lack of study on green synthesised FeNPs and AOPs as hybrids in the oxidation and degradation of micro-pollutants; secondly, the past papers fail to mention the extraction process from natural sources because in most cases laboratory methods were used and lastly, there is lack of research on other alternative nanoparticles for the same purpose. Therefore, the main future scope of the study is to apply both green synthesised FeNPs and AOP hybrid method in the oxidation and reduction of certain micro-pollutants under controlled environment to compare the efficacy to previous publications.

Conflict of Interest

None.

REFERENCES

Ajitha, B., Reddy, Y.A. and Reddy, P.S. 2015. Green

- synthesis and characterization of silver nanoparticles using Lantana camara leaf extract. *Materials Science and Engineering: C*. 49 : 373-381.
- Alvarez-Ayuso, E., Garcya-Sánchez, A. and Querol, X. 2003. Purification of metal electroplating waste waters using zeolites. *Water Research*. 37 : 4855-4862.
- Arslan, I., Balcioglu, I.A. and Tuhkanen, T. 1999. Advanced oxidation of synthetic dyehouse effluent by O₃, H₂O₂/O₃ and H₂O₂/UV processes. *Environmental Technology*. 20 : 921-931.
- Atharizade, M. and Miranzadeh, M.B. 2015. Evaluation of efficacy of advanced oxidation processes fenton, fenton-like and photo-fenton for removal of phenol from aqueous solutions. *J Chem Soc Pak*. 37 : 266.
- Avisar, D., Lester, Y. and Mamane, H. 2010. pH induced polychromatic UV treatment for the removal of a mixture of SMX, OTC and CIP from water. *Journal of Hazardous Materials*. 175 : 1068-1074.
- Bethi, B., Sonawane, S.H., Bhanvase, B.A. and Gumfekar, S.P. 2016. Nanomaterials-based advanced oxidation processes for wastewater treatment: a review. *Chemical Engineering and Processing-Process Intensification*. 109 : 178-189.
- Bhattacharjee, A., Ahmaruzzaman, M. and Sinha, T. 2014. Surfactant effects on the synthesis of durable tin-oxide nanoparticles and its exploitation as a recyclable catalyst for the elimination of toxic dye: a green and efficient approach for wastewater treatment. *RSC Advances*. 4 : 51418-51429.
- Choi, J.W., Yoon, J.Y., Park, J.D. and Lee, H.S. 2012. Removal Characteristics of Phenol at Advanced Oxidation Process with Ozone/Activated Carbon Impregnated Metals. *Applied Chemistry for Engineering*. 23 : 302-307.
- Cui, B., Peng, H., Xia, H., Guo, X. and Guo, H. 2013. Magnetically recoverable core-shell nanocomposites γ -Fe₂O₃@ SiO₂@ TiO₂-Ag with enhanced photocatalytic activity and antibacterial activity. *Separation and Purification Technology*. 103 : 251-257.
- Das, P., Ghosh, S., Ghosh, R., Dam, S. and Baskey, M. 2018. Madhucalongifolia plant mediated green synthesis of cupric oxide nanoparticles: A promising environmentally sustainable material for waste water treatment and efficient antibacterial agent. *Journal of Photochemistry and Photobiology B: Biology*. 189 : 66-73.
