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Chapter

An Overview of Carbon-Based Materials for the Removal of Pharmaceutical Active Compounds

Mazen K. Nazal

Abstract

Carbon-based materials, namely activated carbon, carbon nanotube and graphene, are considered as one of the most effective adsorbents for pollutant removal and wastewater treatment. Due to their high surface area and distinct chemical and physical properties of the carbon-based materials, particularly activated carbon and carbon nanotube are rapidly emerging as one of the most effective adsorbents for wastewater treatment. Various studies have reported the applications of activated carbon, carbon nanotubes and graphene as promising adsorbents for removing organic and inorganic pollutants. In this chapter, an introduction about the activated carbon, carbon nanotubes and graphene and their production, prosperities and usage for the removal of pharmaceutical active materials from aqueous media are highlighted and summarized. Challenges and future opportunities for application of these carbon-based materials as adsorbents in wastewater treatment are also addressed in this chapter.

Keywords: adsorption, aquatic environment, pollutants, activated carbon, carbon nanotube

1. Introduction

In recent years, there is great concern about the occurrence and the impact of the pharmaceutical active compounds in water, in addition, development of efficient and cost-effective technologies for the removal of these compounds and treatment of industrial effluent, surface water and ground water. Pharmaceutical active compounds are natural or synthetic chemicals that can be found in over-the-counter therapeutic drugs and veterinary drugs. They induce pharmacological effect and give significant benefits to human beings. A continuous release of these chemical compounds into aquatic environment has been increased due to the increase of general use of pharmaceutical compounds in human and veterinary medicines. **Figure 1** illustrates the routes of releasing the pharmaceutical compounds into water. These routes include wastewater effluents, human and animal excreta, sewage sludge, medical and industrial waste and land fill leaching [1].

Depending on the biodegradability and hydrophobicity of these pharmaceutical active compounds, they are naturally reduced by dilution, degradation and

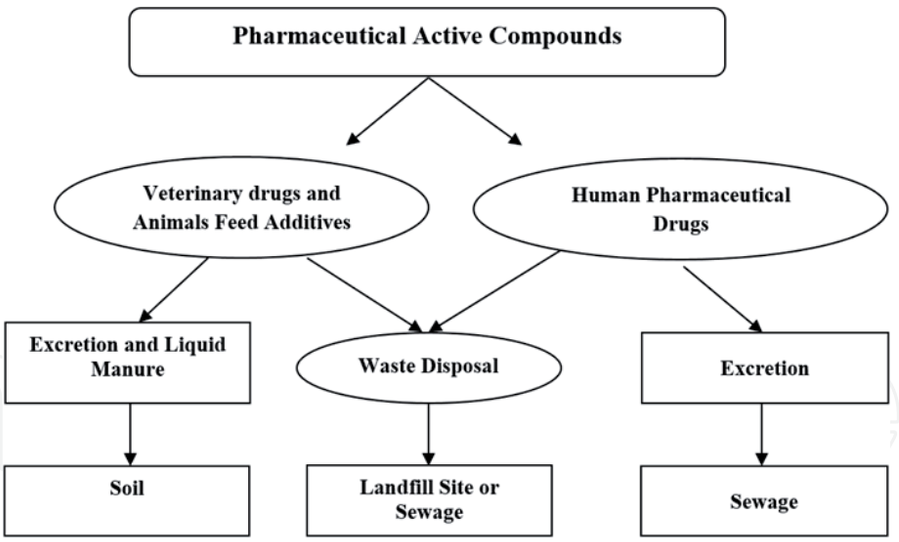

Figure 1.
Routes of releasing the pharmaceutical compounds into the environment.

Pharmaceutical active compounds	Maximum detected concentration (ng/L)	Aquatic environment type
Bleomycin	19 (United Kingdom)	Sewage
Clotrimazole	34 (United Kingdom)	Stream or river water
Diclofenac	1200 (Germany) 41 (France) 40 (Finland) 64 (Austria)	Surface water
Carbamazepine	110 (Germany) 800 (France) 370 (Finland) 64 (Austria)	Surface water
Iopromide	910 (Germany) 17 (France) 211 (Austria)	Surface water
Roxithromycin	560 (Germany) 37 (France)	Surface water
Ibuprofen	530 (Germany) 120 (France) 65 (Finland)	Surface water
Erythromycin	80 (United Kingdom)	River water
Fluoxetine	290 (United Kingdom)	Sewage
Mefenamic acid	1440 (United Kingdom)	Sewage
Paracetamol	< 20 (United Kingdom)	Sewage
Propranolol	215 (United Kingdom)	River water
Tamoxifen	42 (United Kingdom)	Sewage
Tetracycline	1000 (United Kingdom)	River water
Trimethoprim	1288 (United Kingdom)	Sewage

Table 1.
The measured concentration of some pharmaceutical active compounds in some of the aquatic environment in European countries.

adsorption in the environment. Thus, these compounds in water exist in a trace concentration level [2].

Some of the pharmaceutical active compounds used for birth control, heart medication and painkilling were detected in wastewater in the United State of America (USA) since more than 40 years ago [3–5]. Literature shows that the pharmaceutical active compounds enter the surface water through different sources such as excretion, bathing, effluent discharging, improper disposal of these compounds and veterinary facilities [1, 6–8]. In addition, a study conducted in the United Kingdom by Drinking Water Inspectorate reported that many classes of pharmaceutical active compounds are present in wastewater influent [9]. **Table 1** represents several pharmaceutical active compounds that were detected in the aquatic environment of United Kingdom (UK) and other European countries [10, 11].

There is no international standard method for drinking water sampling and method of analysis for pharmaceutical active compounds. In addition, a few systematic monitoring studies on measuring the pharmaceutical active compounds in surface water, drinking water and ground water were conducted. Therefore, limited data are available on their occurrence in these aquatic environments to be used in assessing the potential health risk due to the exposure to a trace concentration level of pharmaceutical compounds. However, literature showed that the surface water and ground water sources affected by wastewater discharges have pharmaceutical active compound concentrations less than 100 ng/L, while these compounds were found in the drinking water with a concentration less than 50 ng/L [2].

2. Treatment technologies for pharmaceutical compounds' removal from water

The presence of these compounds at trace concentration levels (nanogram to sub microgram per liter) in the aquatic environment has raised a question concerning the efficiency of wastewater treatment techniques in removing of the pharmaceutical active compounds. Many removal techniques such as chlorination, photocatalysis, adsorption, biodegradation and advanced oxidation or ozonation have been investigated for the removal of pharmaceutical active compounds from the aquatic environment [12–25]. Some of these techniques have different disadvantages such as their high cost, high energy consumption and formation of toxic by-products. Adsorption technique has many advantages over these techniques such as it works at mild operation conditions, requires low energy and is efficient and cost-effective. Therefore, it is a promising technique for the removal of pharmaceutical active compounds.

