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Insights of the Removal of Antibiotics From Water and Wastewater: A Review on Physical, Chemical, and Biological Techniques

Ali Khadir[1]*, Amin M. Ramezanali[2], Shabnam Taghipour[3] and Khadijeh Jafari[4]

[1]Young Researcher and Elite Club, Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch, Islamic Azad University, Tehran, Iran
[2]School of Civil Engineering, College of Engineering, University of Abbaspour, Tehran, Iran
[3]Department of Civil Engineering, Sharif University of Technology, Tehran, Iran
[4]Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran

Abstract

Pharmaceuticals, particularly antibiotics, are rightly regarded as one of the major emerging contaminants of the environment and there is increasing concern over their continuous presence in the aqueous solutions. Extensive research has shown that these compounds have been detected in fresh water of many countries. In this chapter, a brief introduction on pharmaceuticals and antibiotic pollution and also different common methods for antibiotic abatement in aqueous solutions has been studied. The performance of technologies such as membrane bioreactors, aerobic granular sludge, activated carbons, magnetic nanoparticles, Fenton processes, Peroxone, photocatalytic degradation, and electrocoagulation has also been discussed. Each method has its own advantages and disadvantages in which at present no sole system might be the best one.

***Keywords*:** Pharmaceuticals, antibiotic, treatment, pollution, water, wastewater

**Corresponding author*: Alikhadir.research@gmail.com

Inamuddin, Mohd Imran Ahamed, Rajender Boddula, and Tauseef Ahmad Rangreez (eds.) Applied Water Science Volume 2: Remediation Technologies, (1–48) © 2021 Scrivener Publishing LLC

1.1 Introduction

Drugs and their related compounds have been initially utilized to treat living creatures and since their discovery they have rescued lives of many people and animals. In fact, living without drugs seems to be impossible, particularly under present situation that humans are dealing with wide range of contaminants during their daily life. However, rapid population growth, continuous agricultural and industrial development, and establishment of countless pharmaceutical companies have made drugs as a hazardous health components for ecosystem [1,2]. Briefly, these compounds are persistent, recalcitrant, and toxic and many organisms are not able to metabolize and adsorb such compounds [1]. Effluent and wastes by pharmaceutical manufacturing companies, municipal wastewaters, and human/animal excretion are of the main pathways of pharmaceutical compounds entrance the environment [3,4]. Approximately 50–80, 80–90, and 15–30% of ciprofloxacin, tetracycline and sulfamethoxazole are excreted through urine and feces, respectively [5,6]. Unfortunately, present wastewater treatment plants could not remove pharmaceutical completely because of the lack of facilities and technologies. It must be considered that wastewater treatment plants act an integral role for pollution release unless they have proper treatment technique [7,8]. Fernández-López *et al.* [9] investigated the removal of four pharmaceuticals in different five treatment plants (Figure 1.1), and they reported that they have detected the target pollutants in the both influent and effluent of the treatment plants. Carbamazepine and naproxen were the most abundant compounds. Palli *et al.* [10] also found that pharmaceuticals were detected in the influent of wastewater treatment plants of Tuscany (Italy) in which acetaminophen (3,914 ± 2,620 ng/L), diclofenac (2,065 ± 739 ng/L) and amoxicillin (2,002 ± 2,170 ng/L) were the most concentrated followed by atenolol, ketoprofen, clarithromycin, carbamazepine, doxycycline and 17-β-estradiol. Their finding declared that some components had been removed well, but some of the others have exhibited partly elimination. Bagnis *et al.* [11] observations showed that wastewater, landfill leachate and agriculture were the sources of the presence of pharmaceuticals in Nairobi river. Considering these results, pharmaceuticals are generally detected in the effluent of conventional wastewater treatment plants, and to prevent the pollution spread, a full recognition of these system along with other advanced ones are vitally important.

Generally, pharmaceuticals are categorized into different classes including analgesics, antibiotics, psychiatric drugs, anti-hypertensives, beta-blockers,

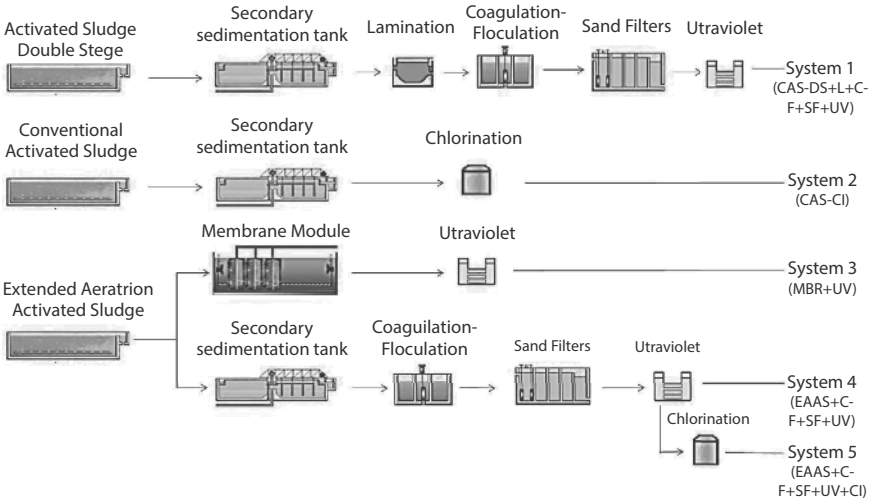

Figure 1.1 The schematic system of various treatment systems. Reprinted and reproduced with permission from Ref. [9].

hormones, contrast media, anti-diabetics, anti-viral, and anti-cancer drugs. Among antibiotics, antimicrobial drugs leading to bacterial growth inhibition, are important environmental pollutants due to their huge consumption. From 2000 to 2010, global antibiotic consumption promoted by 36%, signifying a forthcoming serious environmental issue [12]. Previous studies have confirmed that approximately 70 antibiotics have been detected in various media such as waters, soil, and sediment [13–16]. According to the available reports, in fresh waters of many countries such as Ghana, South Africa, Kenya, Nigeria, Mozambique, USA, Brazil, Canada, Latin America, Australia, Iran, China, Taiwan, Japan, Korea, UK. France, Spain, Germany, Italy, etc. antibiotic compound have been detected, indicating that antibiotic pollution may dominate the entire world, requiring nation and international plans to cease their future consequences [6]. Toxicity, persistence, carcinogenicity, DNA damage and lymphocyte mutagenicity, increasing human allergy, lower biodegradability, spread of antibiotics resistance bacteria and causing undesirable effects on humans and animals are some of the main hazardous side effects of the antibiotic spread [17–19]. Thus, it is obligatory to implement proper treatment systems to prevent further antibiotic release in the ecosystem.

Different treatment methods which have been applied for treatment of oily wastewaters are antibiotic contaminated waters include biological, chemical, and physical processes. In biological treatment (aerobic and

anaerobic) microorganisms are employed to treat wastewater under the presence or absent of oxygen. Activated sludge is one of the oldest bioreactor that has fluctuations in the removal efficiency of persistent compounds. Chemical methods such as advanced oxidation processes (AOPs) often decompose antibiotics into simpler molecules but this technology is very complex and expensive. However, it has generally high removal efficiency under appropriate operation. Physical techniques are one of the most effective methods of removing antibiotics from aquatic environments. Owing to generation of less toxic byproducts and low operational costs, adsorption is considered as a simple, practical, and effective method among other physical processes. In recent years, combination of several methods has been developed to increase the removal efficiency however these methods require further scrutiny to optimize the process. Considering both antibiotic pollution and treatment methods, the aim of present chapter, is studying application of various technology for antibiotics pollution abatement from aqueous solutions.

1.2 Antibiotic Removal Methods

1.2.1 Aerobic Biological Treatment

Aerobic wastewater treatment involves using oxygen for degradation of the soluble and colloidal organic matters into carbon dioxide, ammonia, energy, water, and new cells by means of heterotrophic and autotrophic microorganisms. Heterotrophs are organisms that require organic carbon supply for growth, and those which utilize inorganic carbon such as carbon dioxide are known as autotrophic microorganisms. A mix of these organisms as a unite culture can degrade compounds effectively. Since supplying oxygen is costly, aerobic processes are feasible if the COD of the input wastewaters is less than 1,000 mg/L [20,21]. In high-strength effluent such as industrial wastewater (e.g. pharmaceutical companies effluents), a hybrid system of anaerobic/aerobic could bring satisfactory results in terms of organic matters removal.

