

Drug contaminants in water and sustainable approach towards their degradation: a short review

Sayed Jaheera Anwar^a, Irshad Ul Haq Bhat^{a,b,*}, Maisara Abdul Kadir^{a,b}, Hanis Mohd Yusoff^{a,b}, Mohd Hasmizam Razali^{a,b}, Lee Khai Ern^c

^aFaculty of Science and Marine Environment, Universiti Malaysia Terengganu, 21030, Kuala Nerus, Terengganu, Malaysia, email: jaheeraanwar@gmail.com (S.J. Anwar)

^bAdvanced Nano Materials (ANoMa) Research Group, Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, 21030, Kuala Nerus, Terengganu, Malaysia, emails: irshadbhat78@gmail.com (I.U.H. Bhat), maisara@umt.edu.my (M.A. Kadir), hanismy@umt.edu.my (H.M. Yusoff), mdhasmizam@umt.edu.my (M.H. Razali)

^cInstitute for Environment and Development (LESTARI), Universiti Kebangsaan Malaysia, 43600, Bangi, Malaysia, email: khaiernlee@ukm.edu.my (L.K. Ern)

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ABSTRACT

The presence of drugs has alarmed about the impending hostile effects of drugs on community health and the water ecosystem. The common sources for drug contamination in water are either from human consumption, their partial metabolization, and improper disposal of unused expired drugs. Besides, veterinaries, pharmaceutical plants, hospital wastes also contribute to water pollution. The other sources of drug pollution are dairies, animal husbandry, animal excreta, poultry, and community waste. The pharmaceutical waste can reach the freshwater, thus effecting the drinking water, which in turn can be lethal to the aquatic ecosystem. The drugs contaminating the water are necessary to be detected initially and controlled or eliminated accordingly. Ozonation and advanced oxidation processes have been effectively used to degrade different drugs. The metal nanoparticles as nanocatalyst can be effective in converting drug contaminants to less or non-harmful products via catalytic degradation. The eradication of drugs from contaminated water bodies by conventional management technologies has been extensively flourished but the sustainable degradation approach is highly encouraged. Based on the recent advances presented in the literature obtained from different search engines, we here in report the current scenario about the presence of drug contaminants in water, and various alternatives opted for degradation of drugs. Furthermore, the use of metal nanoparticles can add up new dimensions to control this challenging pollution.

Keywords: Drug degradation; Conventional management technologies; Ozonation; Oxidation; Metal nanoparticles; Catalyst

1. Introduction

The consumption of drugs has been extensively increased worldwide in the past few decades. A relatively huge volume of copious recommended and non-recommended drugs has been consumed annually all over the globe for the treatment of humans as well as for animal complaints.

These drugs cover antipyretics, antibiotics, analgesics, anti-depressants, blood lipid regulators, chemotherapeutic agents, and contraceptives [1,2].

Apart from the medical uses, the drugs have a wide range of agricultural and livestock applications [3]. The wastewaters such as excretion, surfeit water from animal feeding operations, effluents from hospitals, and pharmaceutical

* Corresponding author.

industries are the main sources of drugs [4]. The inappropriate dumping of unutilized and outdated drugs into the domestic wastewaters or in landfills forthwith, accidental leaks at the time of manufacturing, and supply are some of the other key sources responsible for the contamination of the aquatic environment [5]. These waters then pass into sewage treatment plants where the metabolized and un-metabolized drugs along with further organic and inorganic matters in wastewater are laterally treated. But some of these drugs could not be entirely eradicated from the sewage treatment plants thus, leaving behind some of its components in those plants and also in the surface and ground waters [6].

The crucial bacterial processes are disrupted by these drug residues in surface water, which in turn prove hazardous to soil fertility, animal production, and a proper balance in the aquatic environment. Even a minute quantity of drug residues present in the water bodies found to be a major global challenge faced for assessing water quality because of its noxious impact over the aquatic habitats. Moreover, concerns have grown as they may even pass into streams, rivers and groundwater before reaching to the food chain. There is a chance of developing microbial resistance as these tenacious compounds may exercise selective pressure on the microorganisms [7–9]. The situation turns to worse if the intestinal bacteria become drug-resistant, grown in huge numbers, and developed into super-bugs, the infections triggered by these bacteria may be fatal for the innumerable reasons. It would be a major threat to the global human population [10].