2.1 Adsorption technique

The removal of pharmaceutical active compounds from water by adsorption is considered as one of the easiest and safest techniques since it is easy to design and operate and this technique does not produce any toxic wastes as a by-product and is capable of removing most forms of organic material. The adsorption process includes the accumulation of pharmaceutical compounds on the adsorbent's surface. Hence, the selection of adsorbent must be precious. The adsorbent must have a capability to accumulate the pollutant from water with high surface area and high hydrophobicity. The efficiency of this technique is mainly depending on the functional group composition, surface area, pore size and the ash content. It also depends on the chemical parameters like temperature, polarity, pH, concentration

of the adsorbate and the availability of other competing solutes. The adsorption process also depends on the mobility of the adsorbate molecules toward the external boundary layer of the adsorbent, active surface sites and surface pore size.

Pharmaceutical active compound	Carbon-based adsorbent	Adsorption capacity (mg/g)	Reference
Clofibric acid	Mesoporous silica SBA-15	70	[70]
Ofloxacin	Nonporous SiO_2	2.1	[71]
Tetracycline	Mesoporous silica	44.4	[27]
Cephalexin	Amberlite XAD-16 polymer	116	[36]
Nalidixic acid	Polystyrene-divinylbenzene, X16	800	[31]
Penicillin	Polymer Amberlite XAD-16	1401	[34]
Amoxicillin	Bentonite clay	53.9	[38]
Flurbiprofen	Organophilic montmorillonite clay	240	[39]
Tetracycline	Na-kaolinite	29	[40]
	Kaolinite	3.8	[72]
	Rectorite clay	40	[46]
Tetracycline	NaOH-activated carbon produced from macadamia nut shells	455.33	[48]
	H_3PO_4-activated carbon produced from apricot nut shells	308.3	[49]
	Activated carbons produced by KOH activation of tyre pyrolysis char	312	[50]
	Commercial activated carbon	471	[51]
Sulfamethoxazole	AC	185	[53]
Metronidazole	AC	93.21	[53]
	CAC	328	[52]
Amoxicillin	AC	221.8	[73]
Dimetridazole	CAC	186	[52]
Ronidazole	CAC	394	[52]
Tinidazole	CAC	385	[52]
Penicillin G	AC	315	[56]
Oxytetracycline	MWNT10	190.2	[54]
Tetracycline	MWNTs	148	[58]
	SWNTs	370	
Tylosin	K-MWNTs	270	[58]
	K-SWNTs	466	
Carbamazepine	MWNT100	41.4	[58]
Cephalexin	Cellulose oxide	79	[59]
Fluoroquinolone	Goethite	49.6	[61]
Ciprofloxacin	Hydrous oxides of Al (HAO)	13.6	[64]

Table 2.
Different adsorbents and their adsorption capacities for removal of pharmaceutical active compounds.

Many researchers have studied the adsorption of pharmaceutical active compounds from wastewater using different types of adsorbents. Several materials as an adsorbent have been reported in the literature and listed in **Table 2** and were tested and investigated for the pharmaceutical active compounds' removal from aquatic environment, such as silica-based adsorbents [26–30], polymeric materials [31–37], clay [38–47], carbonaceous materials [48–58] and other materials [59–71]. The next sections focus on carbonaceous materials as adsorbents, namely activated carbon and carbon nanotubes.

2.1.1 Activated carbon

Activated carbon is a pure carbon graphite form with amorphous and highly porous structure. It contains different range of pore sizes starting from cracks to slits of molecular dimensions [73]. The first produced commercially activated carbon was in early nineteenth century from wood as a raw material. It has been used for water odor and taste control in 1930 [74]. Nowadays, activated carbon is produced from a wide range of raw organic materials and sources, such as sugar, shells, refinery coke, rice hulls and different types of wood. The main features of activated carbon that make it good as an adsorbent in the adsorption process are the following: (i) its high surface area, (ii) its porosity and (iii) its surface reactivity.

2.1.1.1 Classifications of activated carbons

Activated carbon can be classified based on its activation process or its properties. Based on the activation process, the following are the main two categories based on the activation process:

- Physically or thermally activated carbon: the activation process involves carbonization of organic raw materials at temperature ranging from 500°C to 600°C [75].

- Chemically activated carbon: the activation process involves addition of some inorganic salts such as metallic chloride to activate the surface of carbon [76].

Mattson et al. [77] suggested another classification, which categorizes activated carbon to acidic or basic activated carbon:

- Carbon activated at low temperature range from 200°C to 400°C: this develops an acidic surface that lowers the pH value of the solution. This activated carbon exhibits negative zeta potential and usually adsorbs basic and hydrophilic compounds.

- Carbon activated at a high temperature range from 800°C to 1000°C: this develops basic surface that increases the pH value of the solution. Therefore, this type of activated carbon has a positive zeta potential and is usually used for adsorbing acidic organic compounds.

Commercially, activated carbon can be classified as three main types [78], and they are the following:

- Powdered activated carbon (PAC): it has fine granules or powder with particle size less than 1.0 mm and average diameters ranging between 0.15 and 0.25 mm.

- Granular activated carbon (GAC): it combines powdered activated carbon with a binder and forms cylindrical shape activated carbon particles with diameters from 0.8 to 130 mm. The main application for this form is for gas purification.

- Impregnated activated carbon (IAC): it is impregnated with different inorganic ions.

- Polymeric coated activated carbon, which is used in medical field applications.

2.1.1.2 Physicochemical properties of activated carbon

The properties of activated carbon are influenced by the used raw materials and activation method in its preparation process. The porous graphite and graphene sheets that form the activated carbon are connected together and have π-orbitals in the benzene rings, which enable several modifications to be carried out on activated carbon. For example, cooling the activated carbon in the presence of oxygen can produce activated carbon rich with oxides and acidic functional groups, as a result, alter the positive zeta potential of basic activated carbon to negative to be used for different applications. In addition, the surface chemistry, pore structure (volume and diameter) and surface area of activated carbon depend significantly on the employed temperature in the preparation process [75, 79].