After the advent of membrane processes in 1960s like microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, the development of membrane bioreactors (MBRs) were of great attention. MBRs are hybrid bioreactors of membrane filtration and activated sludge, using a physical–biological treatment system which are effective for municipal and industrial wastewaters [22]. Figure 1.2 illustrates the schematic of two configurations of MBRs which are side-stream MBR and submerged MBR. The main

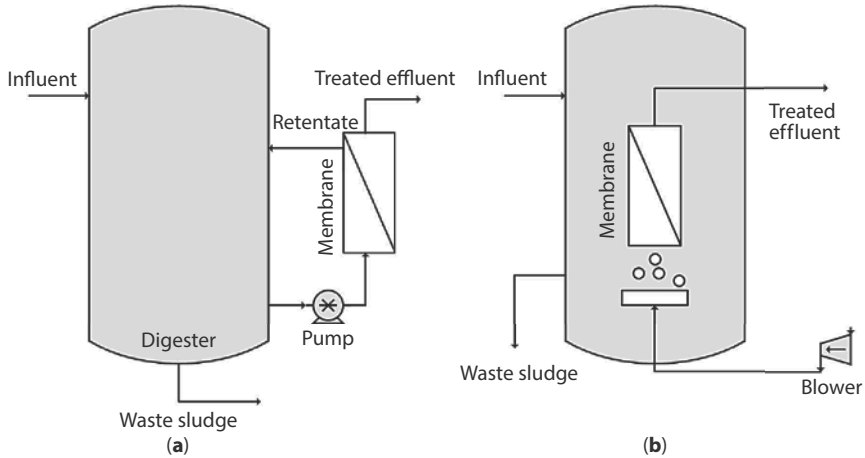

Figure 1.2 Two configurations of MBRs. Reproduced with permission from Ref. [31].

benefits of MBRs over activated sludge processes are their less required space for operation and also their ability to eliminate distinctive compositions of wastewaters [23]. Bentmen *et al.* [24] proved that MBR effluent has better quality than single activated sludge process and the mean BOD, COD, and turbidity removal was greater than 90% [25]. Sahar *et al.* (2011) found that MBRs could result in about 15–42% higher removal efficiency in comparison to conventional activated sludge [9]. In the drug production centers using MBR technology for the treatment of their wastewater, high removal of COD and BOD has been reported [23]. For example, with a capacity of 1 m^3/day for MBR operated at a pharmaceutical center in Taiwan, 95% COD and 99% BOD were eliminated. The initial values of COD and BOD were 800–11,800 and 100–6,350 mg/L, respectively [26]. Song *et al.* [27] successfully used biofilm MBRs for simultaneous removal of COD, nitrogen and veterinary antibiotics from digested piggery wastewater. The initial concentration of COD and total nitrogen (TN) was 1,101 ± 185 and 1,492 ± 132 mg/L, respectively. They found that COD/TN ratio played an important role that could highly affect the quality of effluent. Under optimum ratio of COD/TN (2.3 ± 0.5), 92.1 and 97.1% of COD and NH_4^+-N were removed, respectively. Also, the effect of hydraulic retention time (HRT) on the removal of 30.41 μg/L antibiotic was studied and observed that by decreasing HRT from 5 to 1 d, the removal efficiency reduced from 86.8 to 45.3%, respectively. However, Prasertkulsak *et al.* [28] observed complete removal of ibuprofen, 17β-Estradiol and triclosan at days 42 and 76.

MBRs have a unique advantage compared to many biological systems that make this technique to be extensively utilized. Fluctuations in the characteristics of the influent could deteriorate the quality of the treated water since many biological systems could not endure such variations. However, MBRs have proved their appropriate performance even under such circumstances. Zhu *et al.* [29] expressed that 100 μg/L sulfamethoxazole and tetracycline hydrochloride could not affect the performance of the systems and pollutants were removed perfectly. Even at antibiotic dosage up to 2,000 μg/L, COD and ammonia removal were not affected; however, denitrification was hindered. In another investigation, it was found that after tetracycline addition to the system, COD removal was approximately the same (changed from 92 to 88%), and of ammonium it was constant (99%) [30]. Similar to Zhu *et al.* [29] finding, denitrifies were affected by the antibiotic toxicity.

Activated sludge is one of the oldest biological wastewater treatment system that has been extensively utilized over a century for treatment of various contaminants [31, 32]. In the time of invention, it is fair to say that activated sludge was a breathtaking technology and paved the way for further development. By population growth and generation of countless recalcitrant organic matters, activated sludge may face some limitations such as installation of multiple units for carbon, nitrogen and phosphorous removal, flow recirculation, low biomass concentrations in the aeration tank, the necessity of clarifier to separate solids, large area requirement, much energy required for oxygen supply, and poor settling (may be because of sludge bulking) [33–35]. It has been more than two decades from the first usage of aerobic granular sludge and the findings demonstrate that it could be a novel and promising development in the field of biological treatment, and it has been predicted that aerobic granular sludge will overtake activated sludge [36,37]. Aerobic granules consist of highly compacted microbial aggregates containing millions of microorganisms per gram of biomass that their densities are much higher than that of conventional activated sludge. Tolerance to toxicity, high biomass retention, withstand at high organic loading, lower operational cost, less electricity requirement, and smaller land requirement (in comparison to activated sludge) are some of the main advantages of aerobic granular sludge over conventional activated sludge [38]. Table 1.1 compares some other features of aerobic granular sludge and conventional activated sludge. Figure 1.3 illustrates a schematic diagram of conventional activated sludge and aerobic granular sludge. Researchers tried to employ such a system for antibiotics removal.

Wang *et al.* (2019) studied the removal and fate of 5 antibiotics (C_{in} = 29.4–44.1 μg/l) and antibiotic-resistant bacteria (C_{in} = 80.9×10^4–111.6×10^4 CFU/ml) from piggery wastewater by aerobic granular sludge. The total

Table 1.1 Comparison of aerobic granular sludge and conventional activated sludge.

Parameters	Aerobic granular sludge	Activated sludge
Settling velocity	10–90 m/h	2–10 m/h
Size	0.2–5 mm	<0.2 mm
Degree of compactness and density	High	Low
Shape	Regular and spherical	Irregular and Filamentous
Layers	Aerobic, anoxic and Anaerobic	Aerobic
Tolerability	High	Low
EPS production	High	Low

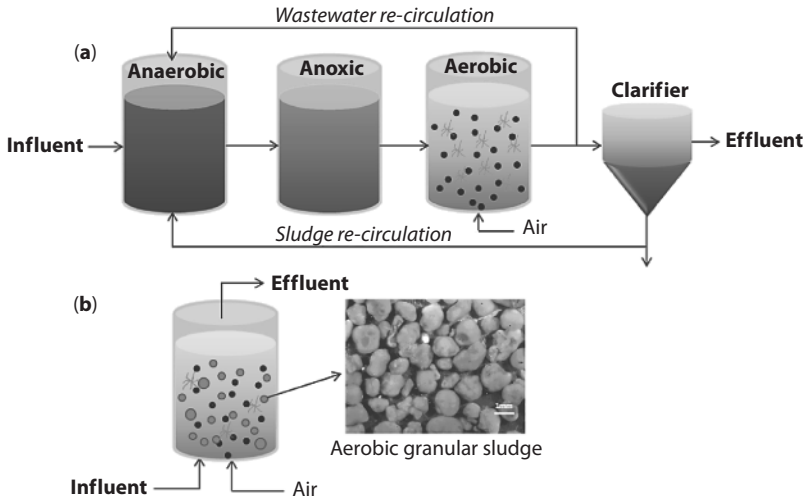

Figure 1.3 Schematic diagram of (a) conventional activated sludge and (b) aerobic granular sludge. Reproduced with permission from Ref. [35].

antibiotics and antibiotic-resistant bacteria removal were up to 88.4±4.5 and 89.4±3.3%, respectively. Moreover, 62.5 and 32.3% of total antibiotics were degraded and adsorbed by aerobic granular sludge, respectively. Bioadsorption and biodegradation were introduced as the main removal pathway of the drugs. In this study COD, NH_3-N, and TN removal

efficiencies were 98.0, 97.0, and 92.4%, respectively. Also, presence of antibiotics did not affect the performance of the system [39]. In another study, tetracycline injection at μg/L level did not affect the removal efficiency of COD and nitrogen, but microbial community and diversity of aerobic granular sludge were altered. Removal efficiency of aerobic granular reactor for tetracycline at initial concentrations of 100 and 500 μg/L were equal to 84.4 and 94.2%, respectively [40]. Kang *et al.* [41] verified that 2 μg/L sulfamethoxazole could not affect the performance of aerobic granular sludge and conventional suspended activated sludge; however, within two months' bacterial community of both biological systems were altered. In addition, sulfamethoxazole (C_{in} = 2 μg/L) showed higher elimination (84 ± 8%) by granular sludge than suspended sludge (73 ± 10%). Wang *et al.* (2018) studied degradation of 300 μg/L oxytetracycline in an aerobic granular sludge sequencing batch reactor. Until day 33 oxytetracycline removal curve exhibited an increasing trend, and then remained constant (89%), and for COD, NH_4^+-N, and total phosphorous it was 8.0, 90.0 and 97.9%, respectively. The microbial community was also altered after oxytetracycline addition [42]. Based on the reported results, aerobic granular sludge is a suitable and effective technique for antibiotics removal with high removal efficiency; however, the changes in the microbial community must be considered well to prevent further issues.

1.2.2 Anaerobic Biological Treatment

Anaerobic process, as its name defines, is a biological wastewater treatment technique to degrade organic matters in the absence of a free or molecular oxygen source with the contribution of anaerobic microorganisms. Anaerobic process is different from anoxic process since it is a reducing media with greatly negative values of oxidation reduction potential. In this environment, nitrate and sulfate are reduced to ammonia (or nitrogen gas) and hydrogen sulfide, respectively. Bacterial community and chemical–biological reactions of anaerobic processes are much more complicated than aerobic processes because there are several pathways for removal, and still there are few reactions that are not fully understood. Besides its complex nature in both operation and dominant organisms, it has been nominated as a promising wastewater treatment technology.

It is considered that Assyrians were the first employed anaerobic process to heat their water and bath. After that, this process was utilized to digest human and solid wastes. Nowadays, anaerobic application is widely utilized for treatment of industrial effluents, especially those

having recalcitrant organic matters. Such favorability might be attributed to advantages of anaerobic processes over aerobic ones. Some of these benefits are [43]:

1. No aeration is required, so it consumes less energy compared to biological systems.
2. Nutrient balance in aerobic system is vitally important; however, in anaerobic system less nutrient amount is required.
3. Methane (or so-called energy) is a valuable end product of anaerobic processes, which could compensate a part of treatment costs. In aerobic, no valuable product is produced.
4. Sludge management in every biological treatment system is of great concern, and it is tried to reduce its volume as much as possible. Fortunately, anaerobic process produces only 20% of sludge that of aerobic process.
5. Aerobic systems cannot tolerate high organic loading rate since they need a great amount of oxygen to degrade organic matters which is not cost effective. But, anaerobic processes can treat effluents owning high organic matters.
6. Less space is occupied in anaerobic systems in comparison to aerobic processes.

