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Application of Agricultural Waste for the Adsorption of Pharmaceutical Pollutants in Wastewater: A Review

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Abstract

Modernization and growth in population have contributed to the continuous release of new and emerging chemical compounds (such as pharmaceuticals) into water sources. The importance of pharmaceuticals can never be overemphasized due to their great potential and effectiveness in the body system. However, improper management of their effluents which eventually ends up in the water in our environment has always been an issue of great concern. This led to the need for the purification of the contaminated water (wastewater). Over time, many methods of wastewater purification have been employed in the treatment of the wastewater, but yet, adsorption has been found and established to be an optimum option for the task due to its effectiveness, availability, affordability, and durability. Adsorption is a separation technique that takes place on the surface of a material or through a component called an adsorbent, and the effectiveness of this method is a function of the adsorbent capacity, contact time, temperature, and other related parameters. For adsorbent preparation, many materials have been considered and proven to be active and effective. However, in this paper, synthesizing agricultural wastes as the adsorbent in the adsorption of pharmaceutical effluents is reviewed with references, to further attest to its prominence in adsorption.

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Keywords: Adsorption, Adsorbents, Agricultural waste, Pharmaceuticals

Introduction

The application of several materials as adsorbents in the wastewater treatment containing different contaminants has received wide attention in recent years. Because, water pollution has become a serious environmental challenge globally due to the existence of various pollutants including pharmaceuticals, pesticides, and organic pollutants. Pharmaceuticals are compounds with biological activity developed to promote human health and wellbeing. However, because a considerable amount of the dose taken is not adsorbed by the body, a variety of these chemicals including painkillers, tranquilizers, anti-depressants, antibiotics, birth control pills, and chemotherapy agents – are finding their way into the environment via human and animal excreta from disposal into the sewage system and from landfill leachate that may impact groundwater supplies (Sharma and Bhattacharya, 2017).

Most substances of pharmaceutical origins are not biodegradable and often not eliminated due to their ability to escape conventional wastewater treatments. Therefore, residual quantities remain in treated water or have been found in drinking water (Baccar *et al*., 2012). The removal of pharmaceuticals by adsorption on commonly efficient adsorbents is one of the most promising techniques because of its convenience when applied in current water treatment processes. To date, several reports relating to the adsorption of pharmaceuticals onto natural materials or components of natural materials e.g. soils, clays, hydrous oxides, and silica have been published (Rajasulochana and Preethy, 2016; Alade *et al.*, 2012; Sangion and Gramatica, 2016; Vitória *et al.*, 2017). Adsorption is a process where atoms, ions, or molecules from a gas, liquid, or dissolved solid adhere to a surface, i.e. a change in the concentration at the interfacial layer between two phases of the system due to surface forces. This process creates a film of the adsorbate-substance which is adsorbed on the surface of the adsorbent-substance whose surface adsorbs the gas or solute molecules from the solution (Alcaraz *et al.*, 2018). Adsorption is a surface phenomenon. Pressure, temperature, nature of adsorbents, nature of adsorbates, the concentration of adsorbents, concentration of adsorbates, and adsorption isotherms are some of the factors that determine the extent of adsorption (Dada *et al.*, 2020).

In this work, different reliable publications from different sources were reviewed to shed more light on the utilization of agricultural wastes in the adsorption of unwanted pharmaceuticals in the environmental water streams. The scope of this review study is not limited to the removal of harmful pharmaceuticals from wastewater through adsorption only, it also considers the utilisation of agricultural wastes which greatly pollute the environment, as major raw materials in preparation of adsorbents used to remove the pharmaceutical pollutants

Agricultural waste

Agricultural-based industries produce a vast amount of residues every year (Pardeep *et al*., 2018). And most of these residues are released to the environment with no effective or proper disposal procedure and this leads to environmental pollution with a harmful effect on human and animal health (Sangion and Gramatica, 2016). Most of the agro-industrial wastes are untreated and are eventually disposed of either by burning, dumping, or unplanned landfilling. These untreated wastes create different problems with climate change by increasing the number of greenhouse gases. These wastes cause a serious disposal problem (Rodríguez-Couto, 2008). For example, the juice industries produced a huge amount of waste as peels, the coffee industry produced coffee pulp as waste, and cereal industries produced husks

All over the world, approximately 147.2 million metric tons of fiber sources are found, whereas 709.2 and 673.3 million metric tons of wheat straw residues and rice straws were estimated, respectively, in the 1990s (Belewu and Babalola, 2009). Due to their high nutritional content as evidenced by their components, agro-industrial residues are getting more consideration for further utilization (Graminha *et al*., 2008).