2.1.1.3 Activated carbon production

A wide range of raw materials can be used as a starting material for producing activated carbon as stated in Section 2.1.1. The following activation methods are used in activated carbon production:

- Thermal activation: this physical process may involve two main steps: the first one to eliminate the volatile matters in the raw materials by carbonizing them thermally at a temperature ranging from 500°C to 600°C and in the second step the porosity and surface are improved by the gasification process. In the gasification process, a carbon dioxide CO_2, methane or steam as an oxidizing gas is used at a high temperature of 800–1000°C [75].

- Chemical activation: in this process, inorganic salts such as metallic chloride are added before the carbonization step to improve the micro-porosity as well as the surface area of the activated carbon [76].

2.1.1.4 Activated carbon for removal of pharmaceutical active compounds

Activated carbon (AC) is widely used in adsorption processes as filtration and purification materials. For instance, in water treatment, activated carbon is used to control taste and odor and to adsorb undesired suspended metals and pollutants [74]. Due to the high surface area and commercial availability of AC, it was studied for removal of different pharmaceutical active compounds. **Table 3** summarizes some of these pharmaceuticals. For example, different types of activated carbon were used for removal of tetracycline (antibiotic drug) from aqueous media. Martins et al. [48] prepared activated carbon from macadamia shells as precursors, the yield was 19.79% and the prepared activated carbon's surface area was 1524 m^2/g. They used it for the tetracycline removal and it had 455.33 mg/g adsorption capacity. Muthanna et al. [80] reported that the activated

carbon was used for removal of three pharmaceutical active compounds (i.e., tetracycline, penicillins and quinolones) and the used activated carbon has 1340.8 mg/g adsorption capacity for tetracycline. Chen et al. [81] studied the effect of the adsorption parameters (i.e., pH, contact time, initial concentration and temperature) on the removal of tetracycline from aqueous solution using rice husk ash (RHA). They found the adsorption capacity increased from 1.51 to 3.41 mg/g when the initial tetracycline concentration in the solution increased from 5 to 20 mg/l. Another study showed that activated carbon prepared via a chemical activation of apricot shells using phosphoric acid heated in air at 100 °C for 24 hours has 307.6 m^2/g surface area and 308.3 mg/g adsorption capacity [49]. In 2016, an activated carbon (TPC-AC) was prepared from tires waste by their pyrolysis and then activated using potassium hydroxide [50]. The prepared adsorbent was tested for tetracycline removal and it has been found that the adsorption process was spontaneous and has adsorption capacity (312 mg/g) higher than the commercial activated carbon. Carl et al. [51] reported that the adsorption capacity of the commercial activated carbon for tetracycline is directly related to the density of π electrons in the graphene layers on activated carbon and the aromatic ring in the tetracycline.

2.1.2 Carbon nanotube

Single and multiwall carbon nanotube (CNT) materials are graphene sheets rolled-up tubular individually or more than one inside each other. CNTs were discovered by Sumio Ijima in 1991 at NEC Laboratory in Japan using the Arc discharge production method and then characterized using a transmission electron microscope [82]. CNTs have two different structures based on the rolling direction of graphene sheets: (i) armchair nanotube and (ii) zigzag nanotube structure [83] as shown in **Figure 2**.

The cylindrical shape of CNT nanostructure can have a length to diameter ration up to 132,000,000:1, which is significantly higher than any other materials [83]. This property was explained by the sp2 hybridization in the carbon atoms that CNTs are composed of in addition to the natural alignment of CNT into ropes attracted together by Van der Waals interaction [84].

2.1.2.1 Physical properties and chemical reactivity of carbon nanotubes

CNTs form bundles of a highly complex network [85]. They have electrical conductivity that depends on the arrangement of the hexagonal rings along the tubular surface. Due to their extraordinary properties, such as large geometric aspect ratio, nanocavities and electrical conductivity, CNTs are considered as attractive candidates in many nanotechnological applications, including the removal of pharmaceutical compounds in water treatment processes. One of the

Physical property	**Material name**				
	MWCNTs	**SWCNTs**	**Wood**	**Steel**	**Epoxy**
Density (g/cm^3)	2.6	2.6	0.6	7.8	1.25
Tensile strength (Gpa)	150	150	0.008	0.4	0.005
Young's modulus (Gpa)	1200	1054	0.6	208	3.5

Table 3.
Comparison between CNTs and other materials.

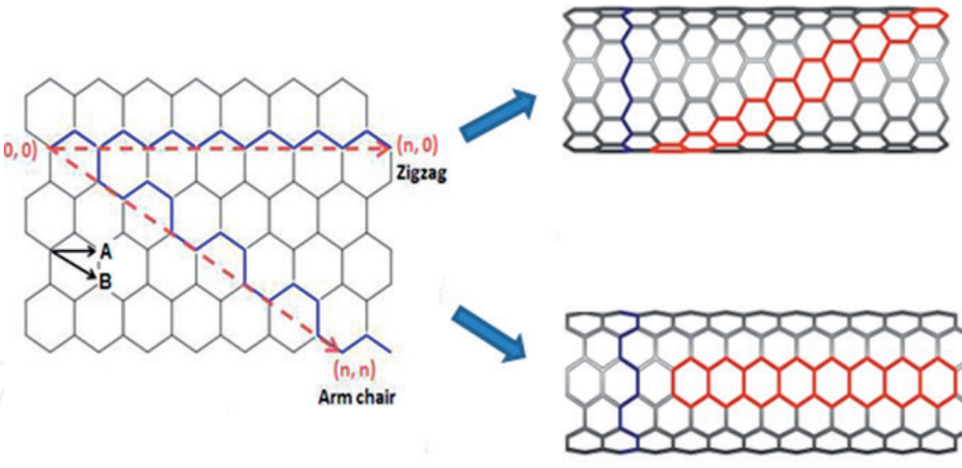

Figure 2.
Armchair and zigzag structural forms of CNTs

main drawbacks of carbon nanotubes is that they do not have good suspension properties in aqueous and organic solvents that in turn has made CNTs' use in industry limited [86]. This disadvantage can be overridden by modifying CNTs chemically with some hydrophilic functional groups that in turn increase CNTs' suspension in water.

The main distinct properties of the carbon nanotubes are categorized into the following:

- Mechanical properties: due to the covalent sp^2 bonds formed between the individual carbon atoms, CNTs have high strength and stiffness. According to the reported results, CNTs have elasticity higher than steel by 10–100 times with an elastic modulus 1Tpa [87]. A comparison between some materials, which have good mechanical properties, with CNTs is shown in **Table 3**.