Above excellences have made anaerobic processes a feasible and efficient treatment system. Considering all these, anaerobic also has some disadvantages that might impede its application. Firstly, quality of treated wastewater could not follow the discharge limit for ultimate disposal. Owning to this fact, it is suggested that anaerobic systems should be coupled with other aerobic processes. Secondly, biomass synthesis rate is not as fast as aerobic process, resulting in longer start-up time. Microbial community in anaerobic processes is sensitive to environmental conditions (especially methanogens) and changes in parameters like pH and temperature could significantly reduce the performance of the system. Aerobic processes are capable of enduring these changes to some extent.

Briefly, organic matters experience some sequential steps to degrade into final products of anaerobic processes which are mainly methane and carbon dioxide. Figure 1.4 depicts the degradation stages of organic matter in anaerobic processes. Hydrolysis, the first stage of anaerobic reactions, could convert large molecules such as proteins, carbohydrates, and lipids into simpler compounds like sugars, amino acids, and fatty acids. This step might be slow depending on the size of the organic matter and operational parameters like pH and temperature [44]. After the formation of

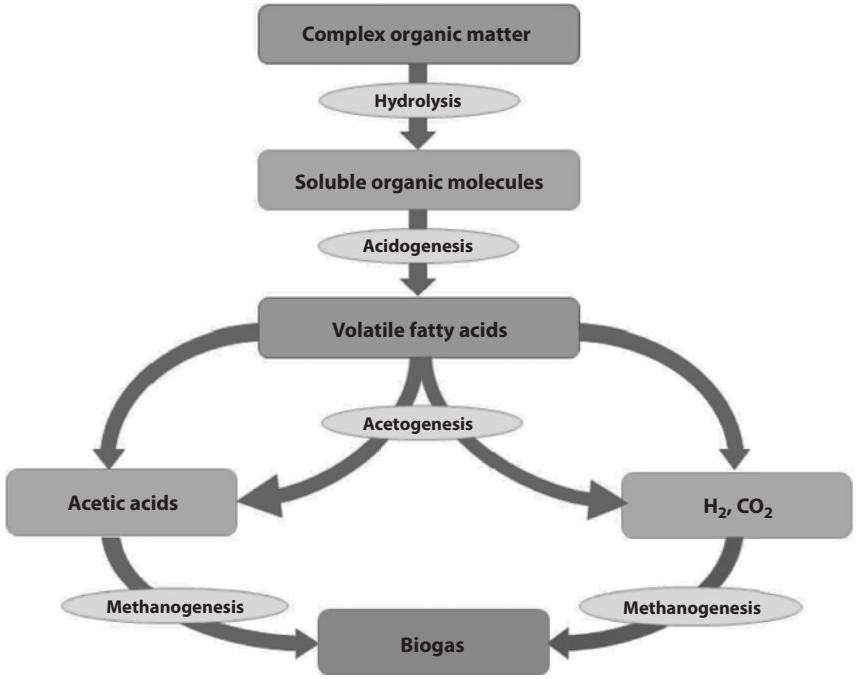

Figure 1.4 Degradation stages of organic matter in anaerobic processes. Reproduced with permission from Ref. [54].

soluble organic matters, they are changed into volatile fatty acids via acidogenic bacteria [45]. Acetogenesis is the third stage involving the production of acetate along with water and carbon dioxide. Approximately 2–3 h is required for bacterial growth and biochemical conversion rate in this step [46]. Uncontrolled production of volatile fatty acids may cause a drop in pH value that could impede methane production. It is recommended to maintain the volatile fatty acids/alkaline ratio lower than 0.3 [47,48]. Methanogenesis is the final step in anaerobic degradation of carbon in which acetic acid and carbon dioxide are converted into methane (Equations (1.1–1.2)). By accomplishment of these reactions at the optimum pH of 6.8–7.2, organic matters are stabilized/removed [46]. Acetoclastic methanogens (72%) are the main responsible for the major CH_4 generation compared to hydrogenotrophic methanogens [46,49]. But, they grow too slowly [50] and are more sensitive to environmental parameters (such as temperature, pH, and ammonia) in comparison with hydrogenotrophic methanogens [51,52]. Thus, a balance between hydrogenotrophic methanogens and acetoclastic methanogens must be

maintained to take the advantages of both and minimize their intrinsic limitations.

$$CH_3COOH \rightarrow CO_2 + CH_4 \quad (1.1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (1.2)$$

As an example, under certain conditions cellulose degradation through anaerobic processes could follow the following reactions (Equations (1.3–1.6)) [53]:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (1.3)$$

$$2CH_3COOH \rightarrow 2CH_4 + 2CO_2 \quad (1.4)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (1.5)$$

$$C_6H_{12}O_6 \rightarrow 2CH_4 + 3CO_2 \quad (1.6)$$

Up to now, various configurations have been proposed by researchers for wastewater treatment. Each has its pros and cons. In the following, some of the most common types of these bioreactors are reviewed and their performance toward antibiotic wastewater will be discussed.

Anaerobic membrane bioreactors (AnMBRs) are deeming to be a promising technology for treatment of pharmaceutical wastewater with the assistance of membrane under anaerobic conditions. Hu *et al.* (2017) investigated the performance of AnMBR at low temperature. Ultrafiltration membrane worked as the physical compartment, and the bioreactor was equipped with internal circulation. The authors found that at HRT> 48 d, COD and tetrahydrofuran removal efficiencies could reach over 95 and 96%, respectively. A combination of biological and physical technique was effective for the drug removal in which at mesophilic temperatures, biological reactions were dominant, and physical removal was influential in low temperatures. This make the bioreactor being capable of adapting temperature shocks [55]. In another AnMBR, the removal of *N*,*N*-Dimethylformamide, m-Cresol and isopropyl alcohol were reported 96.9, 98.2, and 96.4%, respectively [56]. Issues associated by membrane must also be considered, particularly when almost 90% of total energy consumption in AnMBR is related to filtration and membrane fouling [57]. Li *et al.* (2017) reported that presence of benzothiazole could shorten the

membrane fouling cycle [58]. Similar observations were reported for sulfamethoxazole and tetracycline [59].

1.2.3 Adsorption Processes

Among physical treatment techniques, adsorption processes have gained worldwide attention during the last decade. Adsorption is defined as the movement of antibiotic molecules (adsorbate) from the bulk solution to a solid surface called adsorbent. Based on the interaction between adsorbate and adsorbent, adsorption might be classified into two chief groups: physisorption and chemisorption. Briefly, once there is high adsorption energy between adsorbent and adsorbate, it is called chemisorption; otherwise, it is physisorption. The performance of the adsorption is influenced by several parameters, such as contact time, adsorbent dosage, initial antibiotic concentration, pH, solution temperature, interfering anions/cations, and etc. [60]. Among countless adsorbents that have been proposed by researchers, including simple natural materials to engineering ones, activated carbon and zeolite composites are the most utilized adsorbents which are discussed in the following.

1.2.3.1 Activated Carbon and its Composites

Among all carbon based nanomaterials, activated carbon has been highlighted as a promising material because of its large surface area, porous structure, functional groups, tunable surface chemistry, suitable thermostability, and high adsorption capacity [61]. Activated carbons are found in the forms of granular/powdered activated carbon, fibrous activated carbon, extracted activated carbon, and pellet activated carbon [62]. Low-cost materials such as wood, coconut and fruit shells, waste sugarcane bagasse, seed, coal, peat, and lignite might be employed to derive activated carbon. According to the pore size, activated carbon can be categorized to microporous (<2 nm), mesoporous (2–50 nm), and macroporous (>50 nm).

Manjunath *et al.* [63] reported the adsorption of sulfadiazine, metronidazole and tetracycline antibiotics on KOH-treated *Prosopis juliflora* activated carbon from single, binary and ternary adsorption systems. The adsorbent was mesoporous with BET surface area and total pore volume of 259.81 m^2/g and 0.15 cm^3/g, respectively. The equilibrium was attained at 2 h with the removal efficiencies of 79.74, 86.16 and 92.80%, respectively. Optimum dose was set at 1 g/L. Kinetics models including Pseudo-first order, Pseudo-second order, Intra-particle diffusion, liquid-film diffusion, Elovich and Bangham were employed to analyze kinetic data.

It was observed that antibiotic adsorption on activated carbon followed the Pseudo-second-order reaction with high R^2 value of 0.9476, 0.9987, and 0.9863 for sulfadiazine, metronidazole and tetracycline, respectively. Among the isotherm models, the Langmuir assumptions fitted well the experimental data and the maximum monolayer adsorption capacity was found 28.81, 25.06, and 18.48 mg/g for the studied drugs [63]. Tetracyclines removal was also studied by Zhang *et al.* [64] by activated carbon and was seen that at antibiotics concentration of 50 mg/L, the removal efficiencies were greater than 99%.