Several standard wastewater management processes such as adsorption, filtration, oxidation, and combined systems have been used so far but still could not cope up with some of the limitations viz., toxic by-products, the lack of proper treatment, low removal efficiency and relatively high operational costs. Hence, there is an instantaneous need to upgrade the latest treatment technologies to degrade and remove pharmaceutical residues from wastewater and also to provide a solution for neutralizing the drug contaminants [11].

In the past few years, advanced methods in ozonation and oxidation paths have been described in the literature for the removal and degradation of drug residues from the aqueous solution. These approaches encompass photocatalytic ozonation, non-thermal dielectric barrier discharge, photocatalytic oxidation, generation of active, non-selective, and unstable oxidizing species analogous to hydroxyl radicals that oxidize majority of the organic pollutants existing in the water. All these methods proved to be fruitful and boosting for the deduction of drug pollutants present in aquatic bodies [12].

The advances in nanotechnology have been used to generate materials of nanoscale size effectively used against the treatment of pollutants of different origins [13,14]. The focus on nanoparticles as nanocatalyst is one of the achievements [15]. The selective mediation of chemical transformations and improved reactivity of nanoparticles make them highly efficient heterogeneous catalysts, robust, green, and involve safe materials. Similarly, nanoparticles produced via environmentally safe and green biosynthesis approach have also been efficaciously used for the degradation of various organic dyes [16]. Hence, their extraordinary high surface-to-mass ratio and shape-dependent properties and their

ability to increase surface catalytic activity have lead nanocatalysts such as zero-valent metals, semiconductor materials, and bimetallic nanoparticles to be utilized widely in water treatment. They can even improve the degradation of environmental contaminants such as pesticides, halogenated herbicides, azo dyes, polychlorinated biphenyls, and nitroaromatics. The catalytic activities have been confirmed on a large scale for several contaminants [17]. Research works on various metal nanoparticles such as photo-catalyst in photocatalytic degradation for the exposures of the reactions to various wavelengths of light sources has been reported by Bhatt et al. [16].

Therefore, this review provides insight into drug contamination, ecotoxicity and human health risk, detection and analysis, characterization and control measures of drugs in water. Furthermore, the methods for drug degradation in contaminated water by using nanoparticles as one of the sustainable approaches have been documented.

2. Sources of drugs

Drugs have been found in different environmental samples [18]. There are different probable sources and routes for the existence of drug residues in the water bodies. The consumption of numerous prescription and non-prescription drugs for healthcare at households, hospitals, and clinics stands as one of the foremost drug sources. The other eminent source of drugs is from partial metabolism and excreta, unused, surplus, and expired drugs [19,20]. Apart from veterinaries, pharmaceutical plants, hospital wastes, some of the other important sources of drug pollution are dairies, animal husbandry, animal excreta, poultry, and community waste [21,22]. Recently, the application of drugs has found a place in the agricultural field, for enhancing animal husbandry, poultry, bee-keeping, and aquaculture [23] that pollute the ecosystem through the excretion of under-utilized antibiotic and its metabolites from the bodily waste. Besides, domestic and industrial effluents, the pharmaceutical industries add ominously in total drug concentration in the backwater of the wastewater treatment plant [24]. The improper discarding of unused and expired drugs dumped in landfills also can be reflected as key sources of pollution [5]. The overflow from urban centers, fish farms, irrigation with treated domestic water, and fertilizing livestock manure are some of the other sources that introduce the drugs into the ecosystem [10].

The use of these drugs could not be rejected for its demand for the ever-growing population. But one can put check over their release into the environment as they might enter into the surface and ground waters and would become a threat to social health, weather, and water ecosystem. Several drug residues found to be non-biodegradable and resistant to traditional wastewater management methods [25–28].

The manifestation of drug residues in wastewater management plant was reported by Richardson and Bowron [29], Kümmerer [30], and Debska et al. [31] had anticipated these substances as easily biodegradable in the ecosystem as most of them are capable of being metabolized and converted to some extent in the human body but in contrast, a majority of recent literature studies have confirmed the

existence of these drug residues in the water ecosystem [29,30]. In different countries, such as Germany, Switzerland, the Netherlands, Canada, Spain, Italy, Brazil, and the United States, many drugs are found in wastewater management plant effluents and surface waters [32–41].

