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A review on analytical methods and treatment techniques of pharmaceutical wastewater

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ABSTRACT

This review is providing an overview for the analysis and removal of pollutants from pharmaceutical wastewater. Pharmaceuticals are bioactive compounds and they can cause potential effects on living systems. Different classes of pharmaceuticals are enter into the environment after being used or excreted through wastewater and sewage treatment systems. The complexity of these hazards should not be underestimated. In this modern world, 3000 different substances are used in medicines such as painkillers, antibiotics, contraceptives and much more. These pollutants are becoming omnipresent in the environment because they cannot be removed effectively by the typical wastewater treatment plants due to their toxic and poisonous nature. A variety of technologies, including physical, chemical, biological and thermal process have been largely explored for the removal of pharmaceuticals from wastewater. The analytical methods for pharmaceuticals like chromatographic and spectroscopic methods were also briefly described. Rather than the conventionally suggested methods such as biodegradation, ozonation, photocatalysis for the removal of pharmaceuticals from waste water, the applicability of adsorption process for this purpose is simple and a low-cost technique. In this paper, the process of removing pharmaceuticals from wastewater using adsorbents like activated carbon, carbon nanotubes, zeolites and biosorbents (industrial waste or sewage waste, agricultural waste) were briefly analyzed and explained. Lastly, proposals were made for the future research in the field of pharmaceutical wastewater treatment.

Keywords: Analysis; Pharmaceuticals; Removal; Treatment methods; Wastewater

1. Introduction

Pharmaceutical products have been widely used in many fields such as medicine, industry, livestock farming, aquaculture and people's daily life. The presence of pharmaceutical compounds in water comes from two different sources: production processes of pharmaceutical industry and common use of pharmaceutical compounds resulting in their presence in urban and farming wastewaters. Pharmaceuticals can be introduced into the environment by direct and indirect methods. Mompelat et al. reviewed about the various methods of introduction of the pharmaceuticals into the environment [1]. Establishment of pharmaceuticals as noxious substances in the environment and the necessity to judge their environmental risks have greatly increased. Many reviews have been published recently regarding the effects of pharmaceuticals [2–6]. They are becoming universal in the environment due to their extensive applications and poor removal by the conventional wastewater treatment plants. Both industrial and domestic wastewaters contain a variety of organic contaminants such as pharmaceuticals, personal care products and pharmaceutical pollutants (PPs) [7]. It has been confirmed that most of these compounds undergo both inadequate removal in

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wastewater treatment plants and slow natural degradation, thereupon they were found in surface waters receiving effluent from treatment plants. Admitting the fact that the pharmaceuticals and personal care products (PPCPs) were found in the environment at trace concentrations but still their chemical persistence, microbial resistance, and synergistic effects are yet unknown [8]. Existence and the entry of pharmaceuticals into the surface waters depends upon various matters including geological factors, land-run off and veterinary use (manure dispersion and animal excretion). However, release of wastewater treatment plant (WWTP) effluents also seems to play a major role in the release of pharmaceuticals into the environment.

Similarly, pharmaceuticals exist in the environment at a very low concentration but, generally due to their bio-accumulation, they pose a potential long-term risk for both aquatic and terrestrial organisms. Therefore, over the past few years, pharmaceuticals also have been considered an emerging environmental problem. Pharmaceutical drugs in the environment can be classified on the basis of similar chemical structure, the same mechanism of action and many more factors. Table 1 gives the information related to pharmaceutical drug classes. Although, the removal of pharmaceutical residues by conventional treatment methods was widely carried out in the past, it is not that much effective and not well understood [9]. As conventional treatments have several disadvantages like high cost, low efficiency and high energy requirements. At present, the rising contemplation from the world has been paid to the effect of pharmaceuticals in the environment, which can be attributed to the two reasons [10]. One is the omnipresence of pharmaceuticals in the environment resulting from their widespread use and the other reason is the potentially adverse effects of these micro-pollutants on the aquatic and human life. The requirement for the development in the analytical technology and future research, which enables people to detect pharmaceutical pollutants in ultra-trace level [11].

Several surveys worldwide in many countries proved the occurrence of pharmaceuticals, hormones and other organic contaminants in wastewaters. The most frequently occurring contaminants are steroids, disinfectants, caffeine and such compounds [12]. During the last decade, there was a significant amount of research focusing on the removal of pharmaceuticals from wastewaters. The most commonly available treatment options such as flocculation, sedimentation, filtration, activated sludge, chlorination is not an effective treatment in the elimination of these compounds. Recently it has been found that removal of these pharmaceutical pollutants from wastewater can be done using various technologies such as activated sludge treatment [13,14], submerged membrane bioreactor [15,16], pure cultures [17], mixed cultures [18], constructed wetland [19], coagulation [20], membrane technology [21], advanced oxidation processes [10] and adsorption [22]. These different technologies have been investigated and it has been found that they have some drawbacks. For example, advanced oxidation processes results in the formation of toxic intermediates in some cases if the processes is not carried out properly. The membrane technologies are expensive when it was compared with the other technologies [23]. In some cases, these treatment technologies are providing drawbacks when it was approached individually but on combining these treatment technologies they are very pragmatic in the complete elimination of these pollutants [24].

In this context, the removal of pharmaceutical pollutants by adsorption is a very interesting solution due to its versatility and efficiency. Adsorption is a surface phenomenon which may be defined as a unit operation in chemical engineering sense and that operation which deals primarily with the utilization of surface forces and the concentration of materials on the surface of solid bodies is referred as adsorption.

The adsorbents mostly used in wastewater treatments are activated carbon, graphite, silica gel, zeolites, carbon nanotubes and biosorbents. Out of these mentioned adsorbents, activated carbons are the most commonly used adsorbents which can be either in granular or powdered form for the adsorption of organic substances and non-polar adsorbates. It is also widely used in wastewater treatment because of its physical (e.g., pore size distribution and surface area) and chemical properties (e.g., surface groups). In the adsorption technology, the adsorbent material should have some basic parameters which strongly influence the whole adsorption procedure which includes solution pH, contact time requirement, initial pollutant concentration, temperature, volume of adsorbents, agitation speed, the ionic strength of the solution, adsorbent dosage, etc. [2]. Therefore, if any of the above-mentioned parameters vary, the adsorption processes do not occur properly and the results in less efficient adsorption. The objective of this work is to chronically summarize the existing knowledge on the removal of pharmaceuticals from wastewater, as well as the analytic techniques used to determine pharmaceuticals in the environment and to review the major works regarding the removal of pharmaceuticals from wastewaters using various adsorption technologies.

2. Analytical methods for pharmaceuticals

Pharmaceutical residues have been detected in many environmental matrices worldwide (e.g., in waters, wastewaters, sediments and sludge). These compounds are mainly depends on the hydrophilicity which can enter the aquatic environment or remain adsorbed on the solid particles. The most important sources of such compounds in the environment are households, wastewater treatment plants, hospitals, industrial units and intensive animal breeding [25]. Industrial and domestic wastes must be managed effectively to meet the challenges of increasing population, stringent regulatory requirements, and aging water treatment facilities. To meet these challenges, specific analytical methods are available to monitor the chemical compounds in wastewater. However, because of the complexity of the sample matrix, several analytical methods are required to determine polar and non-polar organic compounds in the dissolved and suspended phases that may impact water quality [26]. Here the analytical methods using chromatography and spectroscopy are discussed in detail.