- Thermal conductivity: CNTs have thermal conductivity ranging from 2800 up to 6000 W/m K [88].

- Electrical properties: CNT carbon-based material exhibits extraordinary electrical properties and it can be conducting or semiconducting material. The conductive CNTs are found to carry electrical current thousand times higher than copper material [89].

- Chemical reactivity: CNTs can chemically be modified to make them highly soluble in aqueous and organic solutions as well as more efficient for certain applications. Their reactivity is related to the mismatching of π-orbitals, which are caused by the curvatures in CNTs' structure. In general, smaller nanotube diameters result in increasing their reactivity. Moreover, the reported results showed that chemical modification of sidewalls or end caps of CNTs are also possible [90].

Based on the CNTs' properties that have been discussed above, CNT materials and their modified structures are promising for different applications such as water treatment, environmental protection and pharmaceutical active compound removal, material science, medicinal chemistry and others.

2.1.2.2 Carbon nanotube production

CNTs are produced using different techniques, and the most common and widely used techniques are:

- **Arc discharge technique.** Arc discharge technique is the most common and simplest technique for CNT production. As mentioned earlier, CNTs were firstly discovered using this technique. In arc discharge technique, CNTs are produced at low pressure of helium inert gas or any other neutral gas [91]. They are produced through arc vaporization of two separated carbon rods in an enclosed system filled with inert gas [92]. One of the major disadvantages of CNT production using this technique is that the produced CNTs are not pure containing some of the catalytic metals; therefore, they require purification to remove these metals and get clean CNTs.

- **Laser ablation technique**. In 1995, carbon nanotubes were synthesized using a laser beam to vaporize graphite at 1200°C [93]. The pulsed and continuous laser methods are the main two types of laser ablations. Much higher light intensity (100 kW/cm^2) is used in the pulsed laser, compared to 12 kW/cm^2 in case of the continuous laser type, which is the main difference between these two laser ablation technique types. In the laser ablation method, CNTs are produced and collected on a cooler surface in the reactor system as the vaporized carbon is condensed. In this technique, SWCNTs can be produced from graphite electrodes by adding metal-based catalysts such as Co, Fe and Ni to the system. However, MWCNTs are the main product when a pure graphite electrode is used [94].

- **Chemical vapor deposition (CVD) technique**. Chemical vapor deposition technique is a simple process and it is believed to be the easiest technique for industrial production of CNTs. In this method, the desired CNT type and quality can be produced by controlling the system production parameters such as temperature, type of catalyst and type of carbon source gases. CVD technique consists of two main steps (catalyst preparation step and then CNT synthesis). In general, to produce CNTs, methane and carbon monoxide gases are dissociated into reactive carbon atoms using an energy source, and then these reactive atoms diffuse over a substrate that is coated by transition metals as a catalyst and heated at a temperature range from 500 to 1000°C [95].
  A comparison between the previously discussed methods for CNT production is summarized in **Table 4**.

2.1.2.3 Carbon nanotubes for pharmaceutical active compounds' removal

Carbon nanotubes with their excellent properties show considerable adsorption capability for removal of pharmaceutical active compounds. A study in 2009 found that the single wall carbon nanotubes (SWNTs) are more efficient for removal of tetracycline from aqueous solutions than multiwall carbon nanotubes (MWNTs), graphite and activated carbon [58]. This finding was explained through the molecular sieving effect, whereas the tetracycline is bulky molecules failed to seep through inner pores, which indicates the important role of molecules' size and their accessibility into pores in the adsorbent materials. In 2016, Yu et al. [96] studied the adsorption performance of MWNTs for removal of ciprofloxacin and found the

Method	Yield (%)	SENT	MINT	Concerns
Chemical vapor deposition	20–100%	Long tubes with diameters 0.6–4 nm	Long tubes with diameters 10–240 nm	Nets are usually mints and often riddled with defects
Arc discharge	30–90%	Short tubes with diameters 0.6–1.4 nm	Short tubes with inner diameter 1–3 nm	Short tubes with random sizes and directions and required purification
Laser ablation (Vaporization)	Up to 70%	Long bundles of tubes with diameters 1–2 nm	Not suitable and too expensive	Costly and required high power

Table 4.
Comparison between the three methods in terms of CNT production efficiency, type of CNTs produced, and the current drawback of each technology.

maximum adsorption capacity is 20 mg/g, which was obtained at pH 4 and 240 min that was attributed by the π-π interaction rather than hydrogen bonding and interaction with oxygenated functional groups on MWNTs. Another study by Yu et al. [97] showed that the maximum adsorption capacity of MWNTs for tetracycline was 269.54 mg/g, which achieved at 25°C and pH 5 within 80 min.

In order to improve the performance and adsorption capacity of CNTs, different types of modifications can be performed such as graphitization, hydrolyzation, carboxylation and etching with potassium hydroxide (KOH). For example, Ji et al. [98, 99] modified the SWNTs and MWNTs by etching using KOH and tested the etched CNTs for three pharmaceutical active compounds (i.e., sulfamethoxazole, tetracycline and tylosin). They found the adsorption performance of the KOH modified SWNTs (K-SWNTs) and KOH modified MWNTs (K-MWNTs) for sulfamethoxazole and tetracycline was enhanced by around 56% and 84% compared to the unetched SWNTs and MWNTs, respectively. This has been explained by increasing the surface area of the etched CNTs.

2.1.3 Graphene

Graphene is a two-dimensional carbonaceous nanomaterial formed from a layer of sp2 hybridized carbon atoms. The graphene nanomaterial has exceptional properties such as high specific surface area [98, 99], high electrocatalytic activity [100], great thermal conductivity [101], high stiffness and strength [102] and high speed electron mobility [103]. These unique physical properties attracted great interest of scientist and introduced it for different potential applications. Among these applications is the adsorptive removal of emerging pollutants such as pharmaceutical active compounds.

2.1.3.1 Types of graphene

The following are the common types of graphene:

- Single layer graphene (SLG): it is one thick hexagonally arranged sp2 hybridized bonded carbon atoms. The dimensions of SLG vary from nano- to microscale. It can be suspended in an aqueous solution or adhered on a substrate.

- Multilayer graphene (MLG): it consists of few flaks of single layer graphene and it is useful in the preparation of nanomaterial composites.

- Graphene oxide: it is a single layer or multilayer graphene that has high oxygenated surface and prepared by exfoliation and chemical oxidation of graphite.

- Reduced graphene oxide: it is that same as graphene oxide; however, the oxygenated functional groups are reduced chemically, thermally or biologically.