Chayid and Ahmed [65] analyzed the adsorption behavior of amoxicillin on activated carbon derived by *Arundo donax* Linn via microwave irradiation and KOH chemical activation. Pseudo-first order, Pseudo-second order, and intra-particle diffusion models were utilized to correlate the experimental data. Pseudo-first order and intra-particle diffusion models were not capable of describing the experimental data well which is confirmed by low R^2 value in comparison to Pseudo-second order. In addition, Sips (Freundlich–Langmuir) represented well-fitted with results than, suggesting the heterogeneous surface adsorption. Many pharmaceutical adsorption studies have confirmed that Sips assumptions could successfully expound drugs removal [66]. Sips maximum adsorption capacity was 345.4 mg/g which showed better performance than commercial carbon 261.8 mg/g [67], vine wood carbon 269 mg/g [68], coconut shell carbon 233.7 mg/g [69], organobentonites 27.9 mg/g [70], and chitosan 8.7 mg/g [71].

Nazari *et al.* [72] used batch adsorption experiments for cephalexin antibiotic removal by activated carbon. Walnut shell was chemically activated by $ZnCl_2$ and then was characterized. Figure 1.5 shows the SEM images of the prepared adsorbent before and after treatment process. Evidently, the activated carbon owned a porous and heterogeneous surface which was favorable for adsorption processes. After drug adsorption, the surface of the adsorbent was covered by layers of pollutant molecules. The suitability of the adsorption might also be verified by the FTIR spectra (Figure 1.5c). It looks as if some peaks were deleted or shifted because of the interactions between the activated carbon and cephalexin [72]. Figure 1.6 compares the adsorption capacity of this study with others in terms of cephalexin adsorption [73–79]. It is fair to suggest that under certain experimental conditions, walnut shell activated carbon is a promising material with higher adsorption capacity than other studies. Table 1.2 shows the adsorption capacity of various activated carbons. It can be concluded that activated carbons are promising adsorbent for antibiotics removal which is mainly due to their high surface area and functional groups.

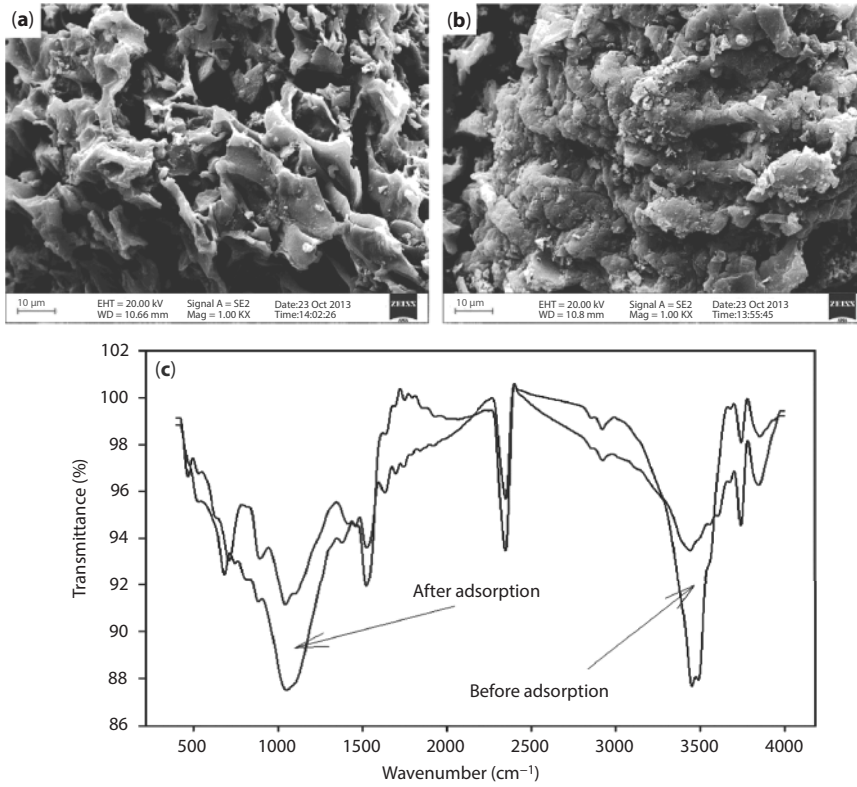

Figure 1.5 The SEM images (a, b) and FTIR spectra (c) of walnut shell activated carbon before/after cephalexin adsorption. Reproduced with permission from Ref. [72].

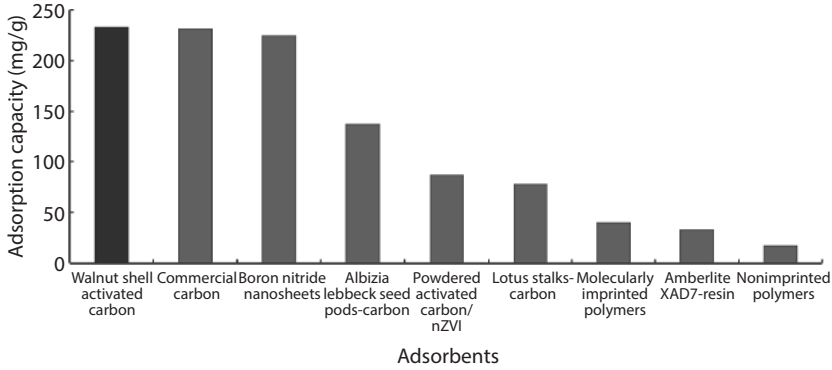

Figure 1.6 The comparison of Walnut shell activated carbon with other adsorbents in terms of cephalexin adsorption.

Table 1.2 Comparison of different activated carbons for antibiotic adsorption.

NO.	Adsorbent	Antibiotic	Adsorption capacity (mg/g)	Ref.
1	Lignin	Tetracycline	931.5	[80]
2	Vine wood	Amoxicillin	2.69	[68]
		Cephalexin	7.08	
		Tetracycline	1.98	
		Penicillin G	8.41	
3	Pomegranate wood	Amoxicillin	1,029.0	[81]
4	Cattail fibers	Norfloxacin	310.71	[82]
5	Magnetic activated carbon/chitosan	Ciprofloxacin	90.10	[83]
		Erythromycin	178.57	
		Amoxicillin	526.31	
6	Macadamia nut shells	Tetracycline	1,524.0	[84]
7	Walnut shell	Cephalexin	1452	[72]
8	Date press cake	Cephalexin	571.5	[85]
9	Lotus stalk	Norfloxacin	1289.1	[86]
10	Amino-functionalized biomass-derived porous carbons	Sulfonamide	95.8	[87]

1.2.3.2 Magnetic Nanomaterials/Adsorbents

Magnetic adsorbents are a wide range of materials that has been greatly utilized in environmental application during the past decades. Numerous magnetic nanomaterials have been developed to remove antibiotics and pharmaceuticals, pesticides, heavy metals, and dyes. The attraction of these adsorbents is due to their high surface area, acceptable adsorption capacity, and facile separation after the completion of the treatment process by means of an external magnetic field (Figure 1.7) [88]. To upgrade the mentioned features, many attempts have been made to prepare magnetic-based composites with higher performance and efficiency.

Figure 1.7 Magnetic separation of the magnetic adsorbents during adsorption processes. Reprinted and reproduced with permission from Ref. [94].

Li *et al.* [89] tested the adsorption behavior of tetracycline onto nitrilotriacetic acid-functionalized magnetic graphene oxide. Within the first 20 min, the process was very fast and then reached the equilibrium state at 600 min. The highest adsorption of tetracycline was achieved at pH of 4, and according to thermodynamic results the process was endothermic. Among the studied kinetics models, the pseudo-second-order kinetics provided the better correlation for the experimental data. The authors reported the maximum adsorption capacity of 356 mg/g which was greater than Fe/biochar (96 mg/g) [90] and MWCNTs (270 mg/g) [91]. In another study, graphene oxide was functionalized with magnetic particles for tetracycline removal, and resulted in the adsorption capacity of 391 mg/g [92]. In another study, sulfamethoxazole removal was investigated by magnetic $CuZnFe_2O_4$–biochar composite. The maximum adsorption capacity was 212.8 mg/g and the process followed pseudo-second order model and Freundlich isotherm [93]. Magnetic graphene nanoplatelets exhibited the adsorption capacity of 14.1 mg/g for amoxicillin [94]. π–π stacking and electrostatic interaction were the dominant adsorption mechanism and the rate determining step was the π–π electron donor–acceptor interaction. Table 1.3 summarizes some of the works that have been carried out for antibiotic removal by different magnetic composites. Adsorption capacities, if is intended as one of the main important choice, own relatively high values which make magnetic composites as satisfactory materials for antibiotic adsorption.

Table 1.3 Comparison of the adsorption capacities of some magnetic adsorbents for antibiotic removal.