Agricultural waste bye products: Agriculture residues can be divided into field residues and process residues (Sushil *et al*., 2018). Field residues are residues that remain in the field after the process of crop harvesting. They consist of leaves, stalks, seed pods, and stems, whereas the process residues are the residues present even after the crop is processed into an alternate valuable resource. These residues consist of molasses, husks, bagasse, seeds, leaves, stem, straw, stalk, shell, pulp, stubble, peel, roots, etc. and used for animal feed, soil improvement, fertilizers, manufacturing, and various other processes (Sushil *et al*., 2018). A huge amount of field residues are generated and most of them are underutilized. Controlled use of field remains can enhance the proficiency of irrigation and control of erosion. In the Middle East region, wheat and barley are the major crops. In addition to this, various other crops like rice, lentils, maize, chickpeas, fruits, and vegetables are also produced all over the world. Agricultural residues are differentiated based on their availability as well as characteristics that can be different from other solid fuels like charcoal, wood, and char briquette (Zafar, 2014).

Industrial wastes: A huge amount of organic residues and related effluents are produced every year through the food processing industries like juice, chips, meat, confectionery, and fruit industries (Michael-Kordatou *et al*., 2015). Generally, there has been a huge growth in the food and beverage industries and this had led to the generation of more wastes because, the more food items, the more wastes generated from them such as peels, husks, etc. (Rudra *et al*., 2015). For instance, in India, approximately, 20% of the fruits and vegetables produced annually go to waste (Rudra *et al*., 2015). Similarly, the waste produced from food industries contains a high value of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and other suspended solids. Most of these wastes are left unutilized or untreated, and they harm the environment, as well as human and animal health, but the composition of these wastes, contains a large number of organic compounds that produce a variety of value-added products and thus reduce the cost of production (Pardeep *et al*., 2018). Some agro-industrial wastes and their types are shown in Figure 1.

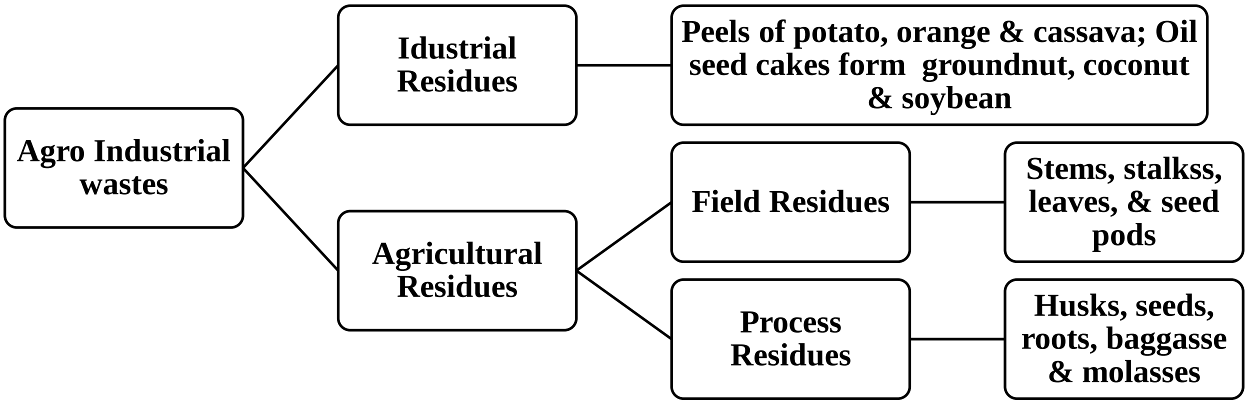

Figure 1: Agro-industrial wastes and their types. Source: (Pardeep *et al*., 2018)