2.1.3.2 Graphene for pharmaceutical active compounds' removal

The graphene nanomaterials and their modified forms have extraordinary surface area and catalytic activity, and as a result, they can be used in several applications such as adsorptive removal of pharmaceutical active compounds [104–111]. Gao et al. [106] investigated the adsorption performance of graphene oxide for tetracycline antibiotic from aqueous solution. They found that the adsorption of tetracycline achieved mainly through a π-π and cation-π interactions with a maximum monolayer adsorption capacity is 313 mg/g and it decreased with an increase in the solution pH or the sodium ions concentration. In 2017, Danna et al. [107] modified a graphene oxide with decafluorobiphenyl and then investigated the prepared adsorbent for removal of six pharmaceutical active compounds from water namely, carbamazepine, sulfamethoxazole, sulfadiazine, ibuprofen, paracetamol and phenacetin. They found that the adsorption capacities for these compounds are 340.5 μmol/g, 428.3 μmol/g, 214.7 μmol/g, 224.3 μmol/g, 350.6 μmol/g and 316.1 μmol/g, respectively. A study in 2014 showed that the adsorptive removal of acetaminophen, aspirin and caffeine from aqueous solution using graphene nanoplates (GNPs) was thermodynamically spontaneous and exothermic with adsorption capacities of 18.07 mg/g, 12.98 mg/g and 19.72 mg/g for acetaminophen, aspirin and caffeine, respectively [105].

The surface area of graphene reduces significantly in solutions due to its aggregation, and as a result, the adsorption capacity of graphene is reduced, which is one of the main disadvantages associated with using graphene as adsorbents. Functionalization or modification of the graphene with certain functional group or metals can be the best solution to overcome that disadvantage as well as increase the adsorption capacity of graphene. Lin et al. [108] functionalized a graphene oxide with magnetic nanoparticles and then studied its adsorptive removal for four tetracycline (TC) pharmaceutical active compounds (i.e., tetracycline, oxytetracycline, chlortetracycline and doxycycline) from aqueous solution. They found that the solution pH and ionic strength had insignificant effect on the TC adsorption and the maximum adsorption capacity is 39.1 mg/g.

3. Conclusions

Pharmaceutical active compounds are continuously released into aquatic environment via different routes (i.e., human and animal excreta, medical industry's waste, wastewater effluent, sewage and landfill leaching). That release increases due to the increase of general use of pharmaceutical compounds in human and veterinary medicines. Therefore, these compounds should be removed from the contaminated water to prevent their accumulation, reduce the environmental pollution and provide an additional source of clean water. Removal of pharmaceutical active compounds from aquatic media can be achieved by either conventional or advanced methods. Among them, the adsorption technique has many advantages over the others. Several materials as adsorbents have been reported and discussed in the literature such as silica-based adsorbents, polymeric materials, clay,

carbonaceous materials and other materials. Activated carbon, carbon nanotube and graphene oxide among carbonaceous materials show excellent performance and high adsorption capacity for pharmaceutical active compounds. As discussed in this chapter, the activated carbon can be activated using different methods (i.e., physical or chemical activation), while the carbon nanotube can be produced through using one of the following methods: (i) arc discharge, (ii) laser ablation and (iii) chemical vapor deposition. The physical (surface area and porosity) and chemical (functional groups) properties are significantly affected by the followed production method for these carbonaceous materials. Using freely available raw materials for the activated carbon and carbon nanotubes production and their modification with different nanoparticles and functional groups is the future prospect for the adsorptive removal of pharmaceutical active compounds from the aquatic environment.

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Conflict of interest

The author declares that there are no conflicts of interest.

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References

[1] Ternes T. Occurrence of drugs in German sewage treatment plants and rivers. Water Research. 1998;**32**:3245-3260

[2] World Health Organization "Pharmaceuticals in Drinking-water" WHO/HSE/WSH/11.05. 2011

[3] Tabak HH, Bunch RL. Steroid hormones as water pollutants. I. Metabolism of natural and synthetic ovulation-inhibiting hormones by microorganisms of activated sludge and primary settled sewage. Developments in Industrial Microbiology. 1970;**11**:367-376

[4] Garrison AW, Pope JD, Allen FR. GC/MS analysis of organic compounds in domestic wastewaters. In: Keith LH, editor. Identification and Analysis of Organic Pollutants in Water. Ann Arbor, MI: Ann Arbor Science Publishers Inc.; 1976. pp. 517-556

[5] Hignite C, Azarnoff DL. Drugs and drug metabolites as environmental contaminants: Chlorophenoxyisobutyrate and salicylic acid in sewage water effluent. Life Sciences. 1977;**20**(2):337-341

[6] Kolpin DW et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environmental Science & Technology. 2002;**36**:1202-1211

[7] Buser HR, Muller MD, Theobald N. Occurrence of the pharmaceutical drug clofibric acid and the herbicide mecoprop in various Swiss lakes and in the North Sea. Environmental Science & Technology. 1998;**32**(1):188-192

[8] Reddersen K, Heberer T, Dünnbier U. Identification and significance of phenazone drugs and their metabolites in ground- and drinking water. Chemosphere. 2002;**49**:539-544

[9] Bound A, Voulvoulis N. Household disposal of pharmaceuticals as a pathway for aquatic contamination in the United Kingdom. Environmental Health Perspectives. 2005;**113**:1705-1711

[10] DWI. "Desk based review of current knowledge on pharmaceuticals in drinking water and estimation of potential levels. Final Report Prepared by Watts and Crane Associates for Drinking Water Inspectorate, Department for Environment, Food and Rural Affairs (Defra Project Code: CSA 7184/WT02046/DWI70/2/213). 2007. Available from: http://dwi.defra.gov.uk/research/completed-research/reports/dwi70-2-213.pdf

[11] Ternes TA et al. Assessment of technologies for the removal of pharmaceuticals and personal care products in sewage and drinking water to improve the indirect potable water reuse. POSEIDON project detailed report (EU Contract No. EVK1-CT-2000-00047). 2005

[12] Bulloch DN et al. Occurrence of halogenated transformation products of selected pharmaceuticals and personal care products in secondary and tertiary treated wastewaters from Southern California. Environmental Science & Technology. 2015;**49**:2044-2051

[13] Bu Q, Wang B, Huang J, Deng S, Yu G. Pharmaceuticals and personal care products in the aquatic environment in China: A review. Journal of Hazardous Materials. 2013;**262**:189-211