NO.	Adsorbent	Antibiotic	Adsorption capacity (mg/g)	Ref.
1	Nitrilotriacetic acid/magnetic graphene oxide	Tetracycline	212	[89]
2	graphene oxide/ magnetic particles	Tetracycline	39.1	[92]
3	magnetic $CuZnFe_2O_4$–biochar	Sulfamethoxazole	212.8	[93]
4	Magnetic graphene nanoplatelets	Amoxicillin	14.1	[94]
5	Nitrilotriacetic acid/magnetic graphene oxide	Ciprofloxacin	230.5	[95]
6	Fe_3O_4-red mud nanoparticles	Ciprofloxacin	111.11	[96]
7	Fe_3O_4/Carbon composite	Ciprofloxacin	90.1	[97]
8	Magnetic chitosan-g-poly(2-acrylamide-2-methylpropane-sulfonic acid)	Tetracycline	806.60	[98]
		Chlorotetracycline	876.60	
9	Magnetite nanoparticles	Chlorotetracycline	476	[99]
10	Magnetic $FeNi_3$/ SiO_2/CuS	Metronidazole	147	[100]

1.2.4 Advanced Oxidation Processes

All removal methods (physical, chemical, and biological) have intrinsic disadvantages that could hinder their application in certain situations. Among these methods, oxidation processes have exhibited virtually better performance in terms of different contaminant elimination (such as drug). AOPs were initially proposed in 1980s for drinking water treatment and afterwards they have been employed for distinctive wastewaters [101]. AOPs require a chemical reagent (such as hydrogen peroxide, ozone, transition metals, metal oxide, etc), and an energy source (such as visible light, gamma, ultraviolet and ultrasonic irradiation) in order to generate free radicals. In fact, during AOPs free radicals mainly hydroxyl radicals (•OH) and sulfate radicals (SO_4^-), commonly named as HR-AOPs and SR-AOPs, respectively, are generated in sufficient quantities to oxidize a large amount of organic and inorganic matters in waters and wastewaters. Similarly, both •OH and SO_4^- could react fast with organic compounds; however, SO_4^- radicals possess higher redox potential, longer half-life, and selective behavior for special compounds [102]. Figure 1.8 shows the oxidation potential of several agents and as can be seen hydroxyl radicals are competitive agents with high energy for matter degradation [103]. Generally, AOPs are carried out by generation of strong oxidant species, interaction between pollutants/oxidant agents, and finally mineralization at near ambient temperature and pressure. Under complete degradations,

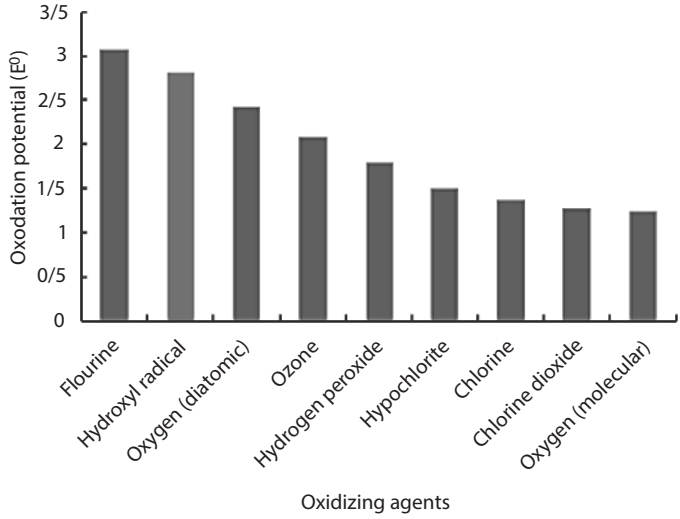

Figure 1.8 Oxidation potential of various oxidizing agents.

CO_2, H_2O, and other inorganic matters are the ultimate products of AOPs (Equation (1.7)).

$$\text{Organic species} + \text{oxidant species} \rightarrow CO_2 + H_2O + \text{inorganic ions} \quad (1.7)$$

Considering the fact that oxidation agents are produced in different ways, AOPs are classified into several types. In the following, some of these techniques are introduced and their applicability for antibiotic removal is discussed.

1.2.4.1 Fenton Type Processes

Fenton process, discovered by the British chemist Henry Fenton in 1894, might be called as one of the most important types of AOPs that has gained much attention due to high degradation efficiency, safe and easy operation, cost-effectiveness, environmentally-friendliness as well as the fact that Fe is inexpensive, abundant and harmless [104,105]. In this method, ferrous salt and hydrogen peroxide are combined with each other to form hydroxyl radicals in an acidic media (pH~2.5–3), as shown in Equations (1.8–1.9) [106]:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + \cdot OH + OH^- \quad (1.8)$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2^{\bullet} + H^+ \quad (1.9)$$

Furthermore, generated $^{\bullet}OH$ could react with Fe^{+2} (Equation (1.10)):

$$OH + Fe^{+2} \rightarrow Fe^{+3} + OH^- \quad (1.10)$$

In view of comparison, $HO_2^{\bullet}$ is less effective than $^{\bullet}OH$ since it has lower oxidation power [107]. Moreover, once the system is operated at non-optimum pH values, other less reactive species are formed that are not as efficient as $^{\bullet}OH$ [108]. It is important to note that once these reactions are occurring in the absence of the required light wavelength, it will be called dark (or thermal) Fenton processes. Ding *et al.* (2019) used heterogeneous dark Fenton reaction for ciprofloxacin degradation by means of g-C_3N_4-iron oxide composite. The BET surface area of iron oxide was 14.53 m^2/g, but after modification it changed to 54.04 m^2/g which could provide greater mass transfer between active sites and antibiotic molecules. At optimum pH of 3 and in presence of 1 g/L composite, 20 ppm ciprofloxacin, and 0.0056 M H_2O_2, maximum ciprofloxacin degradation and mineralization

after 45 min reaction was 100 and 48.5%, respectively [109]. Bobu *et al.*, [110] reported 74 and 37.9% degradation and mineralization of 0.15 mM Ciprofloxacin via homogenous Fenton, respectively. Complete degradation of amoxicillin, ampicillin, and cloxacillin at pH 3 has been reported in the literature [111]. In another investigation, 1,000 ppm amoxicillin exhibited 80% removal efficiency after 70 min reaction [112]. It could be stated that parameters like initial antibiotic concentration, pH value, reaction time, reagent concentration, etc. are imperative elements directly affecting final efficiency of the removal process.

It is noteworthy to mention that Fenton process have been developed by many researchers with the aim of resolving its intrinsic drawbacks such as large volume of Fe-sludge generation, difficulties associated with H_2O_2 storage and transportation, acidification of the wastewater before treatment, neutralization of the treated wastewater, etc. [102,113]. Also, depending on the type of organic matter and in-situ operational parameters, in Fenton process mineralization efficiency can be between 40 and 60% [114]. Therefore, Fenton process experienced an extension with the hope of higher efficiency.

The Photo-Fenton oxidation is referred to common Fenton reagents in which photons/lights are introduced to the system (Equations (1.11–1.12)). This use of irradiation could enhance •OH generation and H_2O_2 photolysis [115].

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + \cdot OH + OH^- \quad (1.11)$$

$$Fe^{+3} + H_2O + hv \rightarrow Fe^{+2} + \cdot OH + H^+ \quad (1.12)$$

Verma and Haritash [116] investigated the removal of amoxicillin (Figure 1.9) via different Fenton processes. It was found that by increasing $FeSO_4$ and H_2O_2 concentration to some extent, the degradation efficiency leveled up; however, excessive H_2O_2 concentration resulted in •OH radicals scavenging and $HO_2^{\bullet}$ generation (Eq. 1.13) [117]. Under optimum conditions (10 ppm amoxicillin, 375 mg/L H_2O_2, pH = 3, and 30 ppm Fe^{+2}), complete degradation of antibiotic was attained within 12.0 ± 2 min. In case of utilization of natural light, artificial light, and ultrasonicator the Fenton process might be named solar-Fenton, photo-Fenton, and sono-Fenton, respectively.

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (1.13)$$

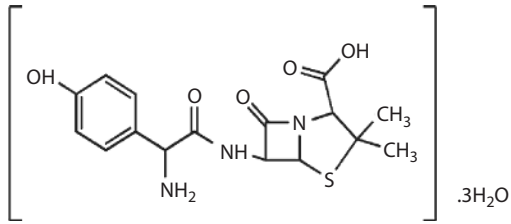

Figure 1.9 The structure of amoxicillin.

A common configuration of photo-Fenton and sono-photo-Fenton is illustrated in Figure 1.10. Figure 1.11 exhibits the degradation efficiency of amoxicillin in different Fenton processes [116]. Accordingly, it seems that photo-Fenton reached the fastest degradation of the antibiotic in 3.5 min; however, sono-Fenton was too time-consuming (20 min).

Ciprofloxacin ($C_{17}H_{18}FN_3O_3$) is known as the most widely prescribed fluoroquinolone antibiotic that is utilized for treatment of many bacterial infections. High concentration of this drug in discharges of hospitals and pharmaceutical factories, have necessitate researchers to investigate its elimination [118]. Recently, Giri and Golder [119] investigated the performance of photo-Fenton for ciprofloxacin removal and they found that under optimum condition of 1.25 mmol/L Fe^{+2}, 10 mmol/L H_2O_2, and pH = 3.5, the obtained removal and mineralization efficiency was equal to 93.1 and 47.3%, respectively. With the aim of higher removal efficiency, Hassani *et al.* [120] proposed heterogeneous Fenton process via magnetic particles. Magnetic particles have become as interesting research area since they are easily withdrawn from the solution after the treatment by means of an external magnetic field. So, no filtration or centrifugal is required which is beneficial in terms of treatment cost [60]. Based on the findings

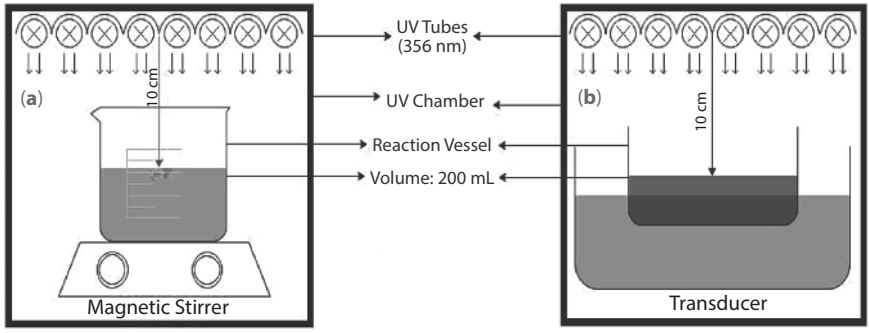

Figure 1.10 Schematic representation of (a) photo-Fenton, (b) sono-photo-Fenton. Reproduced with permission from Ref. [116].