2.1. Chromatographic methods

Chromatography is the collective term for a set of separation techniques that operate based on the differential partitioning of mixture components between a mobile and

Table 1
Pharmaceutical drug classes and examples

Classification property	Drug class	Examples	Uses
Chemical structure	β-lactam antibiotic	• Penams (penicillin derivatives) • Monobactams • Carbapenems	Treatment of bacterial infections
	Fibrate	• Bezafibrate (bezalip) • Clinofibrate (Lipocolin)	Treatment for hypertriglyceridemia and hypercholesterolaemia
	Benzodiazepine	• Alprazolam • Quazepam • Clorazepate	Useful in a variety of indications such as alcohol dependence, anxiety disorders
	Cardiac glycoside	• Oleandrin • Digitoxin	Used in rat poisons, heart tonics and emetics
Mechanism of action	Renin inhibitor	Aliskiren	Treatment for hypertension
	ACE inhibitor	Captopril	Treatment for hypertension
	β blocker	Propranolol	Treatment for hypertension and arrhythmia
	Proton-pump inhibitor	Omeprazole	Reduction of gastric acid production
Mode of action	Diuretic	Acetazolamide	Treat heart failure, liver cirrhosis
	Cholinergic	Acetylcholines	It prevents fat deposits in the liver and facilitates the movement of fats into the cells
	Dopaminergic	Monoamine oxidase (MAO)	Dopamine injection (Intropin) is used to treat certain conditions, such as low pressure
Therapeutic class	Analgesic	• Salicylates • Paracetamol	Provides pain relief in common conditions such as muscle sprains and overuse injuries
	Anticoagulant	• Warfarin	Used to treat and prevent blood clots that may occur in your blood vessels
	Antipsychotic	• Aripiprazole • Clozapine	Antipsychotics are frequently used for the following conditions • Schizophrenia • Bipolar disorder
	Antiviral	• Amantadine	They are designed to help deal with HIV, herpes viruses.

a stationary phase. The mobile phase (a liquid or a gas) travels through the stationary phase (a liquid or a solid) in a defined direction. The distribution of components between the two phases depends on adsorption, ionic interactions, diffusion, and solubility or in the case of affinity chromatography, specific interactions. Depending on the experimental design, the separation in a liquid mobile phase may be carried out via column or planar chromatography, on analytical or preparative scales [27–30]. There are various types of chromatography out of which thin layer chromatography, high performance (high pressure) liquid chromatography (HPLC) and gas chromatography are found to be more suitable for wastewater treatment.

2.1.1. Thin layer chromatography

Thin-layer chromatography (TLC) is a very commonly used technique in synthetic chemistry for identifying compounds, determining their purity and following the progress of a reaction. It also permits the optimization of the solvent system for a given separation problem. In comparison with column chromatography, it only requires small quantities of the compound (~ng) and is much faster as well [31–33]. Stationary phase, a special finely ground matrix (silica gel, alumina, or similar material) is coated on a glass plate, a metal or a plastic film as a thin layer (~0.25 mm). In addition, a binder like a gypsum is mixed with the stationary phase to make it stick better to the slide. In many cases, a fluorescent powder is mixed into the stationary phase to simplify the visualization later on (e.g., bright green when you expose it to 254 nm UV light) [34]. After separation is complete, individual compounds appear as spots separated vertically. Each spot has a retention factor (R_f) which is equal to the distance migrated over the total distance covered by the solvent. The R_f formula [35] is:

$$R_f = \frac{\text{distance travelled by sample}}{\text{distance travelled by solvent}} \quad (1)$$

After the plate is set the selection of solvent is done. Proper solvent selection is perhaps the most important aspect of TLC, and determining the best solvent may require a degree of trial and error. A common starting solvent is 1:1 hexane: ethyl acetate. Varying the ratio can have a pronounced effect on R_f. R_f values range from 0 to 1 with 0 indicating that the solvent polarity is very low and 1 indicating that the solvent polarity is very high [36]. The volatility of solvents should also be considered when chemical stains are to be used. Any solvent left on the plate may react with the stain and conceal spots. Many solvents can be removed by allowing them to sit on the bench for a few minutes, but very nonvolatile solvents may require time in a vacuum chamber. Volatile solvents should only be used once. If the mobile phase is used repeatedly, results will not be consistent or reproducible [37]. The uses of solvent mixtures are:

- A solvent which can be used for separating mixtures of strongly polar compounds is ethyl acetate: butanol: acetic acid: water in the ratio of 80:10:5:5.
- To separate strongly basic components, make a mixture of 10% NH_4OH in methanol, and then make a 1 to 10% mixture of this in dichlormethane.
- Mixtures of 10% methanol or less in DCM can be useful for separating polar compounds [38].

Spots are applied to the plate using very thin glass pipettes. The capillary should be thin enough to apply a neat spot, but not so thin as to prevent the uptake of an adequate quantity of analyte. Here is a popular method of producing TLC pipettes. A capillary tube is used in some cases. After the apparatus is set spotting and developing is done and the final study is done using the plate obtained [39].

2.1.2. HPLC

Liquid chromatography performed using such resins is called high-performance liquid chromatography, abbreviated as HPLC. However, at such particle sizes, the sufficient flow of the mobile phase (eluent) can be achieved only by applying a high pressure of around 10 MPa by using special precision pumps. HPLC thus also stands for high-pressure liquid chromatography according to many researchers, the abbreviation also refers to the high price of the specialized equipment. Due to the application of high pressure, the primary requirement regarding HPLC columns is that they should be incompressible. Silica is predominantly used for this purpose. Under appropriate conditions, silica can be used to create homogeneous column media of sufficient strength and with a well-controlled particle size. For the hydrophilic silica, only hydrophobic mobile phases can be applied. Therefore, HPLC was primarily suitable for the separation of hydrophobic organic solvent-soluble materials [40]. Later, the chemical modification of the silica surface made possible the creation of hydrophobic silica gels. In this case, the hydrophilic-hydrophobic relation of the stationary and mobile phases became reversed, hence it is termed as reverse-phase chromatography (RPC). Reverse-phase chromatography opened the possibility of the separation of water-soluble substances, including the majority of molecules of biological origin. Large pore size gels also allowed the separation of macromolecules. The hydrophobic surface is formed by long alkyl chains linked to the silica. These include octadecyl, octyl, butyl (labeled as C18, C8, and C4) and also phenyl groups. Furthermore, gels containing charged groups can be used for ion exchange [41].

2.1.3. Gas chromatography

Gas chromatography specifically gas-liquid chromatography involves a sample being vaporized and injected into the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid [42]. The instrumental components include carrier gas which should be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependent upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities [43]. It also involves a sample injection port. A microsyringe is used to inject sample through a rubber septum into a flash vaporizer port at the head of the column. The temperature of the sample port is usually about 50°C higher than the boiling point of the least volatile component of the sample [44]. There are two general types of column, packed and capillary (also known as open tubular). Packed columns contain a finely divided inert and solid support material (commonly based on diatomaceous earth) coated with liquid stationary phase. Most packed columns are 1.5–10 m in length and have an internal diameter of 2–4 mm. Capillary columns have an internal diameter of a few tenths of a millimeter. They can be one of two types; wall coated open tubular (WCOT) or support coated open tubular (SCOT). Wall-coated columns consist of a capillary tube whose walls are coated with liquid stationary phase. In support-coated columns, the inner wall of the capillary is lined with a thin layer of support material such as diatomaceous earth, onto which the stationary phase has been adsorbed. SCOT columns are generally less efficient than WCOT columns. Both types of capillary column are more efficient than packed columns [45]. The column temperature is an important aspect to be kept in mind while performing gas chromatography. For precise work, column temperature must be controlled to within tenths of a degree. The optimum column temperature depend upon the boiling point of the sample. There are many detectors which can be used in gas chromatography. Different detectors will give different types of selectivity. A non-selective detector responds to all compounds except the carrier gas, a selective detector responds to a range of compounds with a common physical or chemical property and a specific detector responds to a single chemical compound. Detectors can also be grouped into concentration dependant detectors and mass flow dependant detectors. The signal from a concentration dependant detector is related to the concentration of solute in the detector. Dilution of the sample with make-up gas will lower the response of the detector. Mass flow dependant detectors usually destroy the sample, and the signal is related to the rate at which solute molecules enter the detector. The response of a mass flow dependant detector is unaffected by make-up gas [46].