The agro-industrial wastes can be used as solid support in SSF processes for the production of a range of significant beneficial compounds. The use of agricultural and agro-based industry wastes as raw materials can help to reduce the production cost and contributed to the recycling of waste as well to make the environment eco-friendly (Pardeep *et al*., 2018)

Ioannis *et al*., (2006) carried out an extensive study on the application and use of grape leftovers. The use of grape seed extracts (GSE) has gained ground as a nutritional supplement because of their antioxidant activity (Gonzalez *et al*., 2004). The by-products obtained after winery exploitation, either seeds or pomaces, constitute a very cheap source for the extraction of antioxidant flavanols, which can be used as dietary supplements, or in the production of phytochemicals, thus providing an important economic advantage (Negro *et al*., 2003). Grape pomace represents a rich source of various high-value products such as ethanol, tartrates and malates, citric acid, grape seed oil, hydrocolloids, and dietary fiber. Moreover, grape pomace is characterized by high-phenolic contents because of poor extraction during winemaking, making their utilization worthwhile and thus supporting sustainable agricultural production. Extensive research has demonstrated that many biodegradable organic wastes can be composted conveniently and economically (Epstein, 1997; TiquIa and Tam, 2000; Kadir *et al*., 2016; Ilic-Krstic *et al*., 2018). Composting organic matter is a simple and efficient manner of transforming agro-industrial wastes into products suitable for use as soil conditioners. Different substrates such as tomato waste, cork residues, olive husks, and tannery sludge for composting resulted in end-products adequate as organic fertilizers in terms of their physical-chemical characteristics. Treatment of grape wastes, physicochemical properties, and their use is shown in Table 1.

It has been reported that the grape mark, a primary waste of wine production could be recycled as a soil conditioner because of its organic and nutrient contents (Diaz *et al*., 2002). Besides, compost obtained from winery wastes showed that its chemical values are within the same range as those from other sources, though with a high-calcium value due to the nature of the wine-making process (Bertran *et al*., 2004). Winery waste sludge was shown to be an effective adsorbent for the adsorption of heavy metals from aqueous solutions.

Metal sorption consists of several mechanisms that quantitatively and qualitatively differ according to the metal species in solution and the origin and processing of the sorbent. The properties of winery waste are similar to those of other adsorbents, providing it with the ability to adsorb heavy metals (Yuan *et al*., 2004). Grape skin pulp should be considered as the best substrate for pullulan production. Hot water extracts of the pulp can serve as a good substrate for fermentation with *Aerobasidium pullulans* for the production of pullulan. Moreover, it was shown that the pullulan produced from winery waste was of high-molecular-weight (4.22 · 106) and rather pure as determined by its gel elution profile, glucose content, and the number of residues in repeating units (Table 1).

Ioannis *et al*. (2006) had shown that winery wastes have very high polyphenolic contents, making their utilization worthwhile and thus supporting sustainable agricultural production. In particular, the by-products from vinification are suitable as dietary supplements or as ingredients in functional foods. Furthermore, the compost from winery wastes possesses adequate characteristics for its use as a soil conditioner. Additionally, wine-processing sludge shows to be an effective adsorbent for the adsorption of pollutants. And finally, winery wastes can be recycled and used as a substrate for the production of a high-added-value product, Pullulan.

The characterization and potential uses of fruit peel waste had been studied and reported (Pranav *et al*., 2017). Orange peel (OP) is obtained from an agricultural product, Orange (Citrus *sinensis*, family Rutaceae). OP contains cellulose, hemicellulose, lignin, pectin (galacturonic acid), chlorophyll pigments, and other low-molecular-weight compounds (e.g. limonene). Traditionally, OP is treated to obtain volatile and non-volatile fractions of essential oils and flavouring compounds. Also, OP has been reported to have germicidal, antioxidant, and anticarcinogenic properties, and thus may be effective against breast and colon cancers, skin inflammation, muscle pain, stomach upset, and ringworm (Foo and Hameed, 2012). The outer layer of Lemon (Citrus *limon*, family Rutaceae) peels is called flavedo, its colour may either be green or yellow.