The spotted drug residues in domestic water management plant effluents and surface water comprised antibiotics, painkillers, anticonvulsants, lipid regulators, cytostatic drugs, hormones, antihistamines, X-ray contrast media and beta-blockers in the concentration range of ng/L to mg/L. Whereas numerous polar drug residues and metabolites viz, diclofenac, sulfamethoxazole, carbamazepine, amidotrizoic acid have been noticed at about 1 mg/L concentration in the samples of groundwater [42–44].

Hence, it is has been reported that effluents from wastewater management plants might get released into surface water, and then to groundwater; finally the compounds enter the aquatic environment. Sometimes, the biologically treated domestic water may be treated again for innumerable applications including portable re-use.

3. Drug contamination in drinking water, ecotoxicity, and human health risk

The pharmaceutical waste from wastewater management plants can reach to groundwater through surface water [45]. Occasionally, the biologically treated domestic water is retreated for the production of various reclaimed waters for other commitments along with re-using purpose [6]. The progression of resistance may occur as these persistent drug residues might exercise selective pressure over microorganisms [46]. According to Mutiyar and Mittal [47], drugs get assorted with freshwater sources by way of soil erosion and rains. Le Page et al. [48] have stated the detection of antibiotics frequently in surface water and wastewater at a concentration range of 0.01 and 1.0 µg/L. Therefore, it is evident that antibiotic residues had reached drinking water sources. Macrolides, chloramphenicol, and sulfonamides are some of the drugs identified in drinking water with maximum concentrations whereas; detection frequencies of ciprofloxacin exhibit the value up to 679.7 ng/L as highest concentration level [49]. Drugs such as fluoroquinolones, sulfamethoxazole, macrolides, sulfonamides, lincomycin, beta-lactams, and trimethoprim with a concentration range up to 35,500 ng/L have found to be present in the hospital effluents of many developing countries [50]. The occurrence of other types of drugs, such as anticonvulsants and analgesics in drinking water, is a strong global health concern. Subsequently, the long-term health hazards by the acquaintance to trace drug residues and their metabolites are still unknown. Hence, the mixture of biologically active compounds and its presence in drinking water should be evaded particularly as a preventative measure [51,27].

The risk linked with drug contamination of the aquatic ecosystem is a global challenge. The problem of drug resistance is rising rapidly in developing countries owing to different concerns, for example, improper standards for drug prescription and irregular monitoring. The pharmaceuticals comprising of cytostatic agents, genotoxic antibiotics, and immunosuppressive drugs possess cytotoxic, mutagenic,

embryo-toxic, and carcinogenic properties. Drugs are the chemical substances associated with therapeutic action but certain ecological and public health hazards can be foreseen from their introduction to the environment. Some categories of drugs are harmful to plants, phytoplankton, crustaceans, microorganisms, fish, insects soil microorganisms, and equally humans [6]. Drugs such as macrolides, fluoroquinolones, and tetracyclines are nondegradable and found to be tenacious in the ecosystem [52]. Sarafloxacin has been used to treat poultry infection that binds toughly to soil; so, it is necessary to detect further isoforms that persist in the soil to check the toxicity level of new pollutants [53]. Virginiamycin, a food supplement utilized to enhance the growth of animals and is found in the dung of treated animals which even find its application in fertilization and because of its soil binding capacity [54], it pollutes the water supply and its exposure provides resistance to the soil microbiota [55].

