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INVITED REVIEW PAPER

Sources and impacts of pharmaceutical components in wastewater and its treatment process: A review

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Abstract−Pharmaceutical compounds and their derivatives are major pollutants in the environment, as their metabolites affect the terrestrial as well as aquatic organisms in one or another way. In recent times, many papers have discussed the treatment procedures for single pharmaceutical and mixture of pharmaceutical components, but only few papers have discussed the fate and the exposure of pharmaceutical contaminants in our environment. In this paper, we discuss the sources and the forms of pharmaceutical products and their resultant in the environment and their addition to the microbial and to human communities. A detailed discussion of various treatment techniques from conventional to current techniques, their advantages and disadvantages is given here. Researchers are finding the techniques in order to completely degrade the contaminants and their transformed products from the environment. Among the technique,s nanotechnology was found to be an efficient technique, and the combination of nanotechnology with other conventional technologies gives higher removal efficiency.

Keywords: Derivatives, Metabolites, Exposure, Contaminants, Nanotechnology

INTRODUCTION

In the 21st century, the mortality rate has been reduced gradually due to advancements in the pharmaceutical sector. The commonly used antibiotics can be categorized under common names based on their chemical structure, namely tetracycline, aminoglycosides, macrolides, sulfonamides [1,2]. Tetracycline is mainly used as antibiotic in animal feed [3,4]. These types of components are introduced to the environment as a result of medical and veterinary use and they are environmental contaminants. In our environment by one or the other way the concentrations of contaminants are available [5-7]. Around 2300 active pharmaceutical ingredients [API] in human medicine are found to be toxic and bio accumulative. The leading roles are played by veterinary components, traces of which are often found in surface water, soils etc. In some cases ground water also is affected in major amounts. Antibiotics such as tetracycline, norfloracin are found to be electrostatically negative charged [8,9] and pharmaceuticals such as sertraline and fluoxe-

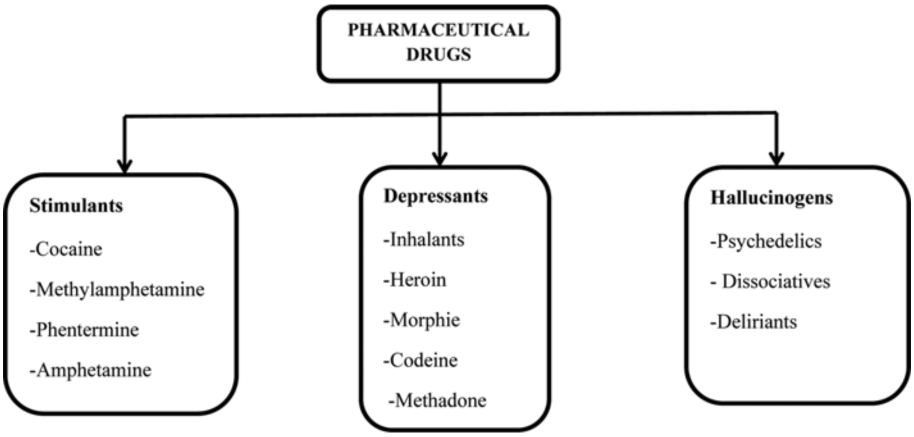

Fig. 1. Major classification of Pharmaceutical components (Source: Ceida, http://www.ceida.net.au/aboutus.asp).

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Table 1. Characteristics and specification of standard drinking water

S. No	Essential characteristics	Requirments	Permisible limt	Undesirable effects
1	pH	6.5 TO 8.5	No relaxation	If changes occurs basic or acidic nature predominates
2	Colour (Hazen units)	5	25	Consumer acceptance decreases
3	Taste	Agreeable	-	-
4	Turbidity (NTU)	5	10	Consumer acceptance decreases
5	Odour	Unobjectionable	-	Tested at heat and cold conditions
6	Total hardness (mg/L)	300	600	Adverse effects to domestic use as well as to living beings
7	Electrical conductivity (μS/cm)	0.7	25	It depends upon the saltiness in water
8	Chloride (mg/L)	250	1000	After this limit corrosivity, palatability are affected
9	Dissolved solids (mg/L)	500	2000	Gastro intestinal effects, palatability decreases
10	Calcium (mg/L)	75	200	Hyperparathyroidism
11	Magnesium (mg/ L)	30	100	Diarrhea, nausea
12	Chloride (mg/L)	250	1000	Increases blood pressure
13	Copper (mg/L)	0.005	1.5	Hypertension,premensturnal tension, childhood hyperactivity and autism
14	Iron (mg/L)	0.3	1	In overloaded condiotn leads to cancer
15	Manganese (mg/L)	0.1	0.5	Increases results in imparedmemeory, Pshychiatric illness, Loss of appetite
16	Sulphates (mg/L)	150	400	Diarrhea and dehydration
17	Nitrates	45	No relaxation	Blue baby syndrome
18	Phenol	0.001	Relaxed upto 0.002	-
19	Mercury	0.001	No relaxation	Muscle weeknes, Impairment in speech, hearing and movement
20	Chromium	0.05	No relaxation	Causes allergic dermatitis when the dosage increases
21	Cadmium	0.01	No relaxation	Gastro interstainal disturbance, nausea, abdominal cramps
22	Selenium	0.01	No relaxation	Diarrhea, finger nail weakening
23	Arsenic	0.5	No relaxation	Damages skin, pigmentation change
24	Fluroide	0.6 to 1.2	1.5	Below 0.6 and above 1.5 it shoud be rejected

Source: Indian standard drinking water - specification (First Revision) IS-10500:1991. BIS, New Delhi, India

tine used for the treatment of central nervous system are lipophilic, and stimulants such as anti-inflammatory drugs are found in sludge due to high mass load [10,11]. Wild life is affected to the great extent due to pharmaceutical compounds like antibiotics, anti-cancer drugs, non-steroidal drugs, beta blockers, lipid regulators, anti-inflammatory drugs etc., and the research on human life based on pharmaceutical waste has been inadequate. The major classifications of pharmaceutical drugs are given in Fig. 1.

1. Sources of Pharmaceuticals in Water

Water as the main abundant resource covers 70 percent of the planet and also in the form of rainwater, polar ice caps, in clouds and also in air. It is essential for all forms of life and makes a two-to-three ratio in our bodies. The world level distribution of water area is as follows: 97 percent covered by ocean and 2.53 percent covered by fresh water, and particularly in fresh water 0.01 percent is found on the surface, 0.76 percent is as ground water and remaining 1.76 percent is glaciers and ice caps. Increase in population and improper use of natural resources has a major impact on the aquatic environment. Water bodies are under threat by rapid industrialization and urbanization. Due to industrialization and deforestation in Maharashtra, India there was no rain for three years; not only in Maharashtra but in many parts of the world water crises are seen in a large extent. Since there are no scientific findings for artificially making of water resources, we are pushed to treat the used or polluted water in the environment. The characteristics and specifications of standard drinking water are listed in Table 1. In India many water resources are polluted due to religious practices, improper agricultural practices, urbanization, and industrialization. Water pollution is a form of environmental degradation when the pollutants enter directly to the water bodies. Entire biosphere is affected by water pollution. Plants and animals which make their living in water bodies as well as the organisms which depend on water are also affected; the individual species alone is not merely affected, but also the biological community to larger extent. Table 2 illustrates the polluted rivers around India and sources of pollution. Drugs in water are considered as one of the source for water pollutants. Many researches have uncovered that feminization in fish has been altered so that the female-to-male ratios in fishes were increased. It is not clear to the point that whether female fishes change to male fishes or male fishes change to female; according to Norris, male fish react with estrogen and additionally female tissues are grown to male fish. During a census male fish were counted as female fish. Antidepressant medications also affect the brain of the fish and the number of inter-sex