2.2. Spectroscopic methods

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. Spectroscopy originated through the study of visible light dispersed according to its wavelength, by a prism. Various spectroscopic methods are used for the treatment of wastewater. Near-infrared spectroscopy (NIRS) and nuclear magnetic resonance (NMR) are suitable for wastewater are discussed in detailed.

2.2.1. NIRS

Near infrared spectroscopy (NIR) is a type of vibrational spectroscopy that employs photon energy in the energy range of 2.65×10^{-19} to 7.96×10^{-20} J, which corresponds to the wavelength range of 750–2,500 nm (wavenumbers: 13,300–4,000 cm^{-1}). This energy range is higher than necessary to promote molecules only to their lowest excited vibrational states (through a fundamental vibrational transition) and lower than typical values necessary for electron excitation in molecules (except for some rare-earth compounds) [46]. It is used in astronomical spectroscopy, agriculture, remote monitoring, material science and medicine.

2.2.2. NMR

Nuclear magnetic resonance (NMR) is a physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation. The principle of NMR usually involves two sequential steps: The alignment (polarization) of the magnetic nuclear spins in an applied and constant magnetic field B_0 and the perturbation of this alignment of the nuclear spins by employing an electromagnetic, usually radio frequency (RF) pulse. The required perturbing frequency depend upon the static magnetic field (H_0) and the nuclei of observation. The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied, an energy transfer is possible between the base energy to a higher energy level (generally a single energy gap). The nuclei of all elements carry a charge. When the spins of the protons and neutrons comprising these nuclei are not paired, the overall spin of the charged nucleus generates a magnetic dipole along the spin axis, and the intrinsic magnitude of this dipole is a fundamental nuclear property called the nuclear magnetic moment, µ. The symmetry of the charge distribution in the nucleus is a function of its internal structure and if this is spherical (ie analogous to the symmetry of a 1s hydrogen orbital), it is said to have a corresponding spin angular momentum number of $I = 1/2$, of which examples are 1H, 13C, 15N, 19F, 31P etc. Nuclei which have a non-spherical charge distribution (analogous to, for example, a hydrogen 3d orbital) have higher spin numbers (e.g., 10B, 14N).

3. Removal of pharmaceuticals

The entry of pharmaceutical components and their fate in the environment are of still high interest. Most pharmaceuticals are deposited in the environment through human consumption and excretion, and are often filtered ineffectively by wastewater treatment plants (WWTPs) which are not designed to manage them. Concentration of these pharmaceuticals is quite low in the environment, but repeated exposure to these compounds can cause serious health issues and anonymous long-term impacts. Therefore, removal of pharmaceuticals from environment is a very crucial factor for reducing the risk of health hazards. Therefore, the review will move over a descriptive presentation of the various technologies for the removal of the pharmaceuticals along with the respective references. Here it is important to note that these pharmaceuticals are not regulated and any method of removal can be assumed based on the specific problem. However, this review makes a detailed analysis on the removal of pharmaceutical pollutants from the wastewater by the adsorption process.

3.1. Various technologies available for removal of pharmaceuticals

Removal of pharmaceuticals from wastewater was done using various treatment methods such as physical, chemical and biological process. Physical treatment methods involve adsorption process, electrodialysis, reverse osmosis (RO), evaporation, filtration, sedimentation [47] and flocculation. Various technologies are adopted in the removal of pharmaceuticals from wastewater such as advanced oxidation process (AOP), the basic principle of this process is that "the strongest oxidants by diffusion can virtually oxidize any compound present in the water matrix". AOP involves ozonation [48]. In AOP, ozonation is the most important and preferred method for the treatment of wastewater. The basic mechanism of ozonation is the non-selective oxidizing activity of OH radicals to eliminate the desired pollutants.

Fenton oxidation [49–51] is an important AOP method which involves iron salts and hydrogen peroxide to effect the removal of the desired pollutants. The operating mechanism of Fenton oxidation is to decompose hydrogen peroxide to generate hydroxyl radicals using several metal-based catalysts. UV treatment [52] is also an AOP method which is usually employed after biological treatment and a sand filtration in the wastewater sector. UV treatment operates on the mechanism of destructing the chemical bonds of the pollutants by direct UV light.

Biological treatment processes includes aerobic and anaerobic methods for the removal of pollutants from wastewater. Sometimes, the biological treatment alone does not suffice the removal of micro-pollutants from the wastewater. Hence it is combined with other conventional treatment methods to improve its efficiency. The best investigated method is the combination of AOP and biological treatment process [53–54]. Membrane technology is one other popular method adopted for treating pharmaceutical wastewater in various ways [55–57]. The process of employing a membrane in the wastewater treatment unit was proved as one of the most efficient treatment methods but the cost of this treatment unit was found to be high. Other method of membrane process which includes nanofiltration (NF) was involved in the pharmaceutical wastewater treatment [58,59]. Apart from the various technologies briefed above, other methods like pre-ozonation, direct photolysis, photocatalysis, and chlorination are also employed in the treatment of pharmaceutical wastewater. Chlorination has been proved as an efficient method for the elimination of pharmaceuticals such as 17α-ethinylestradiol, 17β-estradiol, 17-α-dihydroequilin, trimegestone, estriol, medrogestone, norgestrel, and estradiol valerate [60].

3.2. Adsorption process

Adsorption is the most ubiquitous process which frequently finds application in the process on the removal of trace organic pollutants from water/wastewater and it is one of the major processes involved in the removal of pollutants from the environment. In order to improve the wastewater treatment, various adsorbents have been researched and developed for the adsorption of various contaminants [61]. Sources of different types of conventional and non-conventional adsorbents available are illustrated in Fig. 1. This section of the review gives brief description and explanation about the removal of pharmaceuticals using adsorbents such as activated carbon, zeolites, carbon nanotubes and biosorbents.

3.2.1. Activated carbon

Activated carbon is a form of carbon processed to have low-volume pores which increases the surface area available for adsorption process. Activated carbons can be prepared from various carbon materials, however, the credit for developing commercial activated carbon goes to von Ostrejko [62]. Activated carbon is a conventional adsorbent has a significant role in water treatment, and it has been researched and proved that activated carbon can be used for the adsorption of pharmaceuticals from wastewater. Activated carbon can be classed as follows: (i) powdered activated carbon (PAC), (ii) granular activated carbon (GAC), (iii) bead activated carbon (BAC) is a highly spherical activated carbon with the raw material as petroleum pitch which is highly used in various wastewater treating equipment, and (iv) extruded activated carbon (EAC). The GAC is more adaptable to continuous contact process and there is no need to separate the carbon from the bulk fluid. GAC is widely used for the removal of pollutants from water. On the other hand, the usage of PAC offers some technical problems due to the separation requirement of the adsorbent from the fluid. However, despite the demerits, PAC is also used for wastewater treatment due to its low cost and lesser contact time requirements. GAC and PAC are also used for the treatment of pharmaceuticals from wastewater. Table 2 has compiled the relevant information regarding the removal of pharmaceuticals using activated carbon.