- Deng, Y. and Zhao, R. 2015. Advanced oxidation processes (AOPs) in wastewater treatment. *Current Pollution Reports*. 1 : 167-176.
- Devatha, C.P., Thalla, A.K. and Katte, S.Y. 2016. Green synthesis of iron nanoparticles using different leaf extracts for treatment of domestic waste water. *Journal of Cleaner Production*. 139 : 1425-1435.
- Devi, T.B., Ahmaruzzaman, M. and Begum, S. 2016. A rapid, facile and green synthesis of Ag@ AgCl nanoparticles for the effective reduction of 2, 4-dinitrophenyl hydrazine. *New Journal of Chemistry*. 40:1497-1506.
- Du, Y., Zhao, L. and Su, Y. Tantalum (oxy) nitrides., 2011. Preparation, characterisation and enhancement of photo-Fenton-like degradation of atrazine under visible light. *Journal of Hazardous Materials*. 195 : 291-297.
- Ehrampoush, M.H., Miria, M., Salmani, M.H. And Mahvi, A.H. 2015. Cadmium removal from aqueous solution by green synthesis iron oxide nanoparticles with tangerine peel extract. *Journal of Environmental Health Science and Engineering*. 13:84.
- Goutam, S.P., Saxena, G., Singh, V., Yadav, A.K., Bharagava, R.N. and Thapa, K.B. 2018. Green synthesis of TiO₂ nanoparticles using leaf extract of *Jatropha curcas* L. for photocatalytic degradation of tannery wastewater. *Chemical Engineering Journal*. 336:386-396.
- Hai, F.I., Tessmer, K., Nguyen, L.N., Kang, J., Price, W.E. and Nghiem, L.D. 2011. Removal of micropollutants by membrane bioreactor under temperature variation. *Journal of Membrane Science*. 383 : 144-151.
- Hassan, S.S., Abdel-Shafy, H.I. and Mansour, M.S. 2018 Jan 29. Removal of pyrene and benzo (a) pyrenemicropollutant from water via adsorption by green synthesized iron oxide nanoparticles. *Advances in Natural Sciences: Nanoscience and Nanotechnology*. 9(1) : 015006.
- Herlekar, M., Barve, S. and Kumar, R., 2014. Plant-mediated green synthesis of iron nanoparticles. *Journal of Nanoparticles*. 1-9. <http://dx.doi.org/10.1155/2014/140614>.
- Hoag, G.E., Collins, J.B., Holcomb, J.L., Hoag, J.R., Nadagouda, M.N. and Varma, R.S. 2009. Degradation of bromothymol blue by 'greener' nano-scale zero-valent iron synthesized using tea polyphenols. *Journal of Materials Chemistry*. 19 : 8671-8677.
- Hou, J., Dong, G., Luu, B., Sengpiel, R.G., Ye, Y., Wessling, M. and Chen, V. 2014. Hybrid membrane with TiO₂ based bio-catalytic nanoparticle suspension system for the degradation of bisphenol-A. *Bioresource Technology*. 169 : 475-483.
- Huang, L., Weng, X., Chen, Z., Megharaj, M. and Naidu, R. 2014. Synthesis of iron-based nanoparticles using oolong tea extract for the degradation of malachite green. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 117:801-804.
- Huber, M.M., Göbel, A., Joss, A., Hermann, N., Löffler, D., McArdell, C.S., Ried, A., Siegrist, H., Ternes, T.A. and von Gunten, U., 2005. Oxidation of

- pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. *Environmental Science & Technology*. 39 : 4290-4299.
- Jiang, J.Q., Yin, Q., Zhou, J.L. and Pearce, P. 2005. Occurrence and treatment trials of endocrine disrupting chemicals (EDCs) in wastewaters. *Chemosphere*. 61 : 544-550.
- Jin, X., Peldszus, S. and Huck, P.M., 2012. Reaction kinetics of selected micropollutants in ozonation and advanced oxidation processes. *Water Research*. 46: 6519-6530.
- Joseph, C.G., Puma, G.L., Bono, A. and Krishnaiah, D. 2009. Sonophotocatalysis in advanced oxidation process: a short review. *Ultrasonics Sonochemistry*. 16 : 583-589.
- Joseph, S. and Mathew, B. 2015. Microwave-assisted green synthesis of silver nanoparticles and the study on catalytic activity in the degradation of dyes. *Journal of Molecular Liquids*. 204 : 184-191.
- Kamat, P.V. and Meisel, D. 2002. Nanoparticles in advanced oxidation processes. *Current Opinion in Colloid & Interface Science*. 7 : 282-287.
- Karimi, B., Ehrampoush, M.H., Ebrahimi, A. and Mokhtari, M. 2013. The study of leachate treatment by using three advanced oxidation process based wet air oxidation. *Iranian Journal of Environmental Health Science & Engineering*. 10 : 1.
- Kataria, N. and Garg, V.K. 2018. Green synthesis of Fe₃O₄ nanoparticles loaded sawdust carbon for cadmium (II) removal from water: regeneration and mechanism. *Chemosphere*. 208 : 818-828.
- Katz, B.G., Eberts, S.M. and Kauffman, L.J. 2011. Using Cl/Br ratios and other indicators to assess potential impacts on groundwater quality from septic systems: a review and examples from principal aquifers in the United States. *Journal of Hydrology*. 397 : 151-166.
- Khade, G.V., Suwarnkar, M.B., Gavade, N.L. and Garadkar, K.M. 2015. Green synthesis of TiO₂ and its photocatalytic activity. *Journal of Materials Science: Materials in Electronics*. 26 : 3309-3315.
- Khan, K., Lu, Y., Saeed, M.A., Bilal, H., Sher, H., Khan, H., Ali, J., Wang, P., Uwizeyimana, H., Baninla, Y. and Li, Q. 2018. Prevalent fecal contamination in drinking water resources and potential health risks in Swat, Pakistan. *Journal of Environmental Sciences*. 72 : 1-2.
- Khazaei, E. and Milne-Home, W. 2017. Applicability of geochemical techniques and artificial sweeteners in discriminating the anthropogenic sources of chloride in shallow groundwater north of Toronto, Canada. *Environmental Monitoring and Assessment*. 189 : 218.
- Kumar, K.M., Mandal, B.K., Kumar, K.S., Reddy, P.S. and Sreedhar, B. 2013. Biobased green method to synthesise palladium and iron nanoparticles using Terminaliachebulu aqueous extract, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 102 : 128-133.
- Liu, Z., Hosseinzadeh, S., Wardenier, N., Verheust, Y., Chys, M. and Hulle, S.V., 2019. Combining ozone with UV and H₂O₂ for the degradation of micropollutants from different origins: lab-scale analysis and optimization. *Environmental Technology*. 40 : 3773-3782.
- Lucas, M.S., Peres, J.A. and Puma, G.L. 2010. Treatment of winery wastewater by ozone-based advanced oxidation processes (O₃, O₃/UV and O₃/UV/H₂O₂) in a pilot-scale bubble column reactor and process economics. *Separation and Purification Technology*. 72 : 235-241.
- Machado, S., Pinto, S.L., Grosso, J.P., Nouws, H.P., Albergaria, J.T. and Delerue-Matos, C. 2013. Green production of zero-valent iron nanoparticles using tree leaf extracts. *Science of the Total Environment*. 445:1-8.
- Mansur, A.A., Mansur, H.S., Ramanery, F.P., Oliveira, L.C. and Souza, P.P. 2014. "Green" colloidal ZnS quantum dots/chitosan nano-photocatalysts for advanced oxidation processes: study of the photodegradation of organic dye pollutants. *Applied Catalysis B: Environmental*. 158 : 269-279.
- Moussavi, G., Hossaini, H., Jafari, S.J. and Farokhi, M. 2014. Comparing the efficacy of UVC, UVC/ZnO and VUV processes for oxidation of organophosphate pesticides in water. *Journal of Photochemistry and Photobiology A: Chemistry*. 290 : 86-93.
- Murtaugh, J.J. and Bunch, R.L. 1967. Sterols as a measure of fecal pollution. *Journal (Water Pollution Control Federation)*. 404-409.
- Nasirian, M., Bustillo-Lecompte, C.F. and Mehrvar, M. 2017. Photocatalytic efficiency of Fe₂O₃/TiO₂ for the degradation of typical dyes in textile industries: effects of calcination temperature and UV-assisted thermal synthesis. *Journal of Environmental Management*. 196 : 487-498.
- Njagi, E.C., Huang, H., Stafford, L., Genuino, H., Galindo, H.M., Collins, J.B., Hoag, G.E. and Suib, S.L. 2011. Biosynthesis of iron and silver nanoparticles at room temperature using aqueous sorghum bran extracts. *Langmuir*. 27 : 264-271.
- Pandian, C.J., Palanivel, R. and Dhananasekaran, S. 2015. Green synthesis of nickel nanoparticles using *Ocimum sanctum* and their application in dye and pollutant adsorption. *Chinese Journal of Chemical Engineering*. 23 : 1307-1315.
- Pattanayak, M. and Nayak, P.L., 2013. Green synthesis and characterization of zero valent iron nanoparticles from the leaf extract of *Azadirachta indica* (Neem). *World Journal of Nano Science & Technology*. 2 : 06-09.
- Plakas, K.V., Sklari, S.D., Yiankakis, D.A., Sideropoulos, G.T., Zaspalis, V.T. and Karabelas, A.J. 2016.