Table 2. Some of the polluted river's in India and it's polluted sources

Name of river	Flowing state	Reason for pollution
Bharalu Kalong	Assam	Guwahati sewage nagaon sewage
Yamuna	Delhi	Industrial & Domestic waste from delhi
Sabarmati Amlakadhi Daman Ganga	Gujarat	Discharge from Meshwa & Ahemdabad Industrial & Domestic waste from Ankeshwar Industrial & Domestic waste from Daman, Vapi, Salvas & Kachigeon
Ghagar Markanda Western Yamuna canal	Haryana	Industrial & Domestic waste from Patiala, Derabassi, Sirssi Industrial & Domestic waste Yamuna nagar Industrial & Domestic waste
Sukhna	Himachal Pradesh	Parwanoo sewage
Khan Chambal	Madhya Pradesh	Indore sewage Industrial & Domestic sewage from Grasim township & Nagada
Bhima Godhavari Mula&mutha Pawana indrayani Koyna Mithi Kundalika	Maharashtra	Pune & Daunt sewage Nasik sewage City sewage of Pune Pune sewage Pune sewage Karad sewage Mumbai Roha sewage
Sutluj Ghaggar	Punjab	Sewage from Ludhiana & Jalandhar Municipal & Industrial sewage from Patiala, Chandigarh
Adayar Coovum Cauvery	Tamil Nadu	Chennai industrial & municipal wastewater Chennai industrial & municipal wastewater Erode sewage
Yamuna Hindon Western kali Kali nadi eastern	Uttar Pradesh	Sewage from Agra, Mathura, Bateshwar, Vrindhavan & Etawah Effluent from muzaffarnagar, Ghaziabad & Saharanpur. Sewage & Industrial effulent from Muzaffarnagar & Mansoorpur. Industrial effluent from Meerut, Modinagar, Hapur.

Source: Polluted river stretches in India, Central Pollution control Board

ratio of frogs were increased in urban areas due to pharmaceutical waste [12,13]. Kathryn Arnold, University of New York, who edited a special issue of the journal "Philosophical Transactions of the Royal Society B" gives detailed information regarding benefits of different pharmaceutical products and their environmental risk; and the research published in September revealed that "Half of the wild animals are wiped out for the past 40 years." Another study revealed by Karen Kidd, University of New Brunswick, showed that synthetic estrogen used in the birth control pill wiped out fathead minnows in lakes used for experiments in Ontario, but also seriously affected the whole ecosystem. Professor Joakin Larsson, at the University of Gothenburg, found that "drugs in the effluent may even exceed those found in the blood of people taking medications." Use of birth control pills and postmenopausal treatment, estrogens that women produce naturally, limitations in bulk purchase of medications, and proper drug disposal are to be kept in mind by the users before ongoing medications. The new report was filed by Environmental charity CHEM Trust naming "Pharmaceutical in the Environment: "A growing threat to our tap water and wildlife". Highlighting that pharmaceuticals are polluting rivers, harming birds and animals. Federal Resource Conservation and Recovery Act (RCRA) and State Dangerous Waste Regulations (WAC 173-303) suggested some of the hazardous substance and their toxicity, corrosivity, ignitability, reactivity are mentioned in this act, and it is mentioned that they are not to be used for any purpose. The manufacturing sector of pharmaceuticals has been increased due to invasion of new type of viruses, bacteria etc. To overcome these kinds of single as well as multi cell organisms, new types of drugs have been discovered to safeguard living beings.

Pharmaceutical advancement plays a major role in population growth. Pharmaceuticals and their derived compounds reach water resources by direct as well as indirect means. The excreta from humans as well as animals is considered to be the main source of pollutants; as it is an indirect pollutant, its contribution may be in smaller level, but the transformed components are very difficult to identify from the digestive systems. The source, treatment process up to the final stage in pharmaceutical wastewater is given in Fig. 2. After consumption of drugs once it reaches the sewage tank and

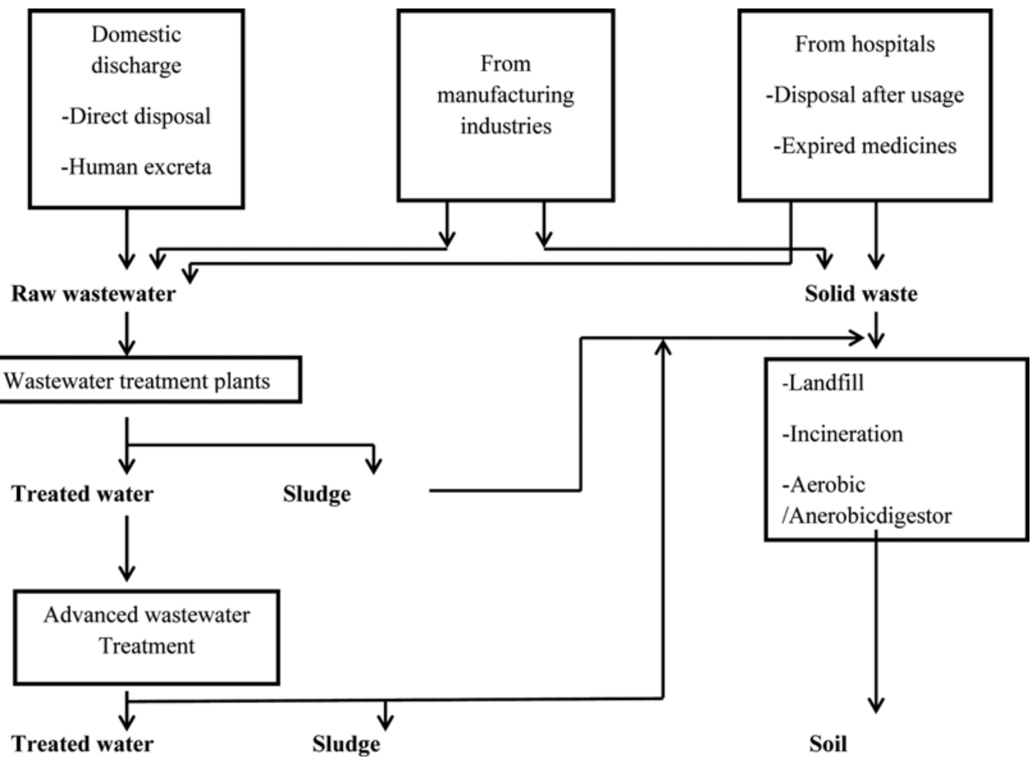

Fig. 2. The sources and the general treatment pattern for pharmaceutical wastewater.

connects with the water treatment plants, we cannot assure proper removal of all types of impurities. Waste water treatment plants are generally comprised of physical, biological and chemical impurities. Different treatments are carried out for the removal of different states, for example, for removing biological components in waste water biological organisms has to be introduced into the system. Generally, water treatment plants are not designed to deal with particular types of chemicals. General treatments are followed while dealing with wastewater treatment plants. Pharmaceutical products and their derivative chemicals affect the water in which they make contact and in due course of time the soil gets polluted. Improper disposal of expired as well as unused medicines affects soil as well as water surface. Release of pharmaceutical products in case of accident during manufacturing and distribution sector contributes the major amount of pollution to water bodies as well as to the environment [14-21]. After conception of pharmaceuticals, certain amounts enter to the body. The quantity depends on the effectiveness of the concerned pharmaceutical products.