Adsorption by activated carbon is a likely technique for the removal of pharmaceuticals and endocrine

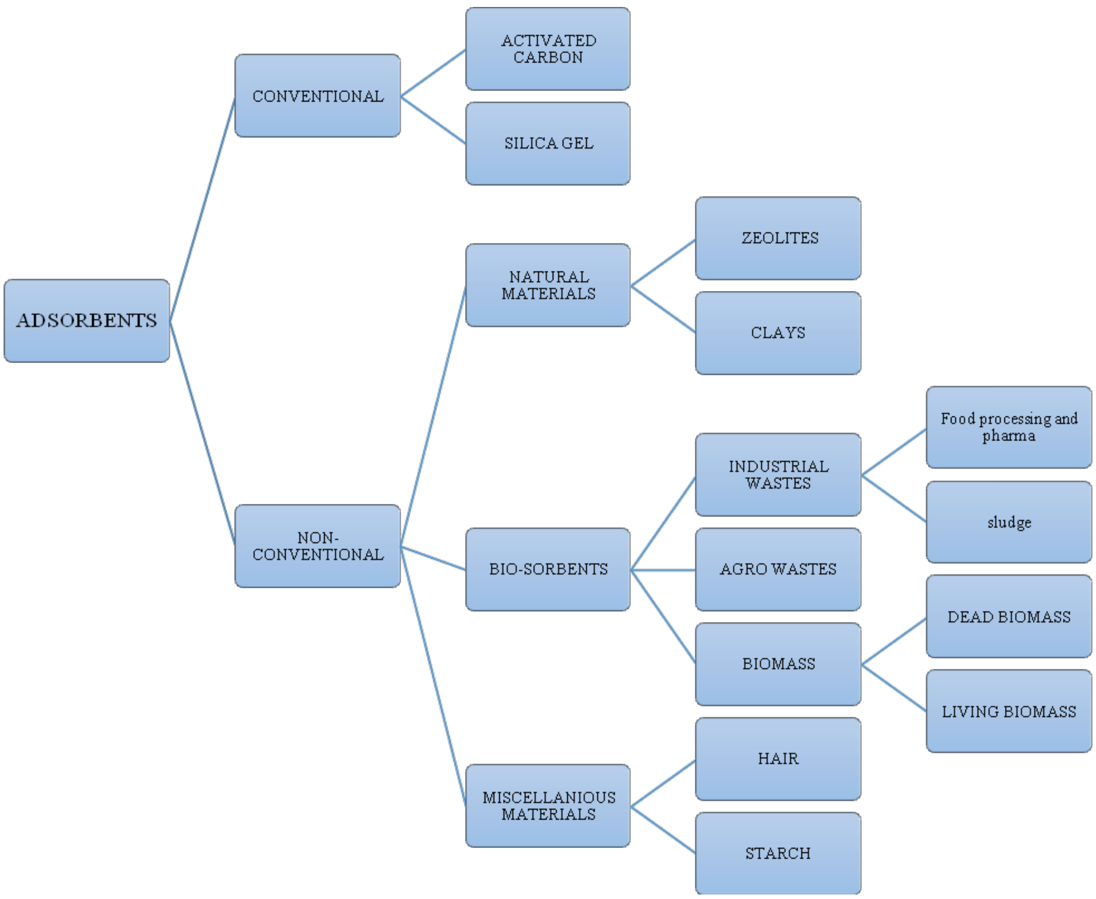

Fig. 1. Types of conventional and non-conventional adsorbents.

disrupting substances (EDS). This was previously studied and explained by Yu et al. [75]. Another similar study had already been reviewed for the adsorptive removal of pharmaceuticals by activated carbon [76]. The adsorption capacities of activated carbon to pharmaceuticals essentially depend on two important factors: hydrophobicity and charge of pharmaceuticals. It was also established that the adsorption capacity of activated carbon was in accordance

Table 2
Removal of pharmaceuticals by activated carbon

Contaminant	Adsorbent used	Initial concentration of the contaminant	Source of water sample	References
Hormone				
Estradiol	PAC	100 ng/L	Surface water	[63]
Estriol	GAC	5 ng/L	Surface Water	[64]
Anti diarrhoeal				
Lopromide	GAC	1 ng/L	Surface water	[64]
Antibiotics				
Nitroimidazole	AC a & b	50 mg/L	Aqueous solution	[65]
Sulfamethoxazole	PAC	600 ng/L	WWTPs effluents	[66]
	PAC	100 ng/L	Synthetic water	[67]
Tylosin	PAC	0.13 mmol/L	Synthetic water	[68]
Tetracycline	PAC	0.19 mmol/L	Synthetic water	[68]
Lipid regulator				
Bezafibrate	PAC	1.3 µg/L	WWTPs effluents	[66]
Gemfibrozil	PAC	100 ng/L	Surface water	[63]
Anti-infective				
Thimerosal (organic mercury compound)	GAC	0.2 µg/L	Pharmaceutical waste water	[69]
Anti-hypertensive				
propranolol	GAC	1 mg/L	Sewage effluents	[70]
Nonsteroidal anti-inflammatory drugs				
Diclofenac	PAC	100 ng/L	Surface water	[63]
	PAC	5.8 µg/L	WWTPs effluents	[66]
	PAC	100 ng/L	Synthetic water	[67]
Paracetamol	PAC	100 ng/L	Surface water	[63]
	PAC	100 ng/L	Synthetic water	[67]
Ketoprofen	ACc	19.28 mg/L	Surface water	[71]
Fenoprofen	PAC	0.1 mg/L	Synthetic water	[72]
Naproxen	PAC	100 ng/L	Surface water	[63]
	GAC	500 ng/L	Synthetic water	[73]
	PAC	100 ng/L	Synthetic water	[65]
Ibuprofen	PAC	40 mg/L	Synthetic water	[74]
Antidepressant				
Diazepam	PAC	100 ng/L	Surface water	[63]
Thioridazine	GAC	1 mg/L	Sewage effluents	[70]
Anti-cancer				
Tamoxifen	GAC	1 mg/L	Sewage effluents	[70]
Anticonvulsants				
Dilantin	GAC	1 ng/L	Surface water	[64]
Carbamazepine	PAC	100 ng/L	Surface water	[63]
	GAC	500 ng/L	Synthetic water	[73]
	PAC	2.5 µg/L	WWTPs effluents	[66]
Primidone	PAC	900 ng/L	WWTPs effluents	[66]

with the hydrophobicity of the selected pharmaceutical (Nortriptyline). In extension to the hydrophobicity and charge of pharmaceuticals, the experiments also established that the water matrix has an effect on the adsorption of pharmaceuticals by activated carbon [77,78]. During the experiments, the adsorption capacity of activated carbon to pharmaceuticals was lowered, due to the competition of organic matter present in the water with the pharmaceuticals to the binding sites of activated carbon [32]. Furthermore, in the pilot-scale experiment, the higher dose of PAC was needed to intensify the removal efficiency of pharmaceuticals that has higher molecular weight compared to others because the pharmaceuticals with high molecular weight are more sensitive to the counteraction of organic matter. Above all this, the removal efficiency of pharmaceuticals from water is affected by critical factors such as contact time, pH and structure of activated carbon [79].