4. Detection, analysis, and characterization of drugs in contaminated water

To eradicate the drug pollutant in contaminated water, drug detection and analysis are pre-requisite steps and have been reported by various researchers. The chemical and structural properties of drugs and their abiotic conversions are responsible for the determination of their existence in the ecosystem [56,57]. A study by Barancheshme and Munir [58] stated the detection of trimethoprim, ofloxacin, and sulfamethoxazole in influents as well as effluents of sewage treatment plants. Pamreddy et al. [59] demonstrated analytical methods to quantify sulfonamides, tetracyclines in wastewater, and also worked on tetracyclines extraction. Neves et al. [60] used ultrasonic aided extraction technology to extract antibiotics from solid samples. The other methods include microwave supported extraction process, fast-tracked solvent extraction process [61] and their strength was long-established by liquid chromatography [62] and mass spectroscopy or tandem mass spectroscopy [63]. Antibiotics ranging from a few hundred to several thousand ng/L can be spotted in sewage water by high-performance liquid chromatography-mass spectrometry (HPLC-MS/MS) [64]. High-performance liquid chromatography (HPLC) is the familiar and well-established chromatography technique utilized for the separation of contaminations in the case of liquid sample. Wang et al. [65] have detected and extracted virginiamycin in soil samples using HPLC. Tetracyclines turn fluorescent when reacted with magnesium ion, the fluorescence is exaggerated with the addition of a base, that is, sodium hydroxide, and hence can be used for antibiotic detection [3]. The drug concentration can be identified using UV-vis spectrophotometer. The degradation products of drugs can be analyzed by using high-performance liquid chromatography-mass spectrometry (HPLC-MS) with Agilent HPLC/Q-TOF MS in strument (Erciyes University, 38280, Talas, Kayseri, Turkey) [11]. The equipment used C18 analytical column along with a mobile phase of methanol and deionized water to degrade drugs [11]. Decomposition products and possible reaction mechanisms can be easily analyzed using general analytical techniques such as liquid chromatography-mass spectrometry (LC-MS), high-performance liquid chromatography (HPLC), and nuclear magnetic

resonance spectroscopy [66]. Gharbani and Mehrzad [67] measured 4-chloro-2-nitrophenol by using HPLC with a Spherisorb ODS-3 of (5 μm , 150 mm \times 4.6 mm i.d) column, and UV absorbance detector at a wavelength of 234 nm in basic and neutral solution and 219 nm in acidic solution. The pH of a solution was measured with pH meter. A total organic carbon analyzer was used to ensure the release of inorganic carbon from the solution as CO_2 . Yi et al. [68] quantified the concentration of diclofenac by a high-performance liquid chromatography equipped with a C18 column and a UV detector at 35°C and a wavelength of 275 nm. They also used HPLC-MS/MS to identify degradation intermediates and mass spectrometer with electrospray ionization (ESI) source to obtain mass spectra data in the negative ion mode by scanning from m/z 100–400. Yi et al. [68] analyzed the degradation products of diclofenac by LC-MS/MS at various irradiation doses. According to Regmi et al. [69], to identify the exact mass, HR-QTOF ESI/MS analysis was carried out in a negative-ion mode using different column systems.

5. Control measures for drug contaminations and drug degradation

It is necessary to treat and eliminate hazardous drug residues and other solid waste from sewage water in a proper way. Wastewater treatment is an important phase to keep the aquatic environment out of pharmaceuticals. Some of the drug components could not be removed effectively; hence, there is a need for advancement and alteration in methods to address this problem. Larsen et al. [70] and Jones et al. [20] suggested the traditional end-of-pipe approach that could be expensive and might not be a practicable choice.

As the traditional wastewater management practices could not meet the need, there arose a need for the introduction of advanced techniques. These technologies include membrane filtration such as nanofiltration, reverse osmosis [19,71–73] advanced oxidation, ozonation, activated carbon adsorption processes [74], chemical oxidation by ozone, ozone/hydrogen peroxide [75,76], activated carbon adsorption, and reverse osmosis [76,71]. The latter two processes are suitable only for the management of clean surface water and groundwater with fewer background pollutants such as natural organic matter. These physical water management methods seek the dumping of wastes such as spent activated carbon generated and membrane retentive while treating the wastewater. The activated carbon adsorption has a restricted ability to get rid of polar organic compounds owing to its removal mechanism of hydrophobic interactions [51] whereas, a lot of drug compounds and its metabolites are found to be polar. On the other hand, chemical oxidation, for instance, advanced oxidation and ozonation processes are considered as a more appropriate treatment method opted for drug residues found in wastewater, surface water as well as groundwater. The ozonation and advanced oxidation methods are introduced before and after feasible biological treatment as the chemical or photochemical oxidation is less toxic, allows more biodegradation of xenobiotics, and improves the degradation in the succeeding treatment process and the ecosystem [77].