[14] Jung C et al. Removal of endocrine disrupting compounds, pharmaceuticals, and personal care products in water using carbon nanotubes: A review. Journal of

Industrial and Engineering Chemistry. 2015;**27**:1-11

[15] Dong S et al. Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: A review. RSC Advances. 2015;**5**:14610-14630

[16] Richardson SD, Ternes TA. Water analysis: Emerging contaminants and current issues. Analytical Chemistry. 2014;**86**:2813-2848

[17] Gadipelly C, Pérez-González A, Yadav GD, Ortiz I, Ibáñez R, Rathod VK, et al. Pharmaceutical industry wastewater: Review of the technologies for water treatment and reuse. Industrial and Engineering Chemistry Research. 2014;**53**:11571-11592

[18] Wu X, Conkle JL, Ernst F, Gan J. Treated wastewater irrigation: Uptake of pharmaceutical and personal care products by common vegetables under field conditions. Environmental Science & Technology. 2014;**48**:11286-11293

[19] Miller EL, Nason SL, Karthikeyan KG, Pedersen JA. Root uptake of pharmaceutical and personal care product ingredients. Environmental Science & Technology. 2016;**50**:525-541

[20] Tanoue R et al. Uptake and tissue distribution of pharmaceuticals and personal care products in wild fish from treated-wastewater-impacted streams. Environmental Science & Technology. 2015;**49**:11649-11658

[21] Subedi B et al. Occurrence of pharmaceuticals and personal care products in German fish tissue: A national study. Environmental Science & Technology. 2012;**46**:9047-9054

[22] Rivera-Jiménez SM, Méndez-González S, Hernández-Maldonado A. Metal (M = Co^{2+}, Ni^{2+} and Cu^{2+}) grafted mesoporous SBA-15: Effect of transition metal incorporation and pH conditions on the adsorption of Naproxen from water. Microporous and Mesoporous Materials. 2010;**132**:470-479

[23] Rivera-Jiménez SM, Hernández-Maldonado AJ. Nickel (II) grafted MCM-41: A novel sorbent for the removal of naproxen from water. Microporous and Mesoporous Materials. 2008;**116**:246-252

[24] Esplugas S, Bila DM, Krause LGT, Dezotti M. Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. Journal of Hazardous Materials. 2007;**149**:631-642

[25] Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. Environment International. 2009;**35**:402-417

[26] Wang CJ, Li Z, Jiang WT, Jean JS, Liu CC. Cation exchange interaction between antibiotic ciprofloxacin and montmorillonite. Journal of Hazardous Materials. 2010;**183**:309-314

[27] Turku I, Sainio T, Paatero E. Thermodynamics of tetracycline adsorption on silica. Environmental Chemistry Letters. 2007;**5**:225-228

[28] Bao Khanh V, Shin EW, Snisarenko O, Jeong WS, Lee HS. Removal of the antibiotic tetracycline by Fe-impregnated SBA-15. Korean Journal of Chemical Engineer. 2010;**27**:116-120

[29] Punyapalakul P, Sitthisorn T. Removal of ciprofloxazin and carbamazepine by adsorption on functionalized mesoporous silicates. World Academy of Science, Engineering and Technology. 2010;**69**:546-550

[30] Lorphensri O, Intravijit J, Sabatini DA, Kibbey TC, Osathaphan K, Saiwan C. Sorption of acetaminophen, 17α-ethynyl estradiol, nalidixic acid, and norfloxacin to silica, alumina, and a hydrophobic medium. Water Research. 2006;**40**:1481-1491

[31] Robberson KA, Waghe AB, Sabatini DA, Butler EC. Adsorption of the quinolone antibiotic nalidixic acid onto anion-exchange and neutral polymers. Chemosphere. 2006;**63**:934-941

[32] María A, Otero RM, Rodrigues AE. Recovery of Vitamin B12 and cephalosporin-C from aqueous solutions by adsorption on non-ionic polymeric adsorbents. Separation and Purification Technology. 2004;**38**:85-98

[33] Scordino M, Di Mauro A, Passerini A, Maccarone E. Adsorption of flavonoids on resins: Hesperidin. Journal of Agricultural and Food Chemistry. 2003;**51**:6998-7004

[34] Chaubal MV, Payne GF, Reynolds CH, Albright RL. Equilibria for the adsorption of antibiotics onto neutral polymeric sorbents: Experimental and modeling studies. Biotechnology and Bioengineering. 1995;**47**:215-226

[35] Lee JW, Park HC, Moon H. Adsorption and desorption of cephalosporin c on nonionic polymeric sorbents. Separation and Purification Technology. 1997;**12**:1-11

[36] Dutta MK, Dutta NN, Bhattacharya KG. Aqueous phase adsorption of certain beta-lactam antibiotics onto polymeric resins and activated carbon. Separation and Purification Technology. 1999;**16**:213-224

[37] Ribeiro MH, Ribeiro IA. Modelling the adsorption kinetics of erythromycin onto neutral and anionic resins. Bioprocess and Biosystems Engineering. 2003;**26**:49-55

[38] KristiaPutra E, Pranowo R, Sunarso J, Indraswati N, Ismadji S. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics. Water Research. 2009;**43**:2419-2430

[39] Akçay G, Kılınç E, Akçay M. The equilibrium and kinetics studies of flurbiprofen adsorption onto tetrabutylammonium montmorillonite (TBAM). Colloids and Surfaces A. 2009;**335**:189-193

[40] Figueroa RA, Leonard A, MacKay AA. Modeling tetracycline antibiotic sorption to clays. Environmental Science & Technology. 2003;**38**:476-483

[41] Wang Y-J, Jia D-A, Sun R-J, Zhu H-W, Zhou D-M. Adsorption and cosorption of tetracycline and copper(II) on montmorillonite as affected by solution pH. Environmental Science & Technology. 2008;**42**:3254-3259

[42] Pils JRV, Laird DA. Sorption of tetracycline and chlortetracycline on K- and Ca-saturated soil clays, humic substances, and Clay–humic complexes. Environmental Science & Technology. 2007;**41**:1928-1933

[43] Bewick MWM. The adsorption and release of tylosin by clays and soils. Plant and Soil. 1979;**51**:363-372

[44] Zhang W, Ding Y, Boyd SA, Teppen BJ, Li H. Sorption and desorption of carbamazepine from water by smectite clays. Chemosphere. 2010;**81**:954-960

[45] Wu Q, Lia Z, Hong H, Yin K, Tie L. Adsorption and intercalation of ciprofloxacin on montmorillonite. Applied Clay Science. 2010;**50**:204-211