A very descriptive study was published by Dickenson and Drewes for the adsorption of five pharmaceutical residues (primidone, carbamazepine, ibuprofen, naproxen, and diclofenac) by the Calgon Filtrasorb 300 powdered activated carbon [80]. The sorption performance was tested in ultra-pure and wastewater effluent organic matter (EfOM) matrices, where the further sorption process was examined in the ultra-pure water for powdered activated carbon of doses greater than 10 mg/L thereby implying the presence of EfOMs that hinders the sorption of the pharmaceuticals to the PAC surface. In this analysis, the adsorption behaviors were described by the Freundlich isotherm model. Another example of the use of adsorbent for drug removal was written by Sheng et al. [81]. It was found by Sheng et al. [81] that an integrated adsorption and filtration system was capable of eliminating the trace pharmaceutical pollutants from wastewater even effectively. Due to the reverberations caused by the weak Van der Waals forces of attraction and chemical bond formation, the pharmaceutical contaminants were adsorbed on the surface of PAC. Then the PACs are in turn filtered by ultra-filtration (UF) process that establishes a physical barrier which restrains the passage of PAC, thereby ensuring the confinement of organic matter adsorbed on PAC. The experiments proved that the log K_{ow} values were found to be higher than 3 for the studied system which provides the high pharmaceutical confinement rates during UF treatment due to the hydrophobic characteristics.

3.2.2. Carbon nanotubes

Various conventional and advanced water and wastewater treatment processes have been investigated for the removal of pollutants from wastewater by high-binding adsorbents [82] like activated carbon (AC) [83], carbon nanotubes (CNTs) [84], biochars [85], and zeolites [86]. Among them, CNTs have drawn much attention because of their unique properties and potential applications. CNTs are a hollow graphitic material composed of one or multiple layers of graphene sheets (single-walled carbon nanotubes SWCNT and multi-walled carbon nanotubes MWCNT, respectively). The length of the CNTs was varied from few hundred nanometers to several microns. The diameter differs if the nanotubes are composed of single or multiple layers. A SWCNT was ranged from 1 to 10 nm, while a MWCNT was thicker, and it was ranged from 5 to 100–200 nm [87]. Thus, effective removal of pharmaceuticals/drugs from contaminated water using carbon nanotubes is of great importance and has attracted significant attention. However, only a few recent reports on their removal by adsorption have been published.

As a result of the higher specific surface area and the larger microspore volume, CNTs are considered as superior adsorbents for the removal of pharmaceuticals. Apart from pharmaceuticals, CNTs had higher adsorption capacities for heavy metals [88,89], dyes [90], phenols [91] and other organic chemicals. Since their discovery in 1991, CNTs have demonstrated such extraordinary mechanical, electrical, thermal, and chemical properties. These quality CNTs become an important candidates for the numerous applications which includes nanocomposites, energy storage, micro- electronics, and medical devices.

Several studies projected the production of CNTs at millions of tons in 2010 and a $1 trillion worldwide market for Nano products by 2015. Additionally, the continuous mass production may provide large quantities of CNTs at economically viable prices for large-scale application in the near future. Although the cost of the CNTs was found to be higher than that of the other studied adsorbents, they are one of the most preferred adsorbents for the removal of pharmaceutical contaminants from wastewaters. Removal of inorganic and organic compounds by CNTs has been studied and reviewed [92]. However, the removal of Endocrine disrupting compounds (EDCs) and drugs by CNTs are affected by their unique properties such as size, shape, pK_a value, functional group, and hydrophobicity (typically assessed in terms of the octanol-water partition coefficient, ''K_{OW}''). Sulfa drugs are one of the most contaminating pollutants in the environment and their removal from aqueous solution using carbon nanotubes was studied [93]. The sulfa drug which includes Sulfapyridine (SPY) and Sulfamethoxazole (SMX) was studied for its removal from the aqueous solution. The adsorption isotherms have been displayed and explained in the corresponding study.

This section also provides a comprehensive analysis on the removal of various inorganic and organic wastes by CNTs [94]. Over the last two decades, either SWCNTs or MWCNTs, have formed a part of extensive and intensive multi-disciplinary research due to their superior properties and a wide range of applications over materials. In fact, they have been designated in several occasions as most investigated materials of the 21st century [84]. It is also mentioned that the EDCs removal from drinking water has attracted considerable attention because of their interference with human reproductive systems by blocking or mimicking the activity of natural hormones. It was also investigated that the adsorption of EDC from artificial seawater, pharmaceutical wastewater, or the combination thereof using SWCNTs. It was reported that the higher removal for 17α-ethyl estradiol (EE2; 95–98%) was observed as compared with the bisphenol A (BPA; 75–80%) [95]. As a result of the excellent adsorption capacity of SWCNTs, a strong linear correlation between the retention and adsorption of BPA and 17β-estradiol (E2) in ultra-filtration (UF) membrane systems blended with SWCNTs (SWCNT–UF) has also been observed [96]. Meanwhile, many works have been done for the removal of pharmaceuticals such as ketoprofen, carbamazepine, and sulfamethoxazole. Table 3 mentions the relevant information regarding the removal of various pharmaceuticals from contaminated water by CNTs. These studies were indicated that carbon nanotubes have high adsorption capacity to the pharmaceutical pollutants.

However, the adsorption capacity varies with the surface chemistry and properties of carbon nanotubes. Moreover, the physiochemical properties of the pharmaceuticals can also influence the adsorption process of carbon nanotubes. It was also investigated that the multi-walled nanotubes (MWCNTs) can effectively remove triclosan, ibuprofen, acetaminophen, caffeine, prometryn, carbendazim and 4-Acetylamino-antipyrine. The removal of PPCPs was increased with the decrease in feeding concentration. The selected pharmaceuticals were adsorbed by multi-walled nanotubes via hydrogen-bonding interaction [112]. Thus, the results were concluded that the multi-walled carbon nanotubes have been widely used in the removal of PPCPs when compared to single-walled carbon nanotubes. Recently, it was mentioned that the CNTs may also able to work as heterogeneous coagulants in the treatment of wastewaters [113]. Thus, it was known that SWCNTs exhibits a strong affinity towards many organic compounds because of their very large specific surface areas. However, a disadvantage with respect to the application of SWCNTs in the adsorption technologies was found to be high cost comparatively which ranges up to almost twice the cost of MWCNT's. Because of this disadvantage, mostly MWCNTs were used for the removal of pollutants in wastewater treatment.

3.2.3. Zeolites

Zeolites are microporous, aluminosilicate materials which find potential use in catalysis process [114] and as adsorbents. Their well-defined structures and adjustable acidity made them highly active in a large variety of reactions. Zeolites can be classified as natural and synthetic. There are over 40 natural zeolites and 100 synthetic zeolites. Some examples of natural zeolites are chabazite, clinoptilolite, analcime and natrolite. While zeolite A and zeolite Y (faujasite) are well-known examples of synthetic zeolites. Jackson et al. [115] carried out the studies on the zeolitic structure and explained the lattice energy minimization to secure structural information about the zeolites. They are being used as selective adsorbents in the recent years, out of the many adsorbents used it has been analyzed and verified that zeolites are more efficient in removing organic and inorganic pollutants from water [116–120]. This section of the review focuses on the removal of pharmaceuticals from water by the usage of zeolites.