2. Occurrences in the Environment

2-1. Water Pollution

Pharmaceuticals are generally seen in surface water. Generally, water is mainly classified into three types: ocean water, fresh water and estuaries. Florida department of Environmental Research names estuaries as "The cradle of the ocean." The land where fresh water and saline water meets is technically known as an estuary. Estuaries are known as nurseries for the ocean living habitat and as connecting point for sea trade and industrial activities; it has been noted that 23% of the population lives in the coastal areas of 100 kilometer distance. Gironde estuary is known as one of the famous estuaries in Europe, by a study conducted to prove that estuaries pave the way for transfer of pharmaceutical containments from land to sea. A total of 52 pharmaceuticals were studied for one year. Among the 52, 36 pharmaceuticals and their concentrations were identified [22]. The components like ibuprofen, ciprofloxacin and chlorophenols were tested using freshwater algae *chlorella vulgaris*. Toxicity ranges are decreased from chlorophenols> ibuprofen>ciprofloxacin. Compounds like autoaminophen, salicylic acid, ketoprofen, carbamazepine, ibuprofen and fluoxetine were studied from collected samples of two types of ground water from Portugal. Among them, salicylic acid, ibuprofen, ketoprofen and carbamazepine were found in both samples with 100% of detection frequency. Twenty-four pharmaceutical compounds were examined in tidal cycles at Yangtze River, China; pharmaceuticals were found to be increased with increase in dissolved organic carbon (DOC). It is suggested that DOC be a carrier for pharmaceutical compounds [23-25]. Chemicals enter into water in the form of drugs that we swallow. Our bodies metabolize certain amount of drug and the remaining drugs are mixed into water in the form of feces and urine to our environment. Pharmaceuticals and personal care products and hormones are found in surface and ground water [26-30]. A number of studies have reported that many pharmaceutical components are found in aquatic systems. Sulfonamides are widely used antibiotics for both human and veterinary medicine. As their soil sorption capacity is weak, sulfonamides percolate inside ground water [31]. Pharmaceutical compounds and their metabolites are found to be in low concentrations in fresh water environment. Several studies have examined aquatic organisms and some traces of pharmaceutical compounds and identified their derivatives. Bioaccumulation factors of 2.2 and 12.6 were found in the algae naming *crustacean*, *thamnocephalusplatyurus* due to the drug carbamazepine [32]. Another study revealed that the accumulation of fluoxetine in snails was found to be 3000 [33,34]. The exposure of goldfish over 14 days concentration of gemfibrozil resulted in plasma bio concentration of 113 [35]. In Eurasian perch fish, the oxazepam concentration was found to be 12 [36]. Studies have attempted to model the toxicity mixtures of β-Blockers and non-steroidal anti-inflammatory drugs. This model was not as much realistic to approach realistic scenarios [37]. Aquatic organisms are the indicators for knowing the information regarding toxicity in the aquatic environment and offer information towards regulatory measures. Eutrophication and algal blooming are considered to be immediate indications on the surface of water due to the interventions of pollutants in water bodies. As a result, sunlight will not pass through the water, so photosynthesis does not occur and finally the food web gets affected. A research paper published in environmental science and technology suggested that activated sludge treatment alone is not sufficient to remove pharmaceutical components. In combination with traditional treatments reverse osmosis, electrochemical treatment, advanced oxidation processes are used.

2-2. Soil Pollution

Soil, whether polluted or unpolluted, contains some variety of compounds naturally. Exceeding limit causes pollution in the soil. There are two types of pollution: anthropogenic and natural. Environmental conditions also play a major role in degrading the contaminants. When the pollutants reach surface water, and due to prolonged exposure the soil beneath the polluted water is affected. The soil bacteria, namely *collembola*, was affected by veterinary products, namely fipronil and fluzuaron, and the reproduction of *collembolan* was affected by pharmaceutical compounds like ivermectin and closantel [38]. There is a research paper which evidences the transport of pharmaceutical compounds from surface water to ground water where soil material is attenuated. Soil has been degraded due to pharmaceutically transformed products due to chemical transformation of parental compounds [39,40]. Pharmaceutical compounds have been transformed mainly due to sunlight exposure and other external forces; the transformed products were to be more persistent and more toxic [41,42]. The accumulation of pharmaceutical compounds in invertebrates like earthworms induces chemically transformed pharmaceutical products into the food web where earthworms are basic food for next level predators via biomagnification or bioaccumulation. The study was focused on single soil type with *eiseniafetida* (Earthworm) and another study has been done using one basic (fluoxetine), one acidic (diclofenac) and two neutral compounds (carbamazepine and orlistat) [43-46]. In veterinary industries sulfonamides are frequently used in medicine, and it has been found that from animal burial sites, as a leachate from wastewater treatment plants, once it comes to contact with soil it percolates inside the ground water and water gets polluted. Soil sorption depends on pH, ionic strength, clay content, organic matter, cation exchange capacity [47-49]. Seven pharmaceuticals half-lives were tested in 13 different soils; among all pharmaceuticals carbamazepine was found to be more stable followed by clarithromycin, trimethoprim, metoprolol, sulfamethoxazole, atenolol. The persistence of pharmaceuticals in soil depends on soil type [50]. Gadolinium has been used as contrasting agent for MRI and roxarsone [arsenic based compound] used as food additive for the poultry industry; it was found that the mobility of these compounds and their salts are affected by the soil type. Gadolinium was found to be stable and it was found in groundwater up to few kilometers [51]. For the four antidiabatic pharmaceuticals glimepitide, glibenclamide, gliclazide and metformin, the behavior of these compounds was tested using three different soils [52]. Avermectins are antiphrastic drugs which are made to absorb on soil pores; when the concentration increases the pores are filled with avermectins so that the concentrations will move deeper towards soil layer [53]. For pharmaceutical compounds clofibric acid, ibuprofen, naproxen, triclosan, diclofenac, biphenol behavior is seen in US agricultural soil along with reclaimed wastewater; the adsorption affinity was found to be in the following order: triclosan>biphenol>clofibric acid>naproxen>diclofenac [54]. Decline in radioactivity was observed in a wide range of soils due to diclofenac and carbamazepine. Our environment comprises a wide range of ionizable chemicals. The presence of pharmaceutical sediments in solid phase depends on sorption of solids [55]. To improve the desorption capacity from the soils and to remove the bioavailability of pharmaceutical compounds from the soil, various enhancement agents such as co-solvents and surfactants are added to the soil; moreover the added solvents reflect environmental hazards [56,57]. Research in Canada states that diclofenac (DCF) reaches agricultural soils, and in Israel diclofenac showed slower mobility in organic rich agricultural soils and higher mobility in fresh water. DCF did not show any toxic effects on earthworms like other pharmaceutical compounds, and risks are seen on soil microbes and it does not show any harmful effect on plant growth [58,59]. Many papers are studied over the pharmaceutical components like estrogen and anti-inflammatory drugs which are deposited as drugs and finally transformed into soil [60,61]. The USGS scientists monitored the sites with reclaimed water. The soil samples were taken before and after treatment on a monthly basis. It was found that the components like erythromycin, carbamazepine, fluoxetine and diphenhydramine were seen in soil and several compounds traveled to deeper depths. The study reveals that the use of reclaimed water unknowingly accumulates the pharmaceuticals in soil. This study was found to be based on understanding the attenuation of soil by pharmaceuticals and particularly the effects in ground water.

2-3. Ocean Pollution

Human-made pollution reaches every square mile in ocean area. In western hemisphere, beluga whales are found to be more toxic pollutants. A 22 year-old-female orca was found dead on Washington, DC and the toxic level was found to be high; some first-born orca calves died due to high toxicity of breast feeding milk and the subsequent calf's accumulated contaminants were low due to low of toxicity in the mother orca. To predict ecological consequences, toxicity has to be measured in terms of long-term exposure, and many studies are carried out in order to predict the toxicity levels. Marine mammals are at the top of food chain; the toxins in their food chains are accumulated mainly on their fatty skins and in breast feeding milk. Marine animals' toxicity towards contaminations scaled from one to ten are bottlenose dolphin, orca, rise's dolphin, harbor seal, beluga Mediterranean monk seal, common dolphin, grey seal, polar bear and the tenth is the steller's sea eagle as listed in "Saving Dolphins and Whales protecting the ocean." Using single stressors, more studies are done in the field of ocean acidification or pharmaceutical drugs and very few papers have been done research on combination of stressors [62-77]. The following compounds are found on the priority list of the UK Environmental Protection Agency like anti-inflammatory drugs, analgesic diclofenac sodium, Lipid regulator clofibric acid and fungicide clotrimazole. From long-term studies researchers came to conclusion that diclofenac was found to be most active pharmaceutical compound. Diclofenac was found to be second most important pharmaceutical compound in UK effluent at maximum concentration of 2.3 μgL^{-1}. Clofibric acid is considered as an emerging pollutant in surface as well as drinking water, and the concentrations around 0.3 ngL^{-1} to 19 ngL^{-1} have been found in the North Sea; a study in the UK showed that the concentration of around 100 ngL^{-1} of clofibric acid was found in estuaries. Concentrations ranging from 3 to 54 ngL^{-1} of clotrimazole are found in UK and Germany marine ecosystems. Studies have been conducted on *slgse*, *cladoceruns* and *macrophytes*, revealing that toxicity has been induced in marine organisms in a large amount. Estuaries are considered as nursery grounds for the growth of larvas and small fishes; if these types of organisms are induced to toxicity in long-term measures, bioaccumulation occurs, but many studies are not available on the toxicity level and the early growth of the embryos and tadpoles [78-81].