Flavedo is a rich source of essential oils, which has been in use since early times in the flavouring and fragrance industries. The major component of lemon peel is the albedo, which is a spongy and cellulosic layer under the flavedo and has high dietary fiber content (Garcia-Perez *et al*., 2008). Also Citrus (Citrus limetta, family Rutaceae) is the world’s largest produced fruit, accounting for 23% of the world’s total fruit

Table 1: Treatment of grape wastes, physicochemical properties, and their use**.**

Grape waste	Treatment	Physicochemical properties	Uses
Grape waste	Composting of grape waste and hen droppings	Organic matter content	Fertilizer for corn seed
Grape seed and Skin extracts	Fractionation of grape seed and skin extracts from grape waste	Phenol content	Dietary supplements for disease prevention
Grape waste	Gasification of waste product from grape	Concentrations of unused residues	Gas production for heating purpose
Pressed grape skin	Composting of solid waste and wastewater	Organic matter content	Fertilizer
Wine pomace and grape seeds	Lyophilisation and extraction of flavanols	Flavanols content	Dietary supplements, production of phytochemicals
Grape marcs, stalks, and dregs	Lyophilisation and extraction of polyphenols	Polyphenolic content	Dietary supplements
Grape skins, seeds, and stems	Acidolysis of a polymeric proanthocyanidins fraction of grape pomace in the Presence of cysteamine	Flavanol content	Source of flavanols
Grapeseed Extract (GSE)	Pre- and post-mortem use of grape seed in a feeding experiment	Phenol content	Feedstuff for dark poultry meat
Grape skin pulp	Fermentation by Aureobasidium pullulan	Ethanol precipitate	Pullulan production
Grape seeds	Solid-state cultivation by trametes hirsute	Lignocellulosic content	Laccase production
Grape pomace	Solid-state cultivation by Pleurotus *spp.*	Pruning content, high phenolic components, and total sugars	Feedstuff for animals
Wastewater	Electrodialysis	Tartaric acid content	Additive in medicines, cosmetics, and acidulants -the compound in soft drinks
Wastewater	Electrodialysis at 60°C	Tartaric acid and malic acid content	Food and pharmaceutical industries

*Source: (*Ioannis e*t al., 2006).*

production. Citrus peel (CP) is a potential source of certain essential oils and yields about 0.5–3 kg oil/tonne of fruit. The essential oils extracted are used for various purposes, such as pharmaceuticals, confectioneries, cosmetics, alcoholic beverages, and also for improving the shelf-life and safety of various foodstuffs. Besides, CP is also rich in pectin (Mohapatra *et al*., 2010).

Likewise, Banana (Musa *spp*., family Musaceae), develops in hanging clusters, with nearly 20 fruits/hand (tier) and 3–20 hands in each cluster. The average fruit weight is about 125 g with nearly 25% dry matter and 75% water. Banana peel (BP) comprises about 30–40% (w/w) of fresh banana. The composition of ripe BP is as follows: crude protein (8%), ether extract (6.2%), soluble sugars (13.8%), and total phenolic compounds (4.8%). The main components of BP are cellulose, hemicellulose, chlorophyll, pectin, and other low-molecular-weight compounds (Mohapatra *et al*., 2010). Banana is the second largest produced fruit, accounting for 16% of the total fruit production worldwide. India is the largest producer of bananas, accounting for 27% of the world's total banana production (Kumar *et al*., 2013).

Table 2: Common Pharmaceutical Categories, Functions, and Examples.

Pharmaceutical categories	Functions	Examples
Analgesics	Pain-relieving without causing loss of consciousness	Acetaminophen, ibuprofen, and aspirin
Anaesthetics	Production of a lack of feeling either locally or generally depending upon the type and nature of administration.	Lidocaine and Procaine
Antibiotics	Destruction and or inhibition of the growth of microorganisms	macrolides, lincosamides, tetracyclines, and quinolones
Anticoagulants	Prevention or delay of blood clotting	heparin, warfarin, dabigatran, rivaroxaban, and apixaban.
Antiemetics	Prevention of or relief from nausea and vomiting	trimethobenzamide, dimenhydrinate, metoclopramide, promethazine, and dronabinol.
Anti-inflammatory	Prevention of inflammation	ibuprofen, naproxen, and aspirin.
Antimanic	Treatment of a manic episode of manic-depressive and bipolar disorder	lithium, haloperidol, clonazepam, and lorazepam

Source: Rafik, 2015

Jackfruit (*Artocarpus heterophyllus* L., family Mulberry) is also another fruit of importance. The tree produces around 200–500 fruits annually. At maturity, each fruit weighs approximately 23–50 kg. About 59% of the fruit's outer peel is composed of fiber, which is fairly rich in calcium and pectin. Jackfruit is a popular food ingredient in the tropical parts of the world (Foo and Hameed, 2012). After the consumption of the edible part, the fruit peels (FPs) are dumped indiscriminately and become serious pollution and disposal problems. Hence, the utilization of FP for engineering applications serves two purposes, generating wealth from waste and also an efficient solid-waste reduction.