The drugs present in freshwater and wastewater can be eliminated completely either by mineralization or by

converting them into less harmful products for human health and aquatic ecosystem [77]. Ozonation and various advanced oxidation processes namely photocatalytic non-thermal dielectric barrier discharge, ozonation, and photocatalytic oxidation have been tested for the non-steroidal anti-inflammatory drug degradation [12]. The ability of a method to remove a particular drug is interconnected to its chemical structure [78], and the insufficient degradation procedure can be a risk to environmental balance [79]. The advanced oxidation routes for the degradation and exclusion of drug residues from the aqueous solution is found to be efficacious and promising for the elimination of drug contaminants. It takes in the generation of active, non-selective oxidizing and unstable species viz., hydroxyl radical that is capable of oxidizing most of the organic pollutants present in water [80,81]. The halogenated drugs and nitro intermediates can get blocked in the single oxidative system, and hence for a complete mineralization, the introduction of potent oxidation species is a necessity [82,83].

The electrochemical advanced oxidation process is an efficient way to degrade antibiotics, electro-Fenton process for the degradation of levofloxacin drug [82,84,85], and trimethoprim drug was reported to be degraded by photoelectro-Fenton and solar photoelectro-Fenton processes [86–89]. Methanol, a universal solvent of tetracyclines is used for its detection and can enhance the degradation of tetracycline molecules [90].

The tremendous effort by researchers has been reported to degrade diclofenac by various methods such as sonolysis, ozonation, and their combined application [91–95], electron beam technology [96], UV/ H_2O_2 [97], Fenton and photo-Fenton [98–100], photolysis and photocatalytic degradation, photocatalytic ozonation, pulsed corona, and dielectric barrier discharge [101–109]. Ibuprofen has been degraded by several oxidation processes including photolysis [110], ozonation [111], electron beam irradiation [112], sonolysis and sonocatalytic degradation [113,114], Fenton and photo-Fenton oxidation [115,116], and non-thermal plasma [117,118–120].

The bioelectrochemical system involving redox reactions can be used to reduce the antibiotic pollution involving the action against antibiotic resistance genes and antibiotic resistance-carrying bacteria [57]. But, due to the large-scale abundance of oxygen in the environment, oxidation is considered as the typical and dynamic path for antibiotic degradation while photolysis is another imperative mechanism used for antibiotic degradation [121].

6. Metal nanoparticles for catalytic degradation of drugs

Nanomaterials are widely used for the removal of drugs by adsorption, filtration, and photocatalysis. Nowadays research is focusing on the use of metal nanoparticles to catalyze drugs. Iron (Fe) nanoparticles are often used in the degradation process because they usually possess a core-shell structure and several degradation paths occur within its core-shell structure [15]. The oxidization of the metallic core-shell leads to the formation of iron oxyhydroxide and iron oxide nanoparticles. The removal mechanism is based upon different mechanisms such as strong oxidizing agents followed by diffusion within the core-shell layers and encapsulating the core

area while, reduction pathways at core-shell area being carried out via adsorption, sorption, and encapsulation process at the oxide layer. Co-operative effects of reduction, sorption, and encapsulation mechanisms result in quick reactions and extraordinary treatment competences for several contaminants [122]. Kerkez-Kuyumcu et al. [15] applied magnetic Fe₃C nanoparticles implanted on N-doped carbon (Fe₃C/NC) catalyst for the degradation of ibuprofen.

Metal ions such as cobalt, cadmium, zinc [123], copper, and mercury [124] are known to degrade cephalosporin and penicillin by helping in β-lactam ring-opening and catalyzing the inactivation rate through the formation of intermediate complexes with cephalosporin and penicillin.

Fan et al. [125] reported aromatic ring decomposition of cefradine by the TiO₂/hn process employing a continuous aeration in presence of radiation from 30-W UV lamp. The formation of resulting compounds containing carboxyl and amino groups was confirmed by spectroscopic techniques. Furthermore, the cefradine decomposition was enhanced by adding hydrogen peroxide in the system as a result of hydroxyl radical production via photodecomposition of hydrogen peroxide.