Immunotoxic effects of ten pharmaceuticals on harbor seal are discussed. Lymphoblastic transformation assay was used for analysis. Cell cycle was monitored throughout the four phases to find the impact of pharmaceutical products [82]. Pharmaceuticals in microalgae, bivalves and fish from Italy, Portugal, Spain, Netherlands, and Norway were tested using four analytical protocols. For the first time tamsulosin, hydrochlorothiazide and dimetridazole are presented in biota samples. Hediste diversicolor was used as bio-indicator in the sediments settling the nearby coastal area. Compounds like carbamazepine, ibuprofen, fluoxetine and propranolol were considered to evaluate sublethal concentrations in sea-worms. Five stations are fixed at Belgian harbors which are used for samplings. Seven pharmaceuticals have been detected so far [83,84].

2-4. Uptake to the Microbial Environment

Natural microbial communities play a major role in several processes like controlling the quality of the ecosystem, fate of transport in the environment; and the ultimate process of microbial communities is self-purification in terms of metabolic and co-metabolic pathways. Recovery of microbial communities from the contaminated environment is possible when the contaminations do not inhibit microbial activity. Pharmaceutical compounds such as ibuprofen, diclofenac, gemfibrozil, paracetamol, clofibric acid, carbamazepine etc., are generally found as microbial contaminants in the environment. It has been found that the rate at which the microbial contaminants are removed from the environment depends on the microbial population which is able to degrade them. Pharmaceuticals are found to be active at low concentrations and therefore are transferred to ecotoxiological components at environmentally relevant conditions [85-92]. Only minimum percentage of domestic wastewaters from various sources is treated in developing countries. The domestic wastewater gets mixed with high concentrations of upcoming pharmaceutical waste due to lack of resources and technologies. The wastewater becomes complex, the microbes undergo high genomic transfer, and the microbes turn into multidrug-resistant microbes [93-103]. 38 multi resistant bacteria were found at Puri on the Bay of Bengal, India. These types of bacteria show resistance over various drugs. Puri is a populous tourist place and many tourists visit frequently; as a result, many domestic wastewaters are made to mix in Bay of Bengal without any treatment. Among the world's countries, China has been marked as having the highest growth in resistant microbes [104,105].

2-5. Uptake to Human Environment

Limited number of studies have suggested that commonly used pharmaceuticals pose a risk to sexual reproduction organs. Non-steroidal and anti-inflammatory agents including ibuprofen and naproxen inhibit estrogen sulfotransferase. Some researchers suggested that ibuprofen alters steroidogenesis; diclofenac produces dysfunction in experimental male rates. Suppression in spermatogenesis was tested with dogs and in monkeys when tested with clofibrate. Some researchers found that amiodarone causes adverse effect on gynecomastia [106-115]. Boron-doped diamond electrode are used as electrochemical sensors for detection of penicillin in human urine samples [116]. Human excretions are found to be major sources. Much information regarding uptake to humans is not discussed much, so studies should be taken in this area.

3. Analytical Techniques

Analytical techniques like liquid chromatography coupled with mass spectroscopy and in tandem are generally used to analyze the presence of low concentration of pollutants in liquid as well as in solid states [117]. Instruments such as orbitrap and Time-of-Flight are considered and high resolution mass spectrometry (HRMS) is used in the analysis of pharmaceutical compounds in recent times. Ultra-High performance liquid chromatography (UHPLC) systems coupled with QTOF mass spectrometer are also found to be an efficient technique [118]. In a research work hydrochlorothiazide, enalpril maleate and paracetamol were calibrated using conventional techniques like tri-linear regression-calibration techniques, multi-linear regression calibration and classical least square method and reverse phase high performance liquid chromatography (RP-HPLC); the spectrophotometric method was found to be effective in showing regression parameters [119]. Liquid chromatography coupled with triple quadrupole mass spectrometer were used for analyzing the vegetable extract which was grown using pharmaceutical reclaimed water. Accelerated solvent extraction (ASE) and ultrasonic liquid extraction (ULE) are followed in order to extract the samples. For the samples like acetaminophen, sulfadiazine and sulfamethoxazole, the ASE method was found to be more efficient than ULE method [120-125]. Gas chromatography was found to be efficient for the determination of estrogen and progestin. To understand the molecular ion and resultant fragmentation of unknown impurities, the isolated impurities are analyzed using chemical ionization or electron ionization. The impurities are analyzed as leachate and finally leachate is matched with NIST (National Institute of Science and Technology) library search [126-130].

DIFFERENT TREATMENT METHODS

Several technologies have been adopted to treat pharmaceutically active compounds (PAC) from sewage water. Every technology has its own advantages and disadvantages when every parameter is accounted for. Among all the technologies, nanotechnology has been considered as an emerging and economically efficient technology in recent times.

1. Activated Sludge Treatment

A number of factors such as nutrient, low organic loading rates, low pH, Low temperature, food/microorganisms ratio were considered [131]. 21 pharmaceutical compounds were treated using activated sludge process, and the concentrations of sludge were analyzed using liquid chromatography coupled with orbitrap high resolution mass-spectrometry; 14 compounds were said to be biodegraded and among those compounds eiclofenac and ibuprofen were slowly degraded. The biological activity maintained was seven days [132]. In a research it was noted that a combined system of algae and activated sludge shows the removal efficiency of 97.91% in the removal of *cephalosporins*. *Chlorella pyrenoidosa* has been used as green algae in this combined treatment [133]. Methods like activated sludge, adsorption and biodegradation are used for the removal of benzafibrate; adsorption and biodegradation are found to be efficient methods compared to activated sludge treatment [134]. It's a self-sustaining system, and removal of 97% of organic solids is possible; liquids and solids are separated based on gravity and can be easily handled. Some of the disadvantages are as follows: cleaning of the system makes the condition worse and variation in the temperature affects the system [135-137]. In a research work, activated sludge treatment was used in the removal of diclofenac and carbamazepine along with the component removal. The bacterial strains were also isolated from the sludge, and for the growth of the isolated bacteria, a period of 10 months was provided. In this research 20 bacterial strains on Carbamazepine and 12 bacterial strains on diclofenac were separated from activated sludge treatment and used as a source for biodegradation process. This technique was found to be efficient initially, but the 10 months provided for the growth of bacterial strain was considered as drawback [138,139]. In another research work *Klebsiella oxytoca NBA-1*, bacterial strain was isolated from pharmaceutical wastewater in order to degrade nitrobenzene. In addition to the strain, glucose and p-chloronitrobenzene (p-CNB) were added under both aerobic and anaerobic conditions. Under anaerobic conditions there was no change in both nitrobenzene and p-CNB and in aerobic conditions the removal efficiency was 20%; this evidence proves that the microbial communities can stay in anaerobic condition for 90 days. On the whole, activated sludge treatment will not provide complete removal of pharmaceutical components present in the wastewater [140,141].