- Removal of organic micropollutants from drinking water by a novel electro-Fenton filter: pilot-scale studies. *Water Research*. 91 : 183-194.
- Pomies, M., Choubert, J.M., Wisniewski, C. and Coquery, M. 2013. Modelling of micropollutant removal in biological wastewater treatments: a review. *Science of the Total Environment*. 443 : 733-748.
- Rao, K.G., Ashok, C.H., Rao, K.V., Chakra, C.S. and Rajendar, V. 2015. Synthesis of TiO₂ nanoparticles from orange fruit waste. *Synthesis*. 1 : 82-90.
- Renge, V.C., Khedkar, S.V. and Bhojar, K.S. 2012. Micropollutant removal from waste water treatment plant-a review. *IJAET*. 3 : 27-30.
- Reungoat, J., Macova, M., Escher, B.I., Carswell, S., Mueller, J.F. and Keller, J. 2010. Removal of micropollutants and reduction of biological activity in a full scale reclamation plant using ozonation and activated carbon filtration. *Water Research*. 44 : 625-637.
- Rosenfeldt, E.J., Linden, K.G., Canonica, S. and Von Gunten, U. 2006. Comparison of the efficiency of OH radical formation during ozonation and the advanced oxidation processes O₃/H₂O₂ and UV/H₂O₂. *Water Research*. 40 : 3695-3704.
- Senthil, M. and Ramesh, C. 2012. Biogenic Synthesis of Fe₃O₄ Nanoparticles Using TridaxProcumbens Leaf Extract and its Antibacterial Activity on Pseudomonas Aeruginosa. *Digest Journal of Nanomaterials & Biostructures (DJNB)*. 7.
- Shahwan, T., Sirriah, S.A., Nairat, M., Boyacý, E., Erođlu, A.E., Scott, T.B. and Hallam, K.R. 2011. Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. *Chemical Engineering Journal*. 172 : 258-266.
- Shen, C., Pang, K., Du, L. and Luo, G. 2017. Green synthesis and enhanced photocatalytic activity of Ce-doped TiO₂ nanoparticles supported on porous glass. *Particuology*. 34 : 103-109.
- Sichel, C., Garcia, C. and Andre, K. 2011. Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants. *Water Research*. 45 : 6371-6380.
- Silva, L.L., Moreira, C.G., Curzio, B.A. and da Fonseca, F.V. 2017. Micropollutant removal from water by membrane and advanced oxidation processes—A review. *Journal of Water Resource and Protection*. 9 : 411-431.
- Sirés, I., Brillas, E., Oturan, M.A., Rodrigo, M.A. and Panizza, M. 2014. Electrochemical advanced oxidation processes: today and tomorrow. A review. *Environmental Science and Pollution Research*. 21 : 8336-8367.
- Smuleac, V., Varma, R., Sikdar, S. and Bhattacharyya, D., 2011. Green synthesis of Fe and Fe/Pd bimetallic nanoparticles in membranes for reductive degradation of chlorinated organics. *Journal of Membrane Science*. 379 : 131-137.
- Sood, S., Umar, A., Mehta, S.K., Sinha, A.S. and Kansal, S.K. 2015. Efficient photocatalytic degradation of brilliant green using Sr-doped TiO₂ nanoparticles. *Ceramics International*. 41 : 3533-3540.
- Stamm, C., Räsänen, K., Burdon, F.J., Altermatt, F., Jokela, J., Joss, A., Ackermann, M. and Eggen, R.I. 2016. Unravelling the impacts of micropollutants in aquatic ecosystems: interdisciplinary studies at the interface of large-scale ecology. In: *Advances in Ecological Research*. Academic Press. pp. 183-223.
- Szabó, R.K., Megyeri, C., Illés, E., Gajda-Schranz, K., Mazellier, P. and Dombi, A., 2011. Photo-transformation of ibuprofen and ketoprofen in aqueous solutions. *Chemosphere*. 84 : 1658-1663.
- Thakur, S. and Karak, N. 2014. One-step approach to prepare magnetic iron oxide/reduced graphene oxide nanohybrid for efficient organic and inorganic pollutants removal. *Materials Chemistry and Physics*. 144 : 425-32.
- Torres, R.A., Abdelmalek, F., Combet, E., Pétrier, C. and Pulgarin, C. 2007 A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in deionised and natural waters. *Journal of Hazardous Materials*. 146 : 546-551.
- Venkateswarlu, S., Rao, Y.S., Balaji, T., Prathima, B. and Jyothi, N.V. 2013. Biogenic synthesis of Fe₃O₄ magnetic nanoparticles using plantain peel extract. *Materials Letters*. 100 : 241-244.
- Wang, F., Smith, D.W. and El-Din, M.G., 2003. Application of advanced oxidation methods for landfill leachate treatment-A review. *Journal of Environmental Engineering and Science*. 2 : 413-427.
- Wang, T., Jin, X., Chen, Z., Megharaj, M. and Naidu, R. 2014. Green synthesis of Fe nanoparticles using eucalyptus leaf extracts for treatment of eutrophic wastewater. *Science of the Total Environment*. 466: 210-213.
- Warner, W., Licha, T. and Nödler, K. 2019. Qualitative and quantitative use of micropollutants as source and process indicators: A review. *Science of the Total Environment*. 686 : 75-89.
- Zietzschmann, F., Altmann, J., Ruhl, A.S., Dünnebier, U., Dommisch, I., Sperlich, A., Meinel, F. and Jekel, M. 2014. Estimating organic micro-pollutant removal potential of activated carbons using UV absorption and carbon characteristics. *Water Research*. 56 : 48-55.
- Zirlwagen, J., Licha, T., Schiperski, F., Nödler, K. and Scheytt, T. 2016. Use of two artificial sweeteners, cyclamate and acesulfame, to identify and quantify wastewater contributions in a karst spring. *Science of the Total Environment*. 547 : 356-365.