Thokchom et al. [126] utilized a hybrid sono-electrolytical treatment system and Pd@Fe₃O₄ to degrade an emerging drug micro-pollutant, ibuprofen. The electro-Fenton process was catalyzed by Pd-Fe₃O₄ using a graphite cathode

and a dimensionally stable anode for the degradation of trimethoprim and levofloxacin antibiotics via oxidation [127]. El-Kemary et al. [128] reported the investigation of photo-degradation of ciprofloxacin drug using ZnO nanoparticle as a photocatalyst, in UV light irradiation under aqueous solutions at varying pH levels; some recent nanoparticles used as metal catalysts are summarized in Table 1.

7. Conclusion and future perspective

The extensive use of pharmaceutical drugs is a leading cause of their accumulation in the environment. This environmentally threatening issue has been reported by different researchers by providing reports of increasing numbers of drugs detected in potable water, river water, seawater, wastewater, and also in treated wastewater. There is an immediate requirement to discover other potential inexpensive and easy handling treatment methods for effective removal and degradation of these drug residues from a relatively large volume of effluents. Apart from ozonolysis and oxidation methods, a paradigm shift towards nanotechnology can open up new avenues for the treatment of drug residues. The development of selective metal nanocatalyst can be a good alternative owing to their size and surface phenomenon properties. Currently, many green synthetic approaches have been adopted for developing various metal nanocatalyst for

Table 1
Metal catalyst used for drug degradation

Drug name	Degradation method	Metal catalyst	Reference
4-Chloro-2-nitrophenol	Heterogeneous catalytic ozonation	ZnO	[67]
Diclofenac	Photocatalytic oxidation	S-TiO ₂	[68]
	Photocatalytic ozonation	TiO ₂	[129]
Ceftriaxone	Electrochemical oxidation	RuO ₂ -TiO ₂ /Nano-G composites	[130]
Tetracycline	*OH-mediation oxidation	US/ZnO/NC	[131]
	Ozonation		[49]
Ibuprofen	Photocatalytic hydroxylation and decarboxylation	N-doped BiVO ₄	[69]
	US/EC degradation or sonoelectro-oxidation	Pd@Fe ₃ O ₄	[126]
	Oxidative degradation	Fe ₃ C/NC	[132]
	Solar photo-Fenton	Fe: ethylenediamine-disuccinic acid (1:2)	[133]
Amoxicillin	Heterogeneous photocatalytic acidic hydrolysis	Fe ³⁺ -TiO ₂ -N,C	[134]
	Fenton and photo-Fenton	Potassium ferrioxalate	[135]
	Photocatalytic ozonation	TiO ₂	[129]
5-Fluorouracil	Solar photo-Fenton	Fe ³⁺ /S ₂ O ₈	[136]
Sulfamethoxazole	Solar photo-Fenton	Fe: ethylenediamine-disuccinic acid (1:2)	[133]
Carbamazepine	Solar photo-Fenton	Fe: ethylenediamine-disuccinic acid (1:2)	[133]
	Photocatalytic oxidation	TiO ₂	[137,138]
Flumequine	Solar photo-Fenton	Fe: ethylenediamine-disuccinic acid (1:2)	[133]
Streptomycin	Heterogeneous photocatalytic alkaline hydrolysis	Fe ³⁺ -TiO ₂ -N,C	[134]
Levofloxacin	Electro-Fenton process	Pd-Fe ₃ O ₄	[127]
Ciprofloxacin	Photocatalytic degradation	ZnO	[128]
	Photo-Fenton	Iron citrate, iron oxalate and iron nitrate	[139]
Dicloxacillin	Photocatalytic oxidation	TiO ₂	[140]
Aspirin	Photocatalytic oxidation	TiO ₂ P ₂₅	[141]
Paracetamol	Photocatalytic oxidation	TiO ₂ P ₂₅	[141]

the degradation of specific contaminants found in water. Similarly, the drugs can be either eliminated or degraded by nanocatalyst. The degraded products can be characterized by various spectroscopic techniques to establish the degrading pathway and determine the structure of resulted products. Thus, a paradigm shift is needed either to modify the current technology or develop an economical and green nanocatalyst that can effectively eliminate drug-based contaminants.

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