Pharmaceutical Pollutants

Pharmaceutical compounds are described as chemical substances used to treat illness, relieve a symptom, or modify a chemical process in the body for a specific purpose. Pharmaceuticals are classified into different groups according to their chemical characteristics, structure, and how they are used to treat a specific disease. There are about eighty such broad categories of pharmaceuticals under therapeutic classification (Rafik, 2015). The table below shows some common pharmaceutical categories, their function, and examples.

Kumari *et al*., (2010) observed that pharmaceutical compounds reach the environment and can be considered as environmental pollution. Pharmaceuticals were thought to reach the environment primarily through usage or inappropriate disposal. Various production facilities were found to be sources of much higher environmental concentrations than those caused by the usage of drugs (Larsson *et al*., 2007). Pharmaceuticals plants generate a large number of wastes during manufacturing, housekeeping, and maintenance operations. While maintenance and housekeeping activities are similar from one plant to the next, the actual processes used in pharmaceutical manufacturing vary widely.

Typical waste streams include spent fermentation broths, process liquors, solvents, and equipment wash waters, spilled materials, and used processing aids. Pharmaceuticals have been detected in wastewater treatment plant effluents, surface water, groundwater, and drinking water. Different classes of drugs such as analgesics, antibiotics, antiepileptic, antihypertensive, antiseptics, beta-blocker heart drugs, contraceptives, hormones, and psychotherapeutics have been documented as environmental pollutants (Halling-Sørensen *et al*., 1998). Pharmaceutical products (i.e. natural or synthetic chemicals designed to have a specific mode of action) are used in human and veterinary medicine and are a class of emerging environmental contaminants (Fent *et al*., 2006). Pharmaceuticals in the aquatic environment have been reported in rivers, sewage, streams, seawater, groundwater, and drinking water. The presence of pharmaceutical wastes in the environment poses a great danger to the health of all the inhabitants, this trend is becoming a contentious phenomenon to both environmental regulators and the pharmaceutical industry (Crane *et al*., 2006). Although, different classes of pharmaceuticals are used in human and veterinary medicine, however, some of them have a higher negative impact on the environment than others due to their high frequency of consumption, volume consumed, and toxicity (Fent *et al*., 2006). A wide range of medications including antibiotics, analgesics, blood lipid-lowering agents, antiepileptic, and β-blockers have been found in different concentrations in the effluents and surface waters globally (Fent *et al*., 2006; Halling-Sørensen *et al*., 1998). Measurable concentrations are usually low, maybe in ng/l to µg/l in range (Fent *et al*., 2006).

Side effects caused by some pharmaceutical products

Antibiotics: Antibiotics are widely used, but studies show that up to 95% of antibiotic compounds may be released unaltered into the sewage system. This phenomenon is suspected to be due to the accelerated resistance of bacterial pathogens against various antibiotics. High concentrations of antibiotics can lead to a change in microbial community structure and affect food chains. Stream surveys document microorganisms that are resistant to a wide array of antibiotics, including vancomycin (Ash et al., 1999). Certain bacteria that are isolated from wild geese near Chicago, Illinois were reported to be resistant to ampicillin, tetracycline, penicillin, and erythromycin (Eichorst et al., 2015). However, contamination of microbial communities in septic tanks, sewers, soil, receiving waters, and other environmental compartments create a widespread pool of antibiotic-resistant microbes, and risk by the widespread use of antibiotics as growth promoters for animals in an aquatic environment is being debated (Carlsson et al., 2009). Antibiotic and other drug resistance is already a major issue in medicine, with significant health and economic impacts as shown in tuberculosis and malaria. The potential of this phenomenon resulting in a great epidemic is high if not curtailed on time (Carlsson et al., 2006).Continuous exposure to antibiotics can increase bacterial resistant strains in the environment. The spread of antibiotic-resistant bacteria can disturb the environmental balance and cause unpredictable effects on humans and animals. Although, pharmaceutical products are necessary and important for human health, however, it should be produced and/or disposed of in such a way that it will cause the least harm to the environment. It is better to control the high consumption of drugs than combating its attendant polluting effects.