In recent years, numerous works have been published by scientists regarding the potential use of zeolites as adsorbents for pharmaceutical pollutants. Braschi et al. [121] analyzed and verified the role of zeolite Y (faujasite) in the removal of sulfonamide antibiotics from water. In this study, in addition to adsorption kinetics, thermogravimetric analysis and diffractometric analysis have also been verified. The adsorption and desorption isotherms have been displayed and explained in the study. Rossner et al. [122] was studied on the removal of emerging pollutants using zeolites. In this research, they observed that

Table 3
Removal of various drugs using CNTs

Pharmaceuticals removed	Type of CNT	K_f (Freundlich affinity coefficient)	References
Amoxicillin	MWCNT	0.0030	[97]
	MMWCNT	0.003013	[98]
Cephalexin	MWCNT	0.3242	[99]
	MWCNT	Not provided	[100]
Diclofenac	MWCNT's	16.3	[101]
Ceftazidime	MWNT's	8.46	[102]
ofloxacin	SWCNT's and MWCNT's	Not provided	[103]
Tetracycline	MWCNT	159.92	[104]
	SWCNT and MWCNT	K_f varies according to different solution chemistry conditions.	[105]
	MWCNT	156.2 for 2.0% oxygen content at 298 K. K_f variation with different oxygen content is explained.	[106]
Carbamazepine	MWCNT	Not provided	[107]
Sulfapyridine	MWCNT	Not provided	[108]
Sulfamethoxazole	FCNT's (functionalized carbon nanotubes)	K_f varies for different SMX species at different pH values.	[109]
Non-Steroidal Anti-Inflammatory drugs (NSAIDs)	c-SWNT (carboxylated single-walled carbon nanotubes)	Not provided	[110]
Norfloxacin	c-MWCNT's	For different temperatures and pH different K_f values were found.	[111]

the adsorption process by zeolites was not as effective in the removal when it was compared with the other adsorbents. Martucci et al. [123] used high silica mordenite for the removal of sulfachloropyridazine sulfonamide antibiotic. In this study, Fourier transform infrared spectroscopy was analyzed for the corresponding adsorption and it was found that the adsorption observed was entirely irreversible in water. Synthetic zeolites such as ZSM 5 and MOR 200, two of the most hydrophobic zeolites were found to have high tendency to remove nitrosamine and pharmaceutical compounds [124], In this study, it was also found that relatively hydrophilic zeolites such as DAY and MOR 30 show lesser tendency to remove nitrosamine and respective pharmaceuticals.

Chabazite, clinoptilolite are some instances of natural zeolites which are considered as more efficient for the treatment and removal of pharmaceutical pollutants on comparison with synthetic zeolites that are discussed above. Standardized adsorption experiments were carried out to regulate the competence of SBDAC modified natural zeolite for the removal of lindane [125]. The potential use of clinoptilolite, a naturally abundant zeolite for the removal of salicylic acid, acetylsalicylic acid and atenolol was studied by Rakic et al. [126]. The results of this study indicated that the removal of salicylic acid, acetylsalicylic acid and atenolol depends on the nature of the zeolite. Attia et al. [127] investigated the adsorption of pharmaceutical compounds from aqueous solutions on synthesized magnetic nanoparticles coated zeolite (MNCZ). Pharmaceutical compounds removal efficiency by MNCZ was found to be higher than that by normal zeolites. The removal efficiency was found to be more than 95% within 10 min. In this study, the synthesis of MNCZ was also briefly explained and the pharmaceuticals used in the experiment were ibuprofen, diclofenac, and naproxen. Nezamzadeh-Ejhieh and Shirzadi [128] explained the photodegradation of tetracycline (TC) from aqueous solution. They carried out the photodegradation by doping FeO onto nano-clinoptilolite (natural zeolite) particles. Nanoparticles of clinoptilolite were obtained by ball milling of the zeolite. In this study, a photocatalytic reactor was used to bring upon the photodegradation of TC. The outcome of this study concluded that the doping of FeO on zeolite increased the photocatalytic reactivity thereby resulting in efficient degradation of tetracycline. Generally, a combination of two individual systems is more efficient in the process on the elimination of pollutants from water than a single system. Kanakaraju et al. [129] investigated and explained the role of integrated photocatalytic adsorbents prepared from titanium dioxide (TiO_2) and natural zeolite for the degradation of pharmaceutical compound amoxicillin (AMX). Similar to the photodegradation of tetracycline (TC) explained above, the degradation of amoxicillin (AMX) was carried out using a photoreactor but in this case, it was an immersion well photoreactor. This study depicted and explained the photodegradation of amoxicillin (AMX) under different conditions.

3.2.4. Biosorbents

The conventional methods of wastewater treatment such as membrane filtration, advanced oxidation, and many other methods present several drawbacks such as the formation of toxic intermediates, high cost and a large amount of energy dissipation. Among the different technologies available biologial degradation and adsorption are among the suggested eco-friendly methods. Adsorption has been proven as the most feasible method of all due to various reasons which have already been discussed in this review. The consistently used adsorbents such as activated carbon, zeolites, and carbon nanotubes have been explained earlier in this section. Even though these adsorbents have been proved as potential adsorbents for wastewater treatment, they have many disadvantages including high operating cost and requirement of regeneration after each operation cycle. Hence there is a thriving necessity for the use of low-cost alternative and economical adsorbents for the elimination of pollutants from water. Table 4 give the information related to various pollutants and the respective biosorbents to remove the pollutants from water along with author references. The complexity of regeneration process has been reduced due to various advantages of biosorbents such as low cost and high availability.

The objective of the topic is to encapsulate the existing knowledge about the removal of pharmaceutical pollutants from wastewater using biosorbents. The removal of pharmaceuticals from the wastewater can be carried out using a wide range of biosorbents including cork powder, agro waste, industrial wastes and chitosan derivatives. This section focuses on the removal of pharmaceuticals using the biosorbents as mentioned above.

3.2.4.1. Adsorbents from agricultural wastes

Agricultural wastes are lignocellulosic materials composed of lignin, cellulose, and hemicellulose. The disposal of waste materials is progressively arousing a purpose for recycling and re-utilization as these materials still consist of unused resources. A major part of this waste is usually put to use as domestic fuel and sustainable construction materials [151]. But these wastes were also find an important application in many fields including the removal of pollutants from water by replacing the commercially available high-cost adsorbents owing to the various advantages such as high availability, high carbon content and low cost. These wastes can be used for the preparation of cheap alternative adsorbents for the elimination of various pollutants such as heavy metal pollutants [152], dyes [153], pharmaceutical contaminants [154–157], and many more organic wastewater pollutants. This topic focuses on the removal of various pharmaceutical contaminants from water by alternative adsorbents prepared from agricultural wastes.

Over the past few years, many researchers have analyzed the potential use of agro wastes for the elimination of pharmaceutical pollutants such as anti-inflammatory drugs (ibuprofen, diclofenac, naproxen), antibiotics (ciprofloxacin, sulphamethoxazole, tetracycline) and other drugs such as paracetamol, pramipexole. Many researchers studied and explained the removal of several antibiotics from water by activated carbon prepared from various agro wastes. Chayid and Ahmed have prepared the activated carbon from *Arundo donax Linn* (Giant Reed) for the removal of Amoxicillin (AMX) antibiotic [154]. The adsorption isotherms were studied by using