2. Coagulation

Electrocoagulation was considered 20 times more effective than chemical coagulation. In electrocoagulation under optimizing, potential sacrificial anodes are used to treat pollutants; the formed active coagulants are responsible for the degradation [142,143]. Dexamethasone was removed using electrocoagulation, where the removal efficiency was achieved with increase of current applied and decrease in inter electrode distance [144]. In a research work electrocoagulation combined with electro floatation was illustrated. In electrocoagulation process, cathode and anode are made up of aluminum and in electroflotation stainless steel anode and graphite cathode were used; the removal of doxycycline hyclate (DCH]) was inversely proportional to the distance between the electrodes [145]. Peroxi-electrocoagulation was used to treat biological wastewater effluent, petrochemical wastewater etc., Removal of sodium dodecyl sulfate (SDS) to the percentage of 80 was achieved using this treatment. In addition to peroxi-electrocoagulation treatment, UV or visible lights were illuminated so that the production of hydroxyl radicals was increased, which are responsible for the degradation of pollutants [146-149]. Hydrolyzed peptone residues from pharmaceutical industries were removed using electrocoagulation followed by photo-oxidation, about 91% and 86% of turbidity and COD was removed. In a research work fenton oxidation and conductive-diamond electro-oxidation were compared in treating 60 different real effluents from pharmaceutical wastewater. Bebeerine pharmaceutical wastewater was treated using electro-coagulation; Fe and Al electrodes were compared in this process. It was mentioned that Fe electrode was efficient in removal. Graphene containing ceramic composite tubular membrane was coupled with electro filtration and electrocoagulation process for the removal of phthalates and pharmaceutical compounds. Removal efficiencies were found to be high in caffeine, sulfamethazole, cephalexin. Several advantages are available in electrocoagulation treatment like easy maintenance. No addition of chemicals, small colloidal particles were removed from wastewater stream. The use of electricity makes the process uncomfortable and sacrificial electrodes are needed to be replaced due to occurrence of oxidation of electrodes which are dissolved in wastewater. For the pretreatment process, generally coagulation and filtration process are done for pharmaceutical waste water. It has advantages like removing the total dissolved solids and organic content before entering into effluent treatment plant. Generally, aluminum sulfate and ferric sulfate are used as coagulants and coagulant aids such as calcium carbonate, bentonite, sodium silicate, which are known as supporting agents added to main coagulants. The chemicals which are added as coagulants are a major problem. The ultimate disposal is tedious [150-152].

3. Fenton Reaction

For the generation of hydroxyl radical, Fenton reactions are used. Generally, hydroxyl radicals are referred to as pollutant killing agents. The combination of electrochemical reaction and Fenton produces electrical hydroxyl radicals [153]. The radicals produced are low selective and used to oxidize a wide range of pollutants; further modification in Fenton reactions increases the degradability of pollutants. Fenton is a homogeneous process where there is a transfer of electrons between metal and hydrogen peroxide [154], and thiamethoxam, neonicotinoid pesticide was targeted. Boron doped diamond was used as anode and carbon was used as cathode, iron was used as catalyst to degrade thiamathoxam [155]. A combination technique of interior micro-electrolysis and Fenton oxidation was analyzed. Steroid hormone pharmaceutical components such as hydroxylamine, pyridine, cyclohyxenone, toluene in aqueous media are treated. In appropriate pH this combination is found to be effective [156]. To treat carbamazepine with higher concentrations, granulated activated carbon cum Fenton reaction was conducted; it paved the way for zero discharge effluent by removing carbamazepine up to 99.51%. Here, the Fenton reaction was made as pretreatment step to increase hydroxyl radical concentration; around 49 percent of CBZ was found to be removed from this treatment, then the effluent was combined with granulated activated carbon for filtration purpose [157]. Comparison between heterogeneous and homogeneous Fenton process was analyzed in this study. When compared to a homogeneous system that is only an iron combination of iron sulfate and copper sulfate solutions and the parameters such as heat, catalyst, energy inputs, hydrogen peroxide were analyzed. Reduction of sludge seems to be difficult in a heterogeneous system when compared to homogeneous [158]. Low cost, low toxicity, simple mechanisms, COD/BOD removal and odor removal are some of the advantages of the Fenton reaction [159]. Additional components are generated along the targeted degradation of pollutants, but the identification and removal of extra compounds is tedious. The possible combination of treatment technologies with Fenton is given in Fig. 3.

4. Membrane Bioreactors

Fluidized bed reactor was inoculated by *trametes versicolor* in sterilized and non-sterilized conditions. From sterilized conditions it is concluded that fungus needs a source of nutrient to maintain the biological activity for better degradation [160]. Many reports suggest that membrane technologies are better than activated sludge process. In this research work two anoxic-aerobic membrane bioreactors are used to treat pharmaceutical wastewater; components such as proteins, fulvic acid, humic substances were highlighted. The concentrations of proteins and polysaccharides are found to be in higher concentration in aerobic reactors when compared to anoxic reactors [161]. The bacterial strain *paracoccus denitrificans*, which could utilize pyridine as its sole source of carbon and nitrogen was added into a membrane reactor, and the removal efficiency was found to be good [162]. The quality of treated water is high, less investment, and wide spectrum of organic pollutants is removed using membrane bioreactors; membrane fouling was considered as major disadvantage, and cleaning of membrane is also considered as tedious process [163-165]. Bio-entrapped membrane reactor and salt marsh sediment membrane bioreactor are used for the removal of pharmaceutical components from the wastewater. Some of the bacteria like *Bacteroidetes*, *Actinobacteria*, *Firmicutes* contributed towards the degradation process. Aggregates of laccase are used in hybrid bioreactors for the removal of acetaminophen, mefenamic acid and carbamazepine; overall 85% of removal efficiency was achieved [166,167]. In a study for the removal of diazepam, carbamazepine, naproxen, ibuprofen combination of stirred tank reactors and fixed bed reactors with *phanerochaete chrysoporium* are used. *P. chrysoporium* was introduced using free pellets or immobilized polyurethane foam; complete removal of diazepam and ibuprofen was seen during the period of 100 days under continuous stirring and 60-90% of removal was seen in carbamazepine and naproxen, high oxygen level was maintained throughout the process [168]. To remove ibuprofen and ketoprofen, aerobic suspension batch reactor was used; during the screening *Bacillus pseudomycoides*, *Rhodococcus ruber* and *vibrio mediterranei* were found which are toxic towards ibuprofen (IBU) and ketoprofen (KETO). This system allows oxygen flow to the activated sludge which allows microbes to have more surface area so that IBU and KETO are degraded efficiently. Under four phases operation were done from day one to 135 days and their efficiencies were reported. COD removal was found to be in increasing order for all the phases. In fourth phase IBU and KETO were removed efficiently, and it was found that when the loading rate increases the removal rate also increases [169-171]. In another research work an aerobic granular sludge sequencing batch reactor (AGS-SBR) was used. A mixture of chiral pharmaceutical compounds namely metoprolol, propranolol, venlafaxine, salbutamol, alprenolol, bisoprolol and norfluoxetine. AGS-SBR showed highest removal efficiency towards norfluoxetine. Ionically crossed linked

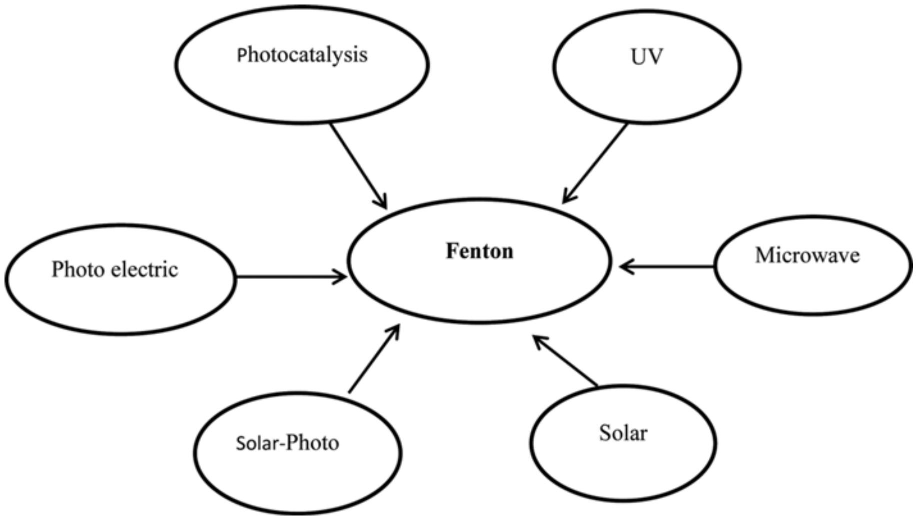

Fig. 3. The possible combination of technologies with Fenton process.