Analgesics and nonsteroidal anti-inflammatory drugs: Non-steroidal anti-inflammatory drugs (NSAIDs), such as ibuprofen, naproxen, and diclofenac, are widely used medications and consequently are often detected in sewage, surface water, and maybe in groundwater. Diclofenac, ibuprofen, acetyls alicyclic acid, ketoprofen, naproxen, indomethacin, and phenazone have all been found in surface water. Diclofenac, ibuprofen, and propyphenazone are the most commonly found drugs in the water systems after clofibric acid. Diclofenac has been proven to be acutely toxic for vultures and cattle. Ibuprofen is one of the most commonly used drugs in the world and causes high levels of environmental pollution. The most sold drugs worldwide, NSAIDs have an estimated annual production of several kilotons (Cleuvers, 2004). NSAIDs such as ibuprofen, naproxen, and aspirin are the most common drugs which are usually found in significant quantities in municipal effluents.

Table 3: Occurrence of commonly detected pharmaceuticals in different water sources

Pharmaceutical	Water source	Concentration (ng/L)
Amoxicillin	Hospital effluents	900
	WWTP influents	9.94×10^3
Ampicillin	Industrial effluents	5.8×10^3
Atenolol	River	250–600
Bezafibrate	WWTP influents	0.3–87
Caffeine	Urban effluents	23–776
	Surface water	2.9–194
	WWTP influents	2,448–4,865
	River	38–250
Carbamazepine	WWTP influents	33–1,318
	Urban effluents	73–729
	Surface water	4.5–61
	River	56–160
Cefaclor	WWTP influents	6.15×10^3
Cefazolin	Industrial effluents	4.2×10^3
Cefotaxime	Industrial effluents	4.2×10^3
Cephalexin	Hospital effluents	1×10^4
	WWTP influents	6.4×10^4
	Industrial effluents	3.1×10^3

Ciprofloxacin	WWTP influents	27–514
	Hospital effluents	1.5×10^4
Clarithromycin	WWTP influents	nd-724
Clofibric acid	WWTP influents	nd-82
	Liao River	18
Demethyl diazepam	WWTP influents	nd-62
Diclofenac	Urban effluents	8.8–127
	Surface water	1.1–6.8
	WWTP influents	9–13
	River	21–98
	Liao River	717
Dilantin	Urban effluents	8.8–181
	Surface water	1.1–8.9
Enrofloxacin	Hospital effluents	100
Erythromycin	WWTP influents	9–353
	Urban effluents	8.9–294
	Surface water	1.8–4.8
Gemfibrozil	WWTP influents	181–451
Ibuprofen	Liao River	246
	Urban effluents	10–137
	Surface water	11–38
	River	35–270
Iopromide	Urban effluents	1,170–4,030
	Surface water	20–361
	River	780–8,100
Lincomycin	WWTP influents	11–629
	Hospital effluents	1.7×10^3
	Industrial effluents	1.1×10^5
Metronidazole	Industrial effluents	7.8×10^3
Nalidixic acid	Industrial effluents	6.7×10^3
Naproxen	Urban effluents	20–483
	Surface water	1.8–18
	River	81–360

Norfloxacin	Hospital effluents	200
Ofloxacin	WWTP influents	150–1,081
	Industrial effluents	1.3×10^3
Oxytetracycline	Industrial effluents	1.5×10^4
Salicylic acid	WWTP influents	433–8,036
	Liao River	295
Spiramycin	WWTP influents	11–129
Sulfadiazine	Industrial effluents	353
Sulfamethoxazole	WWTP influents	46–253
	Urban effluents	3.8–407
	Surface water	1.7–36
	River	9–190
	Hospital effluents	300
	Industrial effluents	5.8×10^3
Sulfanilamide	Industrial effluents	207
Sulfathiazole	Industrial effluents	9.6×10^3
Tetracycline	Industrial effluents	1.5×10^3
Trimethoprim	Urban effluents	10–188
	Surface water	3.2–53.
	River	11–94
	Hospital effluents	300
	WWTP influents	4.3×10^3