Table 4
Removal of various pollutants from water by corresponding bio sorbents

Pollutants	Bio-sorbents	References
Heavy metals		
Copper	Cashew nut shell	[130]
Copper	fishtail palm Caryota urens seeds	[131]
Lead and nickel	*Rhizoclonium hookeri*	[132]
Lead, nickel and chromium	*Rhizoclonium tortuosum*	[133]
Chromium	Dunaliella Algae	[134]
Chromium and nickel	Mixed biosorbent (custard apple seeds and *Aspergillus niger*)	[135]
Lead	Cashew nut shell	[136]
Dyes		
Congo red dye	Raw date fruit waste	[137]
Methylene blue dye	Saw dust	[138]
Methylene blue dye	Orange peel	[139]
Pharmaceuticals		
Paracetamol	Cork powder	[140]
Ibuprofen	Granulated cork	[141]
Penicillin G	Rhizopusarrhizus	[142]
Dorzolamide	Chitosan nanocomposite	[143]
Sulfonamides	Activated sludge	[144]
Phenolic pollutants	Rubber seed coat	[145]
1 butyl 3 methyl imidazonium chloride	Biochars	[146]
Pharmaceutical pollutants	Lignocellulosic materials	[147]
Pharmaceutical pollutants	Bentonite	[148]
Metronidazole(antibiotic)	Siris seed pods	[149]
All types of pollutants (pharmaceutical, heavy metal and dye pollutants)	Agro waste such as saw dust, palm fibers	[150]

the Langmuir, Freundlich, and Sips equations. These isotherms were analyzed and displayed for the corresponding adsorption of AMX. This study was also examined the suitability of *Arundo donax Linn* for the adsorption process. It was found that the adsorption capacity of AMX was increased from 277 to 345 mg/g with an increase in temperature. The activated carbon from lignocellulosic biomass (*Albizia lebbeck* seed pods) was prepared to remove the fluoroquinolones antibiotics (Ciprofloxacin (CIP) and Norfloxacin (NOR)) from water [155]. In this study, the apt equilibrium adsorption data for both the antibiotics was found to be Langmuir isotherm. It was reported that the NOR was adsorbed in larger amounts compared to CIP. Antibiotic CIP can also be eliminated from wastewaters by using chemically prepared carbons synthesized from date palm leaflets through sulphuric acid carbonization [156]. The chemically prepared carbon from date palm leaflets was found to be more efficient in the removal of CIP than in the previous case. The AC prepared from *Albizia lebbeck* seed pods can also be applied for the removal of cephalexin [157]. It was found that *Albizia lebbeck* seeds showed higher efficiency towards the removal of cephalosporin antibiotics like cephalexin. In this study, the adsorption process was found to follow pseudo-second order kinetics and all the adsorption data was represented by Langmuir isotherm model. Another constantly appearing pharmaceutical contaminant in the environment is Metronidazole antibiotic whose elimination from wastewater was also explained by Ahmed and Theydan [155]. Similar to the previous cases, Langmuir isotherm model was adopted to represent the adsorption data for the process. Zhanguang Liu et al. [158] explored and published about the biosorption of chlorofibric acid (CA) and carbamazepine (CBZ) by agricultural waste rice straw. In this study, the adsorption process followed the pseudo-second order kinetics. It was also reported that the adsorption isotherms of CA and CBZ by biosorbents was best obeyed with Frieundlich model. They also determined that the solution pH was the most important factor for CA adsorption. Kyaz and Deliyanni [159] studied the use of potato peel for the preparation of activated carbon and it was used as a green environmental-friendly adsorbent for the removal of dorzolamide and pramipexole. The adsorption and desorption of these two drugs have been displayed and explained in the study as a function of pH and contact time.

Some agricultural wastes such as cocoa shell, wheat barn, and bamboo wastes are involved in the preparation of low-cost adsorbents for the removal of anti-inflammatory drugs. Antunes et al. [160] examined and explained the removal of diclofenac by Isabel grape bagasse. The adsorption process was best explained with the pseudo-second order kinetics and Freundlich isotherm model. This study shows the adsorption and desorption isotherms of diclofenac on grape bagasse. Activated carbon prepared from olive waste cakes are used for the adsorption of ibuprofen, ketoprofen, and diclofenac from the water system [161]. The adsorption data fitted both Langmuir and Freundlich isotherm models and the report indicated that the process followed pseudo-second order kinetics. Mukoko et al. [162] explained the elimination of drugs such as ibuprofen and aspirin by rice hull activated carbon. In this study, it was found that the AC prepared from rice hull was efficient as compared with the other biosorbents for the removal of the respective pharmaceuticals from wastewater. The experimental data of adsorption fitted with the Freundlich isotherm model and the process followed pseudo-second order kinetics. Besides these several other agricultural wastes such as tea and coffee wastes, the waste from coconut, corncob waste and much more can also be adopted for the removal of pharmaceutical contaminants from the wastewater system.

3.2.4.2. Adsorbents from cork powder and granules

Silva et al. [163] published the details about the occurrence of cork in the outer bark of the tree botanically known as *Quercussuber L.* Based on the origin there are different types of cork produced namely grinding powder from granulation, the cleaning powder and the finishing powder from cut and sanding operations. Villaescusa et al. [140] studied and published about the potential use of vegetable wastes such as cork bark for the removal of paracetamol from water. Adsorption isotherm of paracetamol on the respective adsorbent was given as a proof of the experiment and the kinetic results of paracetamol sorption were explained. The removal of consistently used drug ibuprofen from water was reviewed and the results were published by Mestre et al. [164]. In this study, the capabilities of low-cost highly porous activated carbons, obtained from cork powder, for the removal of a widespread used drug (ibuprofen) were investigated. The adsorption kinetics for the respective pollutants on the corresponding biosorbent was analyzed and explained briefly and the kinetic results were given in the study.

Removal of another consistently occurring pollutant in the environment was of clorofibric acid. This clorofibric acid is a precursor for the several drugs such as antibiotics, antidepressants [165]. The removal of clorofibric acid was carried out by using the cork based activated carbon. The results was analyzed and explained for the adsorption isotherms on the activated carbon prepared from cork powder. The removal of chlorofibric acid was mainly influenced by the pH of the solution.

3.2.4.3. Adsorbents from chitosan and chitosan derivatives

Chitosan is a linear polysaccharide composed of randomly distributed β-linked D-glucosamine and N-acetyl-D-glucosamine. Chitosan was manufactured commercially by deacetylation of chitin, a biopolymer available in nature. Among several biowaste materials, chitosan is one of the most preferred biosorbents for many pollutants such as heavy metal [166], pharmaceuticals and dyes. Chitosan has been utilized effectively in drug delivery systems and it is a renowned carrier for pharmaceutical drugs [167,168]. Kyzas et al. derived a grafted chitosan nanocomposite and it was used for the removal of the pharmaceutical compound (dorzolamide) from biomedical synthetic waters [169]. Modified chitosan cross-linked with glutaraldehyde and grafted with sulfonates were incorporated and reviewed as economical adsorbents for the elimination of pharmaceuticals from water. The pharmaceutical that was selected as the representative compound for this study was pramipexole dihydrochloride (PRM) [169]. This study also explained the adsorption kinetics of PRM. This study indicated that environment-friendly modified chitosan adsorbents are efficient than commercially developed adsorbents for the removal of pharmaceutical pollutants from water.

3.2.4.4. Adsorbents from industrial wastes

Since the start of industrial revolution, there has been a major crisis due to the production of a large amount of waste materials every year. Of this large quantity, only a small percentage is put to proper usage while the rest is left un-handled and dumped elsewhere. A major portion of these wastes is generally used for the production of construction materials [170] but they also have a significant role of replacing commercial adsorbents by low-cost alternative adsorbents in the field of wastewater treatment by the elimination of various harmful pollutants. Industrial wastes can be used for the elimination of heavy metal pollutants [171], pharmaceutical pollutants and dyes [172]. This topic focuses on the removal of various pharmaceutical contaminants from water by alternative adsorbents prepared from industrial wastes. In the past few years, a number of industrial wastes have been investigated and developed for the removal of pollutants from water considering the various benefits of these wastes such as high adsorption tendency, high availability and almost free of cost. Among the various industrial waste materials considered for the purpose of wastewater treatment fly ash is one of the most abundantly available and highly preferred for the elimination of pharmaceutical contaminants from water. The major solid waste materials produced as a byproduct of the thermal power plants is fly ash. Fly ash, also known as "pulverized fuel ash", is one of the coal combustion products, composed of the fine particles that are driven out of the boiler with the flue gases. Maheshwari et al. [173] established research studies for the removal of a class of drugs called quinolone antibiotics by adsorption on coal fly ash. The ciprofloxacin hydrochloride (CPH) was used as a pharmaceutical contaminant in this research. They carried out batch adsorption experiments to study the effect of various viable parameters such as pH, contact time, initial concentration and temperature. The removal of CPH by coal fly ash was found to be 48.89%. More studies were carried out for the removal of the consistently used antibiotic CIP from wastewater using fly ash. Zhang et al. [174] examined and explained the ability of modified coal fly ash to eliminate the antibiotic ciprofloxacin from the wastewater. This experiment pointed out the usage of modified fly ash is far more advantageous than using the unaltered fly ash due to the enhanced properties and better adsorption characteristics. This study displayed and explained the adsorption isotherms of ciprofloxacin.