chitosan with *pentasodium tripolyphosphate* was prepared inorder to treat pharmaceutical components [172,173]. Modified cellulose acetate nanofiltration membrane was utilized for the removal of carbamazepine, ibuprofen and sulfamethazine. It was found that modified nanofiltration provides good removal rate for ibuprofen and sulfamathazine and poor removal rate to carbamazepine [174, 175]. Phase changes do not occurr in membrane technology so that energy consumption is minimum; it uses simple and non-harmful materials, so its ecofriendly. It is used to remove most valuable components which are at minor level. Many research works were done using different chemical combinations of membranes even though major disadvantages like fouling and cleaning of membranes make it a tedious process.

5. Photocatalysis

Acceleration of photoreaction in presence of catalyst is known as photocatalysis. Photocatalysis does not require high pressure or temperature or agents such as iron or hydrogen peroxide, but the disadvantage of this process it is very cost effective. The compounds like aldehydes, ketones, nitriles and amides are removed completely from water using TiO_2 as catalyst [176]. For TiO_2 combined with graphene oxide, polycatalytic activity was found to be in increasing manner with increasing concentration [177]. Multiwalled carbon nanotubes combined with TiO_2 has been carried out in a research work. This type of nanoparticle provides superior degradability over plain TiO_2 [178]. Because of biocompatibility, low cost, wide band gap, zinc oxide is also used as photo catalysis, The rate of degradation depends upon the pH of the solution, contaminants present in the solution, type and amount of zinc oxide [179]. To maximize the surface area of the system, catalysts are used as nanoparticles. Major compounds are degraded by using ZnO as catalyst, but ZnO when it's not properly degraded affects the environment as it induces photo toxicity [180]. They are non-toxic, relatively low cost and they indirectly produce hydroxyl radical and directly generate holes. Handling of instruments is tedious except zinc oxide and titanium oxide, other photo catalyst products like zirconium are costly [181,182].

6. Ozonation

Ozonation treatment has been added has additional treatment to increase the removal efficiency of pollutants in wastewater effluent treatment plants [183,184]. It's a colorless unstable gas, used as disinfectant over a wide range of organic and inorganic pollutants. This type of treatment would not use chemical substance to treat water. It is effective a over wide range of pH; here are some of the disadvantages of ozonation. Operational costs are very high, pretreatment is necessary to continue with ozonation. By-products produced by ozonation may be of carcinogenic type, so that effective treatments are adopted after ozonation to remove the by-products. Ozone is less soluble in water so that high efficiency mixing equipment is needed to mix the substances. Combination of H_2O_2 and ozonation was adopted for the pharmaceutical pollutants which are influenced by greater dissolved organic carbon and pH. An investigation was carried to increase the lifetime of ozone in low pH by addition of hydrogen peroxide [185]. Another research focuses on decomposition of aqueous ozone due to the effect of UV-visible radiation of different wavelengths. It is considered as cost effective technique. UV lamps are replaced with electromagnetic waves with the wavelength of 300 nm, and at the wavelength of 320 nm the photo-radiation was found to be effective [186]. The compounds like Phenol, 1,4-chlorophenol, formaldehyde and dyes are removed in considerable amount using MgO as a catalyst in catalytic ozonation [187]. Photocatalytic ozonation with membrane technology, TiO_2 has been used as catalyst. Salts and organic substance are removed using membrane systems [188,189].

7. UV/H_2O_2 Process

Due to the removal of organic contaminants from aqueous solution UV/H_2O_2 treatment has gained attention. By photolysis of H_2O_2, OH radicals are produced which are used for the degradation of pollutants. The quantum yield of this reaction was found to be one. Several research works have been published under the treatment of UV/H_2O_2 process for surface waters and the contaminants in laboratories. Some substances like ciprofloxacin, trimethoprim and antineoplastic drug cyclophosphamide are found to be sensitive to both UV and H_2O_2, and some do not respond to both of them and some respond to anyone [190,191]. A research work mentioned the degradation of six pharmaceuticals under low pressure (LP) and polychromatic medium pressure [MP] UV lamps [192,193]. Under stimulated sunlight five amino drugs and five sulfa drugs were analyzed [194]. The organic contaminants are degraded using electrophilic addition, electron transfer and hydrogen abstraction. Any hindrance in UV light transmission to the waste content affects the production of OH radicals, so the light has to be cleaned periodically. The system is sensitive to pH, basicity has to be maintained throughout the process; sodium hydroxide should be used instead of carbonate, because carbonate reacts with OH radicals [195-199]. It shows efficiency in mineralizing organic pollutants, but has disadvantages like poor UV adsorption capacity, and it does not utilize solar light as the source of UV light because of inadequate UV energy for photolysis of oxidizer from the solar spectrum [200-202].

8. Plasma Treatment

Thermal and non-thermal plasma treatments are available. In thermal plasma, the plasma constituents are permitted to sustain in thermal equilibrium by providing sufficient energy. While, less energy is required to perform non plasma treatment. Non-thermal plasma treatments are generated using electric discharges in liquid or at gas-liquid interface. Many endocrine disrupting compounds and pharmaceutical compounds are treated using plasma and are discussed in terms of removal efficiency and energy yield [203-207]. Traditional Chinese medicines wastewaters are treated using non plasma treatment. Radix aconite was purchased and the filtrate was used as effluent; the results showed that the effluent has to be treated by biological unit finally after plasma treatment. They are considered efficient treatment because of consumption of high amount of electrical energy and plasma treatment has to be done as pretreatment in order to convert organic compounds into biodegradable elements [208-211]. It reduces the water consumption and energy for drying the treated materials, is environmentally friendly, but disadvantages like high cost in initialization, scaling up and maintaining optimal process parameters make it a tedious process [212].

9. Ultrasonic Treatment

Sono-chemical treatment is mainly based on the principle of acoustic cavitation. Many research works were carried out using single pharmaceutical components triclosan, ibuprofen, and diclofenac individually [213-216]. Mixtures of these three components were treated using ultrasonic at a frequency of 20 KHz. It was found that in presence of dissolved air, increased acidic conditions and power densities, there is enhancement in pharmaceutical conversion. The reaction rate increases for single pharmaceuticals and it remains constant for mixtures [217]. It disintegrates and reduces the sludge, improves bio-solid quality and biodegradability, reduces sludge retention time. It is a very costly and time consuming technique, and huge amount of solids cannot be handled [218,219].