[46] Chang P-H, Jean J-S, Jiang W-T, Li Z. Mechanism of tetracycline sorption on rectorite. Colloids and Surfaces A. 2009;**339**:94-99

[47] Chang P-H, Li Z, Jiang W-T, Jean J-S. Adsorption and intercalation of tetracycline by swelling clay minerals. Applied Clay Science. 2009;**46**:27-36

[48] Martins AC, Pezoti O, Cazetta AL, Bedin KC, Yamazaki DAS, Bandoch GFG, et al. Removal of tetracycline by NaOH-activated carbon produced from macadamia nut shells: Kinetic and equilibrium studies. Chemical Engineering Journal. 2015;**260**:291-299

[49] Marzbali MH, Esmaieli M, Abolghasemi H, Marzbali MH. Tetracycline adsorption by H_3PO_4-activated carbon produced from apricot nut shells: A batch study. Process Safety and Environment Protection. 2016;**102**:700-709

[50] Acosta R, Fierro V, Martinez de Yuso A, Nabarlatz D, Celzard A. Tetracycline adsorption onto activated carbons produced by KOH activation of tyre pyrolysis char. Chemosphere. 2016;**149**:168-176

[51] Carl JR-U, Sánchez-PoloJesús VG-PM, Ocampo-Pérez JL-PR. Tetracycline removal from water by adsorption/bioadsorption on activated carbons and sludge-derived adsorbents. Journal of Environmental Management. 2013;**131**(15):16-24

[52] Rivera-Utrilla J, Prados-Joya G, Sánchez-Polo M, Ferro-García MA, Bautista-ToledoI.Removalofnitroimidazole antibiotics from aqueous solution by adsorption/bioadsorption on activated carbon. Journal of Hazardous Materials. 2009;**170**:298-305

[53] Çalışkan Salihi E, Göktürk S. Adsorption characteristics of sulfamethoxazole and metronidazole on activated carbon. Separation Science and Technology. 2010;**45**:244-255

[54] Oleszczuk P, Pan B, Xing B. Adsorption and desorption of oxytetracycline and carbamazepine by multiwalled carbon nanotubes. Environmental Science & Technology. 2009;**43**:9167-9173

[55] Mestre AS, Pires J, Nogueira JMF, Carvalho AP. Activated carbons for the adsorption of ibuprofen. Carbon. 2007;**45**:1979-1988

[56] Aksu Z, Tunç Ö. Application of biosorption for penicillin G removal: Comparison with activated carbon. Process Biochemistry. 2005;**40**:831-847

[57] Erdinç N, Göktürk S, Tunçay M. A study on the adsorption characteristics of an amphiphilic phenothiazine drug on activated charcoal in the presence of surfactants. Colloids and Surfaces B. 2010;**75**:194-203

[58] Ji L, Chen W, Zheng S, Xu Z, Zhu D. Adsorption of sulfonamide antibiotics to multiwalled carbon nanotubes. Langmuir. 2009;**25**:11608-11613

[59] Zimnitsky DS, Yurkshtovich TL, Bychkovsky PM. Adsorption of zwitterionic drugs on oxidized cellulose from aqueous and water/alcohol solutions. The Journal of Physical Chemistry. B. 2004;**108**:17812-17817

[60] Zhang H, Huang C-H. Adsorption and oxidation of fluoroquinolone antibacterial agents and structurally related amines with goethite. Chemosphere. 2007;**66**:1502-1512

[61] Wunder DB, Bosscher VA, Cok RC, Hozalski RM. Sorption of antibiotics to biofilm. Water Research. 2011;**45**:2270-2280

[62] Kikuta TUT. Separate estimation of adsorption and degradation

of pharmaceutical substances and estrogens in the activated sludge process. Water Research. 2005;**39**:1289-1300

[63] Chen W-R, Huang C-H. Adsorption and transformation of tetracycline antibiotics with aluminum oxide. Chemosphere. 2010;**79**:779-785

[64] Cheng G, Karthikeyan KG. Sorption of the antimicrobial ciprofloxacin to aluminum and iron hydrous oxides. Environmental Science & Technology. 2005;**39**:9166-9173

[65] Cheng G, Karthikeyan KG. Interaction of tetracycline with aluminum and iron hydrous oxides. Environmental Science & Technology. 2005;**39**:2660-2667

[66] Kahle M, Stamm C. Sorption of the veterinary antimicrobial sulfathiazole to organic materials of different origin. Environmental Science & Technology. 2006;**41**:132-138

[67] Feitosa-Felizzola J, Hanna K, Chiron S. Adsorption and transformation of selected human-used macrolide antibacterial agents with iron(III) and manganese (IV) oxides. Environmental Pollution. 2009;**157**:1317-1322

[68] Fang Z, Chen J, Qiu X, Qiu X, Cheng W, Zhu L. Effective removal of antibiotic metronidazole from water by nanoscale zero-valent iron particles. Desalination. 2011;**268**:60-67

[69] Caroni ALPF, de Lima CRM, Pereira MR, Fonseca JLC. The kinetics of adsorption of tetracycline on chitosan particles. Journal of Colloid and Interface Science. 2009;**340**:182-191

[70] Bui TX, Choi H. Adsorptive removal of selected pharmaceuticals by mesoporous silica SBA-15. Journal of Hazardous Materials. 2009;**168**:602-608

[71] Goyne KW, Chorover J, Kubicki JD, Zimmerman AR, Brantley SL. Sorption of the antibiotic ofloxacin to mesoporous and nonporous alumina and silica. Journal of Colloid and Interface Science. 2005;**283**:160-170

[72] Li Z, Ackley LSC, Fenske N. Adsorption of tetracycline on kaolinite with pH-dependent surface charges. Journal of Colloid and Interface Science. 2010;**351**:254-260

[73] Hamerlinck Y, Mertens DH. In: Vansant EF, editor. Activated Carbon Principles in Separation Technology. New York: Elsevier; 1994

[74] Mantell CL. Carbon and Graphite Handbook. New York: Interscience; 1968

[75] Mohan D, Singh KP. Granular activated carbon. In: Lehr J, Keeley J, Lehr J, editors. Water Encyclopedia: Domestic, Municipal, and Industrial Water Supply and Waste Disposal. New York: Wiley/Interscience; 2005

[76] Otowa T, Nojima Y, Miyazaki T. Development of KOH activated high surface area carbon and its application to drinking water purification. Carbon. 1997;**35**(9):1315-1339