This report indicated that the adsorption process was influenced by initial CIP concentration and contact time. The adsorption data fitted well with the Langmuir isotherm model. Fly ash is also considered as effective sorbent for the removal of other pharmaceuticals such as pentachlorophenol which is an organochlorine compound that is productively used as a disinfectant [175]. Due to their high toxicity and carcinogenicity chlorophenols and their derivatives are considered as one of the critically polluting groups in the environment. The report indicated that the average sorption capacity for pentachlorophenol (PCP) was 2.5 mg/g.

Numerous wastes such as sludge (tar sludge, acid sludge), coal dust and slag are produced in large amounts by steel industry over the recent years. These wastes are also investigated as adsorbents for the removal of various pollutants from water. As discussed earlier chlorophenols and their derivatives being comparatively more toxic than other pharmaceutical contaminants, their removal is a prerequisite for reducing the harmful effects caused to the environment. Apart from the usage of fly ash for the removal of chlorophenols and its derivatives, several other industrial wastes such as blast furnace slag, sludge from steel industry are also used for the elimination of these pollutants [176]. In this study the adsorption isotherm for the chlorophenol derivatives are clearly depicted and explained. The adsorption process for this study followed the pseudo-second order kinetics and the data fitted with Langmuir isotherm model. Rui Ding et al. [177] analyzed the sewage sludge and waste oil sludge derived materials as potential adsorbents for the removal of antibiotics from water. In this study, the concurrent retention of eleven antibiotics and two anticonvulsants were inspected through batch adsorption experiments. This study shows the examples of adsorption isotherm for few of the antibiotics used in the experiment. Jossa et al. [178] examined and published the results on the removal of pharmaceuticals from wastewater system by adsorption onto sludge which behaves as a potential adsorbent. The seven pharmaceuticals along with some other compounds were considered for the experiments. Gobel et al. [144] used activated sludge to check its adsorption behavior for sulfonamides, macrolides, and trimethoprim. The sorption constants were estimated and the analytical methods were also investigated. Further studies were carried out regarding the usage of activated sludge for the removal of specific pharmaceutical contaminants. Urase and Kikuta [179] investigated about the removal of pharmaceuticals like ibuprofen by using activated sludge. The report indicated that adsorption capacity was increased with a decrease in pH.

Red mud, a solid waste from aluminum industry was explored as a potential adsorbent for the removal of chlorophenols and their derivatives were studied by Gupta et al. [180]. Aside from effects of contact time, particle size, temperature; the status of adsorbent on the removal of chlorophenols was also investigated. Xu et al. [181] determined the application of cobalt-modified red mud integrated with catalytic ozonation process for the degradation of bezafibrate which is a fibrate drug used for treating hyperlipidemia. At the end of the experiment, it was quite significantly proved that integrated system was more efficient in the removal of the drug than a single system adopted. In this study, cobalt doped red mud was investigated as a catalyst for the removal process. Besides the industrial wastes discussed, there are several other wastes used for the removal of pollutants from wastewater such as coke dust, waste muds, waste from cement industry and much more.

4. Future prospects

The typical wastewater treatment process cannot adequately remove the pharmaceuticals and endocrine disrupting substances. These may occur regularly in domestic and industrial wastewater or can also be present in the irregular levels which depend upon their production in the particular facility. Adsorption process has been proven as one of the best and economical methods of treating pharmaceutical wastewater and a great deal of funds and research time has been invested in the development of contemporary techniques for the adsorption of pharmaceuticals from wastewater. The review work described different forms of an effective basis and reference for the future model development and investigation into the removal of pharmaceuticals from wastewater by adsorption process. Although adsorption is one of the most preferred wastewater treatment methods, there are lots of problems faced by the industrial society in modern age. For instance, regeneration of adsorbents used for the purpose of treatment is a major drawback faced. Regeneration by hydrothermal technology or electrochemical regeneration can be adopted for activated carbon. Zeolite, a source of low cost resources can be used as effective adsorbents for various pollutants. This can be regenerated by Fenton oxidation or high temperature combustion. Correspondingly, regeneration and recovery methods vary for different adsorbents under different conditions.

There has been a precipitous upsurge in the process of combining more than one technique for improvised removal of pharmaceutical pollutants. As we all know that the adsorption process using activated carbon was one of the most favored adsorbent and which was universally selected for the removal of all kinds of pollutants. This adsorption method can be integrated with the biological treatment for the removal of pharmaceutical pollutants such as carbamazepine and so on. However, despite the several techniques are available, complete elimination of pharmaceuticals from the environment using adsorption process was definitely not possible. Moreover, the prevailing record shows that no single technology can remove pharmaceuticals thoroughly. Very few works have been researched and described for the treatment of wastewater containing organic mercury compound thimerosal which is an antiseptic and antifungal agent polysulphide treated with coconut husk can be used as an effective adsorbent for the removal of thimerosal. One of the major problems encountered in current scenario is the cost and the availability of adsorbents. Not only conventional adsorbents like CNT or zeolites but also some of the biosorbents like siris seeds, almond shells and so on can also be used. Hence other materials which are easily available and cheap as well were found to operate as alternative adsorbents. These adsorbents are termed as miscellaneous adsorbents. Miscellaneous adsorbents like hair, starch and many others are used for the removal of certain pollutants like heavy metals and dyes. Hence it can also be used for the removal of pharmaceutical pollutants.

5. Conclusion

Medicine is one of the major fields in people's day-to-day life in which pharmaceuticals have started to have revolutionary impact. But their presence in the effluents is a major source of pollution in the environment. Wastewaters due to industrial and domestic applications both contain various organic and inorganic pollutants that include PPCPs, EDCs and heavy metal pollution. Thus, their removal from the wastewaters is of great importance to the environment. The major conclusions that can be drawn from this work have been summarized as below:

- This review points out the various analytical methods and removal technologies available for the detection and elimination of pharmaceuticals in the wastewater.
- Several advanced analytical methods have been developed and optimized over the years for the detection of various frequently occurring pharmaceutical pollutants such as Carbamazepine, ibuprofen, paracetamol and much more.
- Chromatographic methods like thin layer chromatography (TLC), high-performance liquid chromatography (HPLC), Gas chromatography and spectroscopic analytical methods like NIRS and NMR have specifically been studied in this review.
- It has been proven to an extent that adsorption process is far more superior to other technologies available for the removal of pharmaceuticals.
- The adsorption of various pharmaceuticals on adsorbents including activated carbon, carbon nanotubes, zeolites and bio-sorbents was investigated.
- Pharmaceuticals like ciprofloxacin, carbamazepine and several others have approximately higher pollution factor than the other pollutants, their removal using the specified adsorbents have been discussed.
- Out of the mentioned adsorbents, it was clearly depicted by various results that adsorbents from wastes and biosorbents are comparatively more preferred for the removal process than the other adsorbents.

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