10. Adsorption

Components like tramadol and doxepin, clay minerals show outstanding adsorption properties in removal of organic compounds. Cohesion and stability of clay mineral are added advantages in the field of adsorption. Wyoming sodium spectate (Mt) obtained from clay are used as adsorbents and two components, namely tramadol and doxepin, are removed from water. Clay minerals are attracted due to its high cation exchange capacity and swelling properties; modifications of clay minerals are also done to increase the efficiency in removal, Three pharmaceutical compounds, naproxen, gemfebrozil and mefenomic acid, are removed in considerable amount using chemically modified clay mineral LECA (Light expanded clay aggregates) and exfoliated vermiculite. Some of the modified well known clay adsorbents are montmorillonite, vermiculite, kaolinite and bentonite; among them vermiculite showed good results on removal of pharmaceutical components like ibuprofen, ketoprofen, carbamazepine, diclofenac; carbonaceous bentonite and montmorillonite K10 showed affinity towards pH where else vermiculite and montmorillonite K30 does not bother pH in removal of pharmaceutical pollutants [220-223]. Biopolymer based magnetic adsorbents such as chitosan and cellulose, are used as adsorbents, and removal efficiency is found to a great extent; as pharmaceutical compounds consist of three compounds such as anion, cation and neutral molecules are available at different pH; according to the compounds three sorts of branches namely polycations, polyanions and neutral polymers are introduced. Diclofenac sodium and tetracycline are removed using modified Chitosan-Fe_2O_4 composite [224]. Tin oxide has two different forms: stannous oxide/Tin oxide (SnO) and as stannic oxide/Tin dioxide (SnO_2). SnO_2 is a well-known semiconductor. This type of semiconductor is added with montmorillonite (Mt) abundant clay material which consists of two layers of tetrahedral silica sheets sandwiching on one layer of octahedral alumina sheet. The components like trimethoprim (TMP) and sulfmethoxazole (SMX) are removed from water [225]. Compared to activated carbon, biochars provide lesser surface area and are proved as an adsorbent for removing micropollutants. The pyrolyzed biochar generally consists of polyaromatic carbon, which shows higher affinity towards organic compounds, and chemically activated biochars are available nowadays, which results in high porosity and less ash content. The source of biochar may be of organic forms such as plants, domestic and industrial waste, sludge etc., depending on the composition and the elements present in the source the production of biochar variy. In a research work combination of magnetic biochar and activated carbon is used in the removal of tetracycline and carbamazepine; for the preparation of biochar coconut, pine nut and walnut shells are used; ball mills are used in order to get ultrafine particles [226-229]. Chlorohexidine digluconate CHD has been considered as micropollutant and was removed using TiO_2 substance; a comparison of photocatalysis and adsorption using TiO_2 was made. It was found that adsorption was a faster technique than photocatalysis [230]. Activated carbons obtained from lignite and anthracite are used for the removal of paracetamol, phenol and salicylic acid. Hydrophobic nature of adsorbent plays a major role in higher adsorption [231,232]. Erythromycin, carbamazepine and levofloxacin compounds are treated using zeolite. Changes in micropore size and the shape of the zeolite will not confirm the adsorption; change in structures results in adsorption [233]. Molecularly imprinted polymer has been used for the removal of diclofenac, ibuprofen and naproxen, and the removal percentages are in the range of 87, 69 and 38 [234]. Bio adsorption is an adsorption technique where biomasses are used for adsorption purpose; small amount of adsorbent will treat huge amount of aqueous solution [235-237]. Adsorption is considered as one of the simplest, cheaper and versatile techniques, and the major disadvantages are that we are just transforming the pollutants from one from to another; spent adsorbent is considered as hazardous waste, adsorbent regeneration requires stream or vacuum source [238]. Some of the biosorption efficiencies with pharmaceutical components are listed in Table 3.

11. Nanotechnology

An emerging technique involves conventional techniques blended with nanotechnology for betterment in sensing and in removal of pharmaceutical compounds. As the component is nano it does not compromise in any form. The recyclability was found to be good enough as nanoparticle productivity was found to be commercially high. Some of the nanoparticles and their advantages are listed in Table 4.

11-1. Nanotubes

Carbon nanotubes are considered as one of the promising adsorption techniques. Oxytetracycline and ciprofloxacine are two targeted pollutants, and adsorbents such as single walled carbon nanotubes (SWCNT), double walled carbon nanotubes (DWCNT), multiwalled carbon nanotubes (MWCNT) are attempted in this study. Many characteristics such as temperature, pH are absorbed; for all variations in temperature CNT seems to have the same range of adsorption capacities. In case of pH the adsorption capacity increases from pH 3 to 7 [239]. Components of different categories such as sulfamethoxazole, carbamazepine, p-nitrophenol, 3,5-dichorophenol and diclofenac are treated using multiwalled carbon nanotubes [240]. In another research work compounds like trickosan (TCS), ibuprofen (IBU), acetominophen (AAP), caffeine (CAF), prometryn (PTN) and carbendazin (CBD) are treated using five different CNT's such as pristine MWCNT, hydroxylated MWCNT, high-purity MWCNT and laminated MWCNT, Thin walled MWCNT [241]. Photochemical degradation was achieved by using ZnO nanotubes; nanotubes were prepared by self-assembling of ZnO nanoparticles using electrostatic interactions between ZnO nanoparticles and the block copolymer template; ciprofloxacin was targeted in this research [242]. Carbocyclic modified multiwall carbon nanotubes are used for removal of lin-

Table 3. Some of the biosorption efficiencies with pharmaceutical compounds are listed below

Raw material	Treatment	Lost efficiency	Characterization analysis	Removal compound	Reference
Agricultural waste					
Potato peel	Pyrolysis or Hydrothermal treatment	11 35	SEM (Zeiss Supra 55 VP) and FTIR (Nicolet 560)	Dorzolamide Pramipexoledihydrochloride	[231]
Activated carbon	NH_4Cl modified	-	Elemental analysis Total and inorganic carbon analysis Point of zero discharge	Carbamazepine Paroxetine Oxazepam	[232]
Pomogranate wood	H_3PO_4 modified	-	UV-spectroscopy (UV-1800)	Acidic triclosan Acidic naproxen Basic atenolol	[233]
Coffee residues Almond shells	Chemical activation	-	SEM (VEGA/TESCAN) XRD (X'pert MPD) HPLC BET EXT	Chlortetracycline	[234]
Petroluem coke	Potassium carbonate as activator	-	BET EXT	Metronidazole Dimetridazole Sodium diatrizoate	[235]
Date stones	H_3PO_4 modified	-	SEM	Nitroimidazole	[236]
Olive stone	Thermal treatment	-	Micromertics (ASAP 2020) FTIR (Nicolet 5700)	Ciprofloxacin Norfloxacin	[237]
Rice straw	$Fe(NO_3)_3/Ca(NO_3)_2/Al(NO_3)_3$ Treated	-	SEM FTIR XRD	Paracetamol Cloffibric acid Carbamazepine	[238,239]
	Trirthoxyphenylsilane treated		XRD FTIR	Ceftazidime Carbamazepine Ibuprofen Clofibric acid	[240,241]
Cross linked chitosan	Sulfonate crafted chitosen	12	SEM (Zeiss Supra 55 VP) FTIR (PerkinElmer-2000) BET (Tri Star 3000)	Pramipexoledihydrochloride	[242]
Magnetic carbonaceous nanomaterial	Coated with β-cyclodextrin	15	TEM (JEOL JEM-2100) SEM (FEI Quanta) FTIR (Bruker Tensor) XRD (Rigaku D/Max-3C) TGA (Q50)	Lopid	[243]

ear alkyl benzene sulfonates (LAS). CMMWCNT shows heterogeneous sorption capacities and it is absorbed so that CMMWCNT depends on temperature and solution chemistry [243]. Carbon nanotubes are emerging technologies in treating endocrine-disrupting compounds (EDCs) and pharmaceutical and personal care products (PPCPs). CNT showed high range of adsorption capacities for wide range of EDCs and PPCPs; due to large surface area PPCPs are readily attached to CNTs. Halloysite is a negative charge