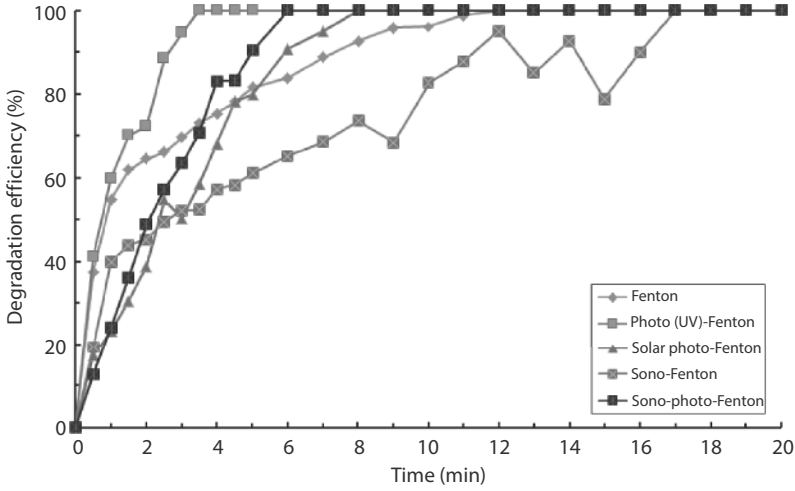

Figure 1.11 The degradation efficiency of amoxicillin via different Fenton type processes.

of Hassani *et al.* [120] it can be deduced that H_2O_2 solely was ineffective for ciprofloxacin removal. Considering Figure 1.12a, it is fair to say that ball-milled particles, whether in adsorption or oxidation, might provide higher effective surface area which contributes the interaction between the nano-sized magnetite particles and antibiotic molecules. Based on this, ball-milled Fe_3O_4/H_2O_2 demonstrated the highest ciprofloxacin removal (88.92%) among the others. Such a claim is well supported in other literatures [121,122]. Figure 1.12b shows the removal pathway of ciprofloxacin in magnetite catalyzed Fenton process.

Briefly, H_2O_2 is adsorbed on the surface of the composite, and then reacts with Fe^{+2}/Fe^{+3}, as the following equations (Equations (1.14–1.16)) [123]:

$$H_2O_2 + \text{composite} \rightarrow [H_2O_2]_{\text{adsorbed}} \tag{1.14}$$

$$Fe^{+2} + [H_2O_2]_{\text{adsorbed}} \rightarrow Fe^{+3} + \cdot OH + OH^- \tag{1.15}$$

$$Fe^{+3} + [H_2O_2]_{\text{adsorbed}} \rightarrow Fe^{+2} + \cdot OOH + H^+ \tag{1.16}$$

After the generation of the oxidant agents, ciprofloxacin is adsorbed by the composite and then degraded to simpler compounds and inorganic ions (Equations (1.17–1.18)) [123]:

$$\text{Ciprofloxacin} + \text{composite} \rightarrow [\text{Ciprofloxacin}]_{\text{adsorbed}} \tag{1.17}$$

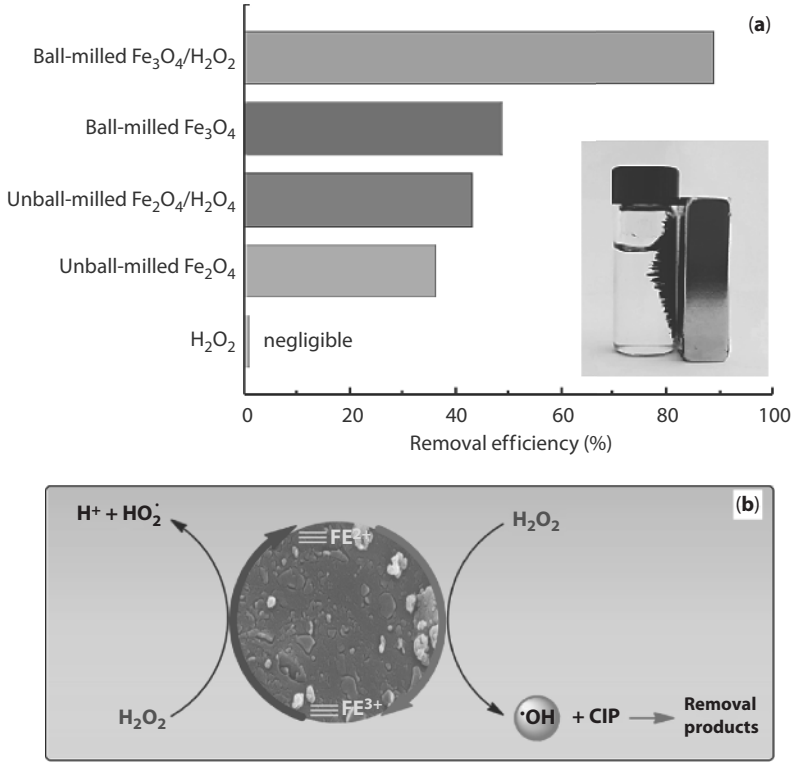

Figure 1.12 (a) Removal efficiencies of ciprofloxacin via magnetic processes (b) removal mechanism of ciprofloxacin through heterogeneous Fenton process. Reproduced with permission from Ref. [120].

$$[\text{Ciprofloxacin}]_{\text{adsorbed}} + \cdot\text{OH} \rightarrow \text{by} - \text{products} \qquad (1.18)$$

The generated by-products are frequently of great matter in which their fate and removal must be studied as well. Logically, high degradation could not guarantee an acceptable degree of mineralization [124]. In fact, during degradation some other compounds may be produced that could be sometimes more harmful and dangerous than the initial pollutant. These compounds are called secondary-pollutants [125]. Kordestani *et al.* [126], employed UV/Fe^{+2}/H_2O_2 system for elimination of 20 ± 1 mg/L meropenem and 20 ± 1 mg/L ceftriaxone antibiotics from pharmaceutical wastewater and reported 99 and 96.2% elimination after 60 min of the irradiation, respectively; however, total organic carbon abatement was 46.2 and 43.6%, respectively. In another investigation, Fenton process was optimized by Taguchi method for degradation of 500 mg/L amoxicillin removal. In

this study, dissolved organic carbons (DOC) was measured as a criterion for mineralization of amoxicillin. The results demonstrated that at the optimal conditions ($C_{amoxicillin}$ = 500 mg/L, $C_{Fe(II)}$ = 5.0 mg/L, C_{H2O2} = 500 mg/L, pH = 3, C_{DOC} = 193.125 mg/L and the reaction time of 15 min) 99.3% of amoxicillin was removed, but the mineralization rate reached to 36.3% [127]. In view of sulfathiazole degradation (47 μmol/L), it was mineralized approximately about 30 and 75% in the Fenton and photo-Fenton reaction and acetic, maleic, succinic and oxamic acids were identified as the main intermediates [128]. These results actually proved the fact that intermediates and/or secondary pollutants are generally produced that require further treatment techniques by considering their toxicity. Despite the fact that degradation processes of antibiotics can produce possible dangerous compounds, advanced oxidation such as Fenton type processes could enhance the biodegradability of the recalcitrant wastewater (such as antibiotics containing pharmaceutical wastewaters) being amendable to biological treatment [113, 114]. Guo *et al.* [112] confirmed that the Fenton pretreatment process excelled the removal capacity of the subsequent activated sludge.

1.2.4.2 Peroxone

Peroxone (a combination of ozone and hydrogen peroxide), is one of the greatest ozone-based advanced oxidation methods that have been extensively utilized for wastewater remediation [131–133]. Figure 1.13 illustrates a simple schematic of a reactor utilized for pharmaceutical degradation by

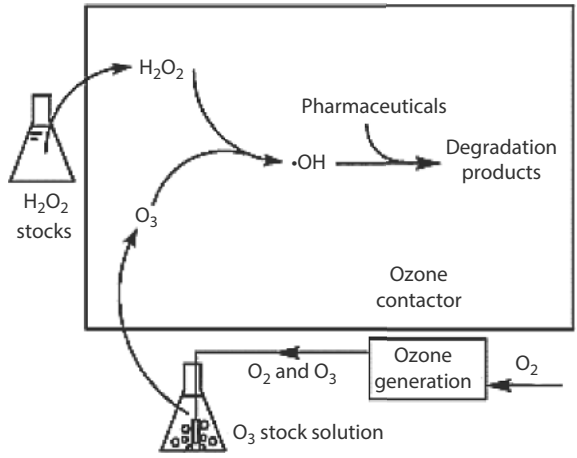

Figure 1.13 Schematic of O_3/H_2O_2 batch system. Reproduced with permission from Ref. [136].

Peroxone system and the reaction is shown in Equation (1.19). Since at acidic conditions, the rate of Peroxone system is slow, it is generally suggested to be conducted at high pH values because O_3 activation is rapid by deprotonated form of H_2O_2 (HO_4^-) (Equation (1.20)) [134,135]:

$$H_2O_2 + O_3 \rightarrow 3O_2 + 2\dot{}_{\square}OH \tag{1.19}$$

$$HO_2^- + O_3 \rightarrow O_2 + \dot{}_{\square}OH + \dot{}_{\square}O_2^- \tag{1.20}$$

Peroxone and ozonation are similar processes with the different in hydrogen peroxide presence, which acts like a key parameter in Peroxone process. The main differences between H_2O_2/O_3 and O_3 processes are listed in Table 1.4. Briefly, ozone decomposition is quicker in Peroxone; however, there is ozone residual in ozonation. In other words, a larger number of very reactive •OH radicals are generated in Peroxone which induces it as a fruitful and cost-effective process [137]. Low water solubility of ozone along with its high cost of generation has obliged the Peroxone process being able to use much ozone at maximum level during oxidation process in compared to ozonation alone [138]. Furthermore, ozonation is more effective in oxidization of iron and manganese, and H_2O_2/O_3 is more reactive for DOC removal [139].