[77] Mattson JS, Mark HB Jr. Activated Carbon. New York: Marcel Dekker; 1971

[78] Hower JC, Senior CL, Suuberg EM, Hurt RH, Wilcox JL, Olson ES. Mercury capture by native fly ash carbons in coal-fired power plants. Progress in Energy and Combustion Science. 2010;**36**:510-529

[79] Fletcher TH, Ma J, Rigby JR, Brown AL, Webb BW. Soot in coal combustion systems. Progress in Energy and Combustion Science. 1997;**23**(3):283-301

[80] Ahmed J. Adsorption of quinolone, tetracycline, and penicillin antibiotics

from aqueous solution using activated carbons: Review. Environmental Toxicology and Pharmacology. 2017;**50**:1-10

[81] Chen Y, Wang F, Duan L, Yang H, Gao J. Tetracycline adsorption onto rice husk ash, an agricultural waste: Its kinetic and thermodynamic studies. Journal of Molecular Liquids. 2016;**222**:487-494

[82] Craig MW. Coping with resistance to copper/silver disinfection. Water Engineering & Management. 2001;**148**(11):27

[83] Wang X, Li Q, Xie J, Jin Z, Wang J, Li Y, et al. Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates. Nano Letters. 2009;**9**(9):3137-3141. DOI: 10.1021/nl901260b

[84] Carbon Nanotube. 2020. Available from: http://en.wikipedia.org/wiki/Carbon_nanotube

[85] Kim, Li H. Fabrication and Applications of Carbon Nanotube-Based Hybrid Nanomaterials by Means of Non-Covalently Functionalized Carbon Nanotubes, Carbon Nanotubes—From Research to Applications. Stefano Bianco: IntechOpen; 2011

[86] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of carbon nanotubes. Chemical Reviews. 2006;**106**:1105-1136

[87] Thoteson E, Ren Z, Chou T. Advances in the science and technology of carbon nanotubes and their composites: A review. Composites Science and Technology. 2001;**61**(13):1899-1912

[88] Zhidong H, Alberto F. Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review. Progress in Polymer Science. 2011;**36**(7):914-944

[89] Collins PG, Avouris P. Nanotubes for electronics. Scientific American. 2000;**283**:62-69

[90] Niyogi S, Hamon MA, Hu H, Zhao B, Bhowmik P, Sen R, et al. Chemistry of single-walled carbon nanotubes. Accounts of Chemical Research. 2002;**35**:1105-1113

[91] Hone J, Whitney M, Piskoti C, Zettl A. Thermal conductivity of single-walled carbon nanotubes. Physical Review B. 1999;**59**:R2514

[92] Ebbesen TW, Ajayan PM. Large-scale synthesis of carbon nanotubes. Nature. 1992;**358**:220-222

[93] The Smalley Group at Rice University. 2020. Available from: https://oit.rice.edu/

[94] Journet C, Bernier P. Production of carbon nanotubes. Applied Physics A: Materials Science & Processing. 1998;**67**(1):1-9

[95] Dai H. Carbon nanotubes: Opportunities and challenges. Surface Science. 2002;**500**(1-3):218-241

[96] Yu F, Sun S, Han S, Zheng J, Ma J. Adsorption removal of ciprofloxacin by multi-walled carbon nanotubes with different oxygen contents from aqueous solutions. Chemical Engineering Journal. 2016;**285**:588-595

[97] Yu F, Ma J, Han S. Adsorption of tetracycline from aqueous solutions onto multi-walled carbon nanotubes with different oxygen contents. Scientific Reports. 2014;**4**:5326

[98] Ji L, Shao Y, Xu Z, Zheng S, Zhu D. Adsorption of monoaromatic compounds and pharmaceutical antibiotics on carbon nanotubes activated by KOH etching. Environmental Science & Technology. 2010;**44**:6429-6436

[99] Stoller MD, Park S, Zhu Y, An J, Ruoff RS. Graphene-based ultracapacitors. Nano Letters. 2008;**8**:3498-3502

[100] He H, Gao C. Graphene nanosheets decorated with Pd, Pt, Au, and Ag nanoparticles: Synthesis, characterization, and catalysis applications. Science China Chemistry. 2011;**54**:397-404

[101] Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, et al. Superior thermal conductivity of single-layer graphene. Nano Letters. 2008;**8**:902-907

[102] Lee C, Wei X, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science. 2008;**321**:385-388

[103] Novoselov KS, Geim AK, Morozov S, Jiang D, Zhang Y, Dubonos S, et al. Electric field effect in atomically thin carbon films. Science. 2004;**306**:666-669

[104] Sinha A, Jana NR. Graphene-based composite with γ-Fe_2O_3 nanoparticle for the high-performance removal of endocrine-disrupting compounds from water. Chemistry. 2012;**8**(4):786-791

[105] Al-Khateeb LA, Almotiry S, Salam MA. Adsorption of pharmaceutical pollutants onto graphene nanoplatelets. Chemical Engineering Journal. 2014;**248**:191-199

[106] Gao Y, Li Y, Zhang L, Huang H, Hu JJ, Shah SM, et al. Adsorption and removal of tetracycline antibiotics from aqueous solution by graphene oxide. Journal of Colloid and Interface Science. 2012;**368**(1):540-546

[107] Danna S, Shubo D, Jin L, Hubian W, Conghui H, Giovanni C, et al. Preparation of porous graphene oxide by chemically intercalating a rigid molecule for enhanced removal of typical pharmaceuticals. Carbon. 2017;**119**:101-109

[108] Lin Y, Xu S, Jia L. Fast and highly efficient tetracyclines removal from environmental waters by graphene oxide functionalized magnetic particles. Chemical Engineering Journal. 2013;**225**:679-685

[109] Kerkez-Kuyumcu O, Bayazit SS, Salam MA. Antibiotic amoxicillin removal from aqueous solution using magnetically modified graphene nanoplatelets. Journal of Industrial and Engineering Chemistry. 2016;**36**:198-205

[110] Kyzas GZ, Koltsakidou A, Nanaki SG, Bikiaris DN, Lambropoulou DA. Removal of beta-blockers from aqueous media by adsorption onto graphene oxide. Science of the Total Environment. 2015;**537**:411-420

[111] Kalantary RR, Azari A, Esrafili A, Yaghmaeian K, Moradi M, Sharafi K. The survey of Malathion removal using magnetic graphene oxide nanocomposite as a novel adsorbent: Thermodynamics, isotherms, and kinetic study. Desalination and Water Treatment. 2016;**57**(58):28460-28473