Table 3. Continued

Raw material	Treatment	Lost efficiency	Characterization analysis	Removal compound	Reference
Graphene	Drawn to planes	71.7 80 81 95.1	Spectro-photometer (UV-vis lambda 12 perkinElmer)	Caffine, Carbamazepine, Ibuprofen, diclofenac	[244]
Silica	Natural surfactant template method	-	XRD (Bruker AXS model D8 Discover FTIR (Nicolet Impact 410) SEM (JEOL-JSM 5410LV)	Naproxen Acetaminophen Clofibric acid	[245]
	Non-ionic template method	-	LC Tandam MS system Mass spectrometer (Quattro Micro API)	Carbamazepine Diclofenac Ibuprofen Ketoprofen	[246]
Silica SBA-15	Calcination	 85.2 49 88.3 93 94.3	XRD TEM	Carbamazepine Clofibric acid Diclofenac Ibuprofen ketoprofen	[247, 248]
Biochar	Pyrolization	-	Elemental analysis (PerkinElmer 2400 series II) Micrometrics (Gemini VII 2390 P)	Diclofenac Naproxen Ibuprofen	[249]
Calotropisgigantia	Ammonium persulfate	30	UV-Spectrophotometer (TU-1810 PC) FTIR (Thermo Nicolet NEXUS) SEM (JSM-5600LV)	Ciprofloxacin	[250]
Zeolite	NaCl treated	45	SEM (Quanta 200)	2-Chlorophenol	[251]
Phoenix dactylifera L. stones	KoH treated	-	SEM FTIR	Levofloxacin	[252]
Polyurethane Foam waste	Pyrolization	-	XRD (Rigaku D/Max diffractometer) FTIR (Nicolet Avtar 330)	Non-steroidal anti-inflammatory drugs	[253]

clay mineral that has been used as a carrier for wastewater treatment and pH dependent. Generally, anticancer drugs are very sensitive halloysite type carriers built for carrier purpose so that the wastage of drugs is avoided [244]. Acetaminophen also known as paracetomol in waste water was quantified using multi walled carbon nanotubes combined with cobalt phthalocyanine modified electrode; in order to increase the surface area and conduction of the adsorbent, gold nanoparticles are used. Overall, it provides good analytical stability and selectivity; it's a pH dependent process with the equal participation of protons and electrons. Carbon nanotubes and powdered activated carbon are used for the removal of sulfamethoxazole, linocomycine. Among those adsorbents single-walled carbon nanotubes due to its high specific adsorption area is seen to be efficient in removing promise, sulfamethoxazole and linocomycine. Papain, which has medicinal use, is extracted from papaya trees, used for pain, swelling and for digestive aids. Papain in multi-nanocarbon is non-covalently immobilized. When compared to free papain nano-enzyme exhibited good thermal response, recycling ability, and it can be separated easily from end product and multiple time usage ability [245]. Carbon nanotubes were imposed on membranes for better removal of pharmaceutical and personal care components. The removal range was found to be 10-95% for triclosan, acetaminophen and ibuprofen. When pH was fixed from 4 to 10 the removal was achieved up to 70%, and the removal rate increases for neutral molecules than ionic molecules because of electrostatic repulsion. Different materials are used as intermediate layers for the formation of tubular carbon nanofibers/carbon/Alumina compos-

Table 4. List of nanoparticles and their properties and advantages (288-291)

Nano materials	Properties	Advantages
Metallic and mixed oxide nanoparticles	High specific area High adsorption capacity High chemical stability	Can be used as magento-optic devices Low cost Low toxicity
Magnetic nanoparticles	Superparamagnet Densimetric separation Large surface area	Biocompatibility Low cost Can be easily synthesized
Carbon nanotubes	High surface area High ability for π-π interactions	Lower price Wider range of accessibility Easy functionalization
Graphene and Graphene oxide	High mechanical strength High surface area	Easy surface modification Less water dispersible
Silicon nanoparticles	Excellent optoelectronic and electronic properties	Biocompatible cheap
Cellulose nano materials	High strength Light weight	Compostable Replaces toxic materials
Zinc oxide nano materials	Optical transparency Luminescence Wider band gap	Environmental friendly Easy to synthesis
Biosensors	Sensitivity High surface energy High reactivity Surface conductivity Surface/volume ratio	Compact size User friendly

ite. Plastic wrap such as polyethylene, polyvinylchloride, polymethylpentene, polyvinylidenechloride are used as base layers on which nanomaterials are fabricated. Adsorption, electrocoagulation and electro filtration were made in order to remove pharmaceutical components such as caffeine, sulfamethoxazole and acetaminophen. Current barrier for using CNTs lies in operational cost and hyperphobicity. It is found to be extraordinary in electrical, chemical, mechanical properties [246,247].

11-2. Electrode Paste and Nanotubes

In a research pyrogallol was blended with multi carbon nanotubes to form a paste and used as electrode in removal of isoproterenol. Platinum was used as auxiliary electrode and Ag/Gal/Kill was used as reference electrode with modified multi carbon nanotubes; it was used as high sensitivity detectivity sensor. In another research multiwall carbon nanotubes were used as paste with the help of plasticizer and with graphene powder, Carbon nano paste has many advantages like low humic resistance, reproducibility, short response time, low cost etc., Many sensors are prepared with the combination of nanotubes for the betterment in determination, and also this type of sensor exhibits good efficiency after multiple attempts [248-251]. $ZnCrFeO_4$ nano composite was blended with multiwall carbon nanotube. Warfarin was determined using this sensor. In another study gentamicin sulfate was determined using prepared electrode paste and methyldopa was quantified using glassy carbon electrode modified by using multi carbon nanotube. In another research bismuth and carbon nanotubes in nafin matrix are used to modify sulfasalazine. This type of sensor was used for the determination of anti-inflammatory drug in human serum without intervention of endogenic species. Ionic liquid and fullerene functionalized carbon nanotubes used for the determination in diazepam. The electro catalytic current increases linearly with the increase in concentration of diazepam. There was excellent repeatability, recovery, long term stability in determining the diazepam component. In each type glassy carbon electrodes were blended with nanoparticles and were made into electrode paste and used as electrochemical sensors for determination of certain pharmaceutical compounds [252-262].

11-3. Nanotubes Based on Metals

Radionuclides and heavy metal are removed using nano-adsorbents like titanium dioxide, iron oxide, aluminum etc.; it's a two-step process in which heavy metal are adsorbed on the external surface followed by intraparticle diffusion [263-267]. Because of its high surface area, this type of nanoparticle has high adsorption capacity and large number of active sites. It was noted that when the particle size is less than 20 nm it shows high adsorption efficiency and is used in two forms such as powder and in pellets. Metals such as arsenic, lead, mercury, cadmium, chromium, arsenic and nickel have also showed. Especially, arsenic showed great removal efficiency when using metal based nanomaterials than carbon nanotubes. Nano-maghemite and nanomagnetite are coming under the category of iron oxide nanoparticles. When the size of magnet decreases to a critical value, ferri or fero magnet changes to super paramagnet, which loses its magnetic moments and responds to an external magnetic field. The magnetic nanoparticles can be used as adsorbents [268-271].

Overall, nanotechnology was found to be an efficient technology despite its commercial value. Once it is synthesized, it can be used for many numbers of times without any deviation from its efficiency.

NEED FOR FUTURE RESEARCH

Due to scientific advancement in our day to day life, many diseases have been raised, the efficiency in treatment techniques has been upgraded to cope up with the new arising diseases. From conventional treatment to the modern treatment, all the techniques are aimed at reducing the pollutant level of pharmaceutical products in various forms. In every treatment, pollutants are made to transfer from one form to another. Complete degradation of pollutants has not been achieved efficiently even though we depend on combined techniques. Many researches have been carried out in the field of water pollution caused by pharmaceutical industries. In every research there is betterment in the outcome over the period. Future work has to be done to overcome the defects.

CONCLUSION

In this research work the source of pollutants from various factors and their occurrence in different fields has been discussed briefly. Specifically, their bioaccumulation and toxicity levels are discussed and the uptake of pharmaceutical pollutants to microbial and to human environment is discussed. Many types of treatment techniques are discussed, and their advantages and disadvantages have been pointed out. In every technique from conventional to modern, some amounts of betterment have been absorbed for the time period, but complete removal was not efficient in each treatment. Among all techniques, the preference was given to nanotechnology because of its high efficiency in removal of pollutants. Hybrid technologies such as combination of nanomaterial with Fenton reaction are also discussed briefly.

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