De Witte *et al.* [140] studied the antibiotic ciprofloxacin removal by ozone-based oxidation methods. They investigated the influential parameters including inlet ozone concentration, temperature, pH, and H_2O_2 concentration. It was observed that high ozone concentration led more antibiotic degradation which can be attributed to generation of higher amount of reactive species. By adding 2, 10 and 50 μmol/L hydrogen peroxide, the efficiency of the process enhanced by 9.5–13.5% compared to ozonation alone [140]. Excess H_2O_2 concentration acts as radical scavengers, resulting in performance abatement as claimed by Gomes *et al.* [141]. Many researchers have reported that addition of hydrogen peroxide during ozonation could excel pharmaceuticals degradation [142–144]. In another interesting study conducted by Martini *et al.* [145], it was reported that H_2O_2 alone was ineffective in removal of sulfamethoxazole which was already expected. In terms of ozonation and Peroxone, they both exhibited the equal sulfamethoxazole removal after 15 min of the reaction [145]. It is fair to suggest that O_3 molecules were the main responsible for sulfamethoxazole elimination [146]. More importantly, sulfamethoxazole mineralization was achieved with higher degree in Peroxone in comparison to single ozonation which is thank to non-selective nature of the hydroxyl radicals [143].

Table 1.4 Comparison between ozone and Peroxone.

Process	Ozone	Peroxone
Ozone decomposition rate	"Normal" decomposition producing hydroxyl radical as an intermediate product	Accelerated ozone decomposition increases the hydroxyl radical concentration above that of ozone alone
Ozone residual	5–10 min	Very short lived due to rapid reaction
Oxidation path	Usually direct aqueous molecular ozone oxidation	Primarily hydroxyl radical oxidation
Ability to oxidize iron and manganese	Excellent	Less effective
Ability to oxidize taste and odor compounds	Variable	Good, hydroxyl radical more reactive than ozone
Ability to oxidize chlorinated organics	Poor	Good, hydroxyl radical more reactive than ozone
Disinfection ability	Excellent	Good, but systems can only receive CT credit if they have a measurable ozone residual
Ability to detect residual for disinfection monitoring	Good	Poor. Cannot calculate CT value for disinfection credit

Recently, application of conventional Peroxone technique has been limited because of H_2O_2 cost, storage, transportation, and handling problems. To overcome these obstacles, electro-Peroxone (E-Peroxone) was developed with the aim of in-situ H_2O_2 generation which requires a DC power, ozone generator, and cathode/anode (Figure 1.14). H_2O_2 is produced via oxygen reduction at the cathode (Equation (1.21)), and like Peroxone the other reactions keep going to generate radical species [147]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1.21}$$

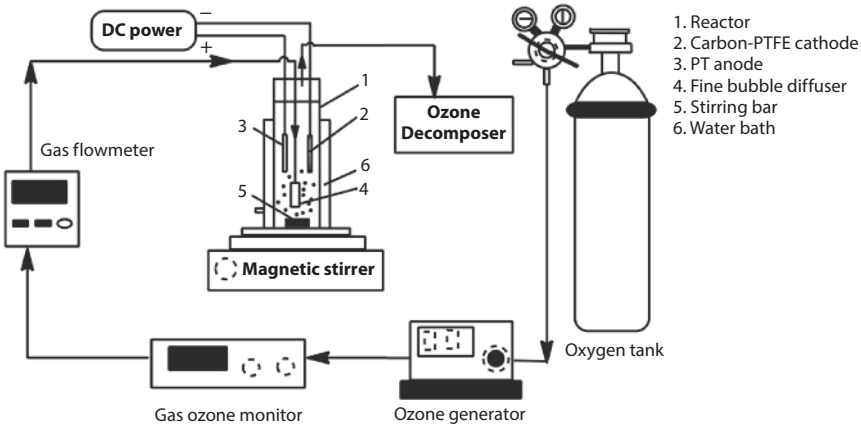

Figure 1.14 Schematic of the reactor used for electrolysis, ozonation, and E-Peroxone [148].

1.2.4.3 Photocatalytic Degradation

Photocatalytic degradation is one of the AOPs for collapsing organic matters in water or air with means of light as the source of energy and photocatalysts as absorbents of photons of the light to initiate the required reactions. Like any other oxidation methods, oxidative photocatalysis also result in generation of highly reactive species. During illumination, the electrons of the catalyst's valence band are excited by the energy of the light and then go forward to the conduction band. After this occurrence which is called semiconductor's photoexcitation state, negative-electron and positive-hole zones are created at conduction band and valence band, respectively [149]. It is the creation of the electron-hole pairs that initiates the photocatalytic degradation process. This phenomenon can only take place when the light energy is either equivalent to or greater than their respective band gap energy [150]. Band gap is defined as the energy difference between conduction band and valence band. The holes (h^+) react with water molecules and hydroxyl ions to generate radical species. On the other hand, electrons may react with oxygen to produced radical species. Equations (1.22–1.27) are the reactions that may happen in a photocatalytic reactor [151]:

$$\text{Semiconductor} + h\nu \rightarrow e^- + h^+ \tag{1.22}$$

$$h^+ + H_2O \rightarrow H^+ + \cdot OH \tag{1.23}$$

$$h^+ + OH^- \rightarrow \cdot OH \tag{1.24}$$

$$e^- + O_2 \rightarrow O_2^- \tag{1.25}$$

$$O_2^- + H_2O + H^+ \rightarrow H_2O_2 + OH^- \tag{1.26}$$

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \tag{1.27}$$

Heterogeneous semiconductors are currently investigated due to their ability to degrade a wide range of organic matters including ZnO, ZnS, Fe_2O_3, CdS, GaP, TiO_2, and BiOX. Solar and UV irradiation may be used as the energy sources. Based on the wavelength, UV lamps are divided into three different groups: UV-A (315–400 nm), UV-B (280–315 nm), and UV-C (100–280 nm).

TiO_2 is by far the most utilized catalyst in water and wastewater technology and is considered as a suitable semiconductor in photocatalytic investigations. Photocatalytic ability of TiO_2 was firstly discovered by Fujishima and Honda in 1972, and since then it attracted attention of researchers. Relatively inexpensiveness, non-toxicity, high photo/chemical stability, strong oxidizing power, and redox selectability are some of unique properties of TiO_2. Besides these advantages, TiO_2 suffers from shortcomings such as large band gap and agglomeration in aqueous solutions. Considering all these, TiO_2 has been extensively employed for degradation of antibiotic solely or along with other materials.

Beheshti *et al.* [152] used TiO_2 and WO_3 nanoparticles for photocatalytic degradation of sulfamethoxazole under various operational parameters. Figures 1.15(a,b) show the SEM images of the semiconductors. They found that by increasing the catalyst dosage, the removal efficiency of antibiotic increased which can be attributed to generation of more radical species. The optimum catalyst dosage for TiO_2 and WO_3 was 500 and 1,000 mg/L, respectively. Also, 25 mg/L sulfamethoxazole was the concentration in which photocatalytic process exhibited the best performance. Figures 15(c,d) show the removal efficiency and remained total organic carbon during sulfamethoxazole degradation. Evidently, it can be seen that halogen/WO_3 could degrade sulfamethoxazole completely during the first 80 min of the reaction, and then UVC/TiO_2 at 90 min. In fact, the influence of irradiation type is observed in this experiment. Furthermore, sulfamethoxazole was totally removed; however, the final concentration of TOC did not reach zero, indicating that photocatalytic degradation process might produce secondary-contaminants during treatment process [152]. Similar observations were reported by Ghenaatgar *et al.* [7] regarding

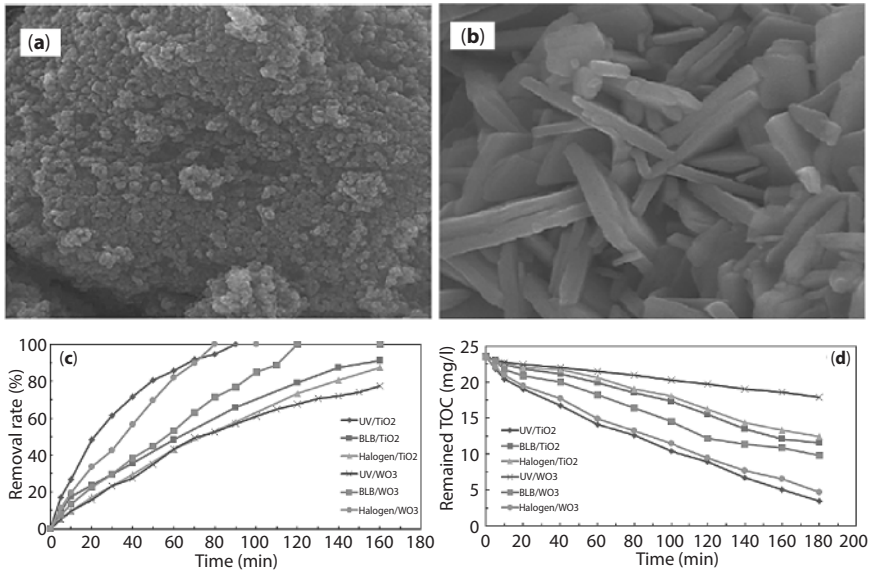

Figure 1.15 SEM images of (a) TiO_2 (b) WO_3, the effect of irradiation on removal rate of sulfamethoxazole (d) Remained TOC concentration at different time. Reprinted and reproduced with permission from Ref. [152].

dexamethasone photodegradation. The authors proposed Figure 1.16 as the degradation pathway [7].

To overcome the main shortcomings of titanium dioxide, some researchers have attempted to synthesize TiO_2-based composites. Hematite is an appropriate photocatalyst because of the narrow energy gap, non-toxicity, availability, and inexpensiveness. Karimi and Habibi (2019) prepared

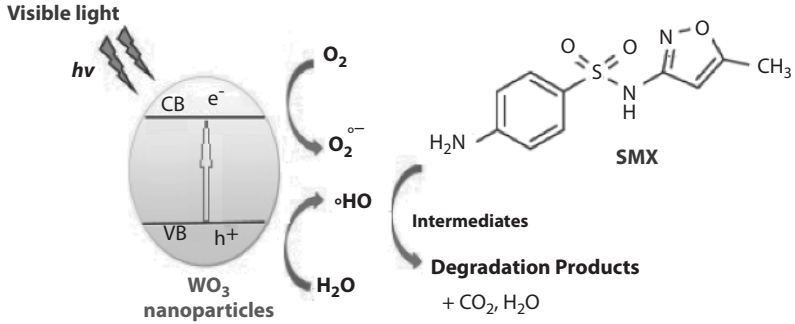

Figure 1.16 Proposed mechanism of sulfamethoxazole degradation. Reprinted and reproduced with permission from Ref. [152].

Fe_2TiO_5 nano-heterostructure via simple surfactant-assisted sol–gel method using CTAB. High surface area, more uniform distribution of the nanoparticles, lower mean size, and assembly of the two metal centers in a structure of Fe_2TiO_5 (100%) resulted in higher degree of metronidazole (12 mg/L) mineralization than TiO_2 (92.1%) and Fe_2O_3 (83.9%) after 120 min reaction time. Accordingly, Fe_2TiO_5 (2.94×10^{-2} 1/min) exhibited a higher rate constant than TiO_2 (2.24×10^{-2} 1/min) and Fe_2O_3 (1.64×10^{-2} 1/min). CO_2, H_2O, and NO_3^- were the final end product of mineralization [153]. In case of $BiVO_4/TiO_2$/RGO, after 120 min the removal efficiency of 96.2%, 97.5%, 98.7% and 99.6% was reported for 10 μg/mL tetracycline, chlortetracycline, oxytetracycline and doxycycline [154]. Wang *et al.* [155] proved that the flower-like $BiOCl/TiO_2$ heterojunction catalyst was able to degrade tetracycline hydrochloride and ofloxacin about 90 and 70% during 10 min of irradiation, respectively.

1.2.5 Electrocoagulation

Electrocoagulation is known as an advanced treatment method for water purification and wastewater treatment, and over the past years it has been employed for the removal of dyes [156], heavy metals [157], arsenic [158], organic matter [159], pharmaceuticals [160], pathogens [161], fluoride [162], and etc. Electrocoagulation technology is an electro-chemical process in which coagulants are generating via sacrificial metallic electrodes with the aim of pollutant destabilization and floc formation. In this method no chemical reagents are used and sludge production and sludge handling costs are lower in comparison to chemical coagulation [163]. The type of electrode plays an integral role during the process. Iron and aluminum are of the best alternatives that have been extensively used because of their availability, inexpensiveness, non-toxicity, and good performance. The clear schematic representation of the electrocoagulation process mechanism is represented in Figure 1.17. Accordingly, by the introduction of current, anode is oxidized and di or trivalent metallic ions are released which are capable of reacting with pollutant molecules. Finally, these flocs might aggregate to become heavier and so precipitate as the sludge [164]. Reaction time, current density, electrode material, and initial pH play crucial role in degradation efficiency.

Electrocoagulation has been utilized for antibiotic removal in several studies. Yoosefian *et al.* [165] tried to remove ciprofloxacin antibiotic from hospital wastewater by electrocoagulation. They found that by increasing ciprofloxacin concentration from 57.65 to 112.3 mg/L, the removal efficiency decreased from 87.8 to 74.1%, respectively. Also, the performance

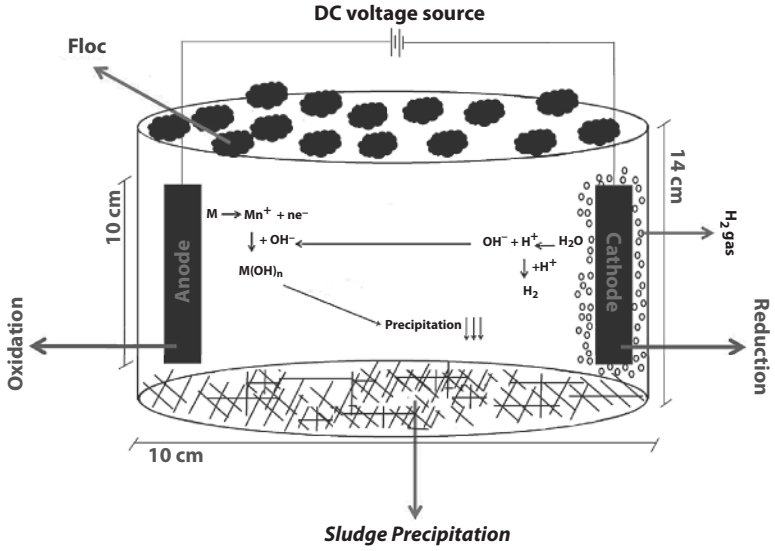

Figure 1.17 Mechanisms of electrocoagulation process. Modified from Ref. [164] with permission.

of the treatment system was limited at low pH values because of the soluble nature of iron hydroxides under acidic conditions. It was observed that by enhancing the current density from 9.35 to 15.65 mA/cm^2, the removal efficiency of ciprofloxacin exhibited an increasing tendency which was attributed to greater generation of Fe^{+3} ions in high currents. Under optimum conditions of ciprofloxacin concentration (60 mg/L), pH 7.5, current density of 15 mA/cm^2, and 1.5 cm inter-electrode distance, after 20 min more than 99% of ciprofloxacin was removed which is a declaration of electrocoagulation effectiveness [165]. In another investigation, approximately 99% of tetracycline (C_{in} = 50 mg/L) was eliminated in optimal conditions (T = 20 ± 1 °C, pH = 4–10) and the removal path was well-fitted with Sips and Pseudo-second order assumptions [166]. Nariyan *et al.* [167] studied the effect of electrode material (0.5 cm distance between electrodes) for treatment of 50 mg/L oxytetracycline hydrochloride with electrocoagulation. They reported that at current density equal to 20 mA/cm^2, iron anode (93.17%) showed better applicability than aluminum anode (87.68%) [167]. In the case of cephalexin antibiotic, at optimum condition including pH = 6, C_{in} equal to 5 mg/L, and electric current intensity of 0.7 A, after 60 min reaction the removal efficiency of 90.1% is reported [168].

Coupling treatment processes have also been an interesting alternative for waters purification. Ahmadzadeh *et al.* [169] proposed a coupling

treatment system of electrocoagulation and adsorption for removal of cefazolin (CFZ) antibiotic from hospital wastewaters. Chitosan was used as the adsorbent because it is biocompatible, biodegradable and non-toxic that owns functional groups favoring the adsorption of pollutants. Under optimal operating condition (15.5 mA cm^{-2} current density, pH~7.8, C_{CFZ} = 60 mg/L, $C_{chitosan}$ = 0.7 g/L, and inter-electrode distance equal to 1 cm), cefazolin was completely removed from the media within 23 min. Results proved that the process has obeyed second-order model and Langmuir. Charge neutralization and sweep flocculation were introduced as the determining mechanism of removal [169].

For some antibiotics, electrocoagulation might not be a suitable choice. Baran *et al.* [170] focused on the elimination of veterinary antibiotics by electrocoagulation. Doxycycline was effectively removed from the solution (~100%); however, in case of ampicillin, sulfathiazole, and tylosin it efficiency was 3.6 ± 3.2%, 3.3 ± 0.4% and 3.1 ± 0.3%, respectively.

In conclusion, electrocoagulation might be introduced as one of the greatest green water and wastewater treatment systems owning its unique advantages. The efficiency of the process relies on some factors. Considering antibiotics, experiment findings would be fluctuated based on the types of the drug and for actual wastewater treatment laboratory tests are unavoidable.

1.3 Conclusion

Antibiotics are known as one of the most hazardous compounds in the environment specially water media, posing serious health problems for animals and humans. Antibiotic elimination has been highlighted by numerous studies during the last decade, and different physical, biological, and chemical technologies have been proposed. In comparison, the physical method such as adsorption could result in high removal efficiency; however, the generated spent-adsorbents require further management and control. Aerobic/anaerobic biological processes might be candidate as the most-utilized techniques for wastewater treatment. The type of the system and in-situ operational parameters directly affect the applicability of biological reactions. Under appropriate operation, biological process could result in acceptable results. Since microorganisms are working in biological treatment, fluctuation in results must be expected, and could be mentioned as one of the disadvantages. Oxidation processes were effective to degrade antibiotic molecules, and frequently have high removal efficiency. But, in some cases secondary pollutants may be generated, requiring

further considerations. Thus, to design an efficient treatment system every aspect of the situation such as treatment cost, environmental conditions, influent characteristics, required removal efficiencies, and so many other parameters must be intended. All methods have their own strengths and weaknesses. These all must be figured out to introduce an efficient system of treatment for antibiotic removal.

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