Source: Javaid *et al.*, 2015

A potential adverse effect of abuse of antibiotics is possible to damage the immune system of animals (Carlsson *et al*., 2009). Antibiotics are widely used in the treatment of diseases in animals and humans, as well as being applied in food rations to increase animal growth rates. Antibiotics have a high antimicrobial activity which is associated with the aromatic structure containing the naphthol chemical group that is antibacterial.

However, approximately 50-90% of the doses of antibiotics administered in health treatment procedures are not absorbed by the organisms and are eliminated by humans and animals in sewage systems (Chayid and Ahmed, 2015). These molecules have a complex chemical structure and the natural environment and sewage conditions are not sufficient to decompose their chemical structure. Thus, the number of antibiotics accumulated in sewage can be a serious environmental problem (Chungombe *et al*., 2014). Due to the chemical structure of antibiotics, they are resistant to many chemicals, oxidizing agents, and heat, and are biologically non-degradable.

Removal of pharmaceutical pollutants in wastewater using agricultural waste

Agricultural wastes adsorbents: Activated carbon has been a popular choice as an adsorbent for the removal of pharmaceuticals from wastewater, but its high cost poses an economical problem (Al-Bayati, 2007; Osorio *et al*., 2012). Therefore, researchers felt the need for the development of low cost and easily available materials, which can be used more economically on a large scale. This opened the doors of research interests into the production of alternative adsorbents to replace the costly activated carbon and this has intensified in recent years. The waste materials and by-products from agriculture and other industries are the sources of low-cost adsorbents due to their abundance in nature and simple processing protocols (Alade *et al*., 2012). In recent years, a new class of adsorbents and specifically lignocellulosic materials have been investigated for the same purposes: their attractiveness resulting from their availability, low cost, and biodegradability (Sulyman *et al*., 2017).

The use of agricultural wastes such as sawdust, rice husk, date stones, watermelon peels, rice bran, pine sawdust, oak sawdust, tea leaves, wood sawdust, chestnut shells, bamboo canes, straw, mango kernel, and peanut shells, in the preparation of adsorbents to efficiently remove heavy metals and various organic compounds such as dyes and pharmaceuticals has been widely reported (Danish *et al*., 2010). Accumulation of these pharmaceuticals on agricultural waste-based adsorbents is generally achieved through interactions with the hydroxyl and carboxyl groups particularly abundant in polysaccharides (cellulose and hemicelluloses) and lignin, both of which constitute about 90% of dry lignocellulosic materials (Ofomaja, 2008). Furthermore, the functionalization of lignocellulosic material by the grafting of organic molecules bearing active groups is primary to the effectiveness of agricultural wastes as an important raw material in the preparation of adsorbents. Interestingly, the use of the resulting hybrid materials as an adsorbent leads to a significant increase in adsorption capacity over that of activated carbon (El-Aziz *et al*., 2009).

Adsorption of pharmaceutical dye from wastewater using litchi peels: Several adsorbent materials containing intrinsic properties such as low cost, high surface area, and magnetic property have been used for the removal of different pollutants in wastewaters (Jiang *et al*., 2015). However, in recent years, magnetic adsorbents have attracted great interest due to their easy separation and recuperation from an aqueous solution by a magnetic field. Vitória *et al*., (2017) used the pyrolysis method to produce Iron-based adsorbent from Lychee fruit (Litchi chinensis) peels for the removal of pharmaceutical pollutants from synthetic aqueous solution. Lychee fruit is a Sapindaceae and known to be of the soapberry family. Vitória *et al*., (2017) showed that the iron-based material prepared from litchi peel biomass presented a mesoporous structure and magnetic property. The Pseudo-second-order model was the best to fit the pharmaceutical dye (amaranth) adsorption kinetics, and the Brunauer, Emmett, and Teller (BET) model were well suited to fit the adsorption isotherm data. The maximum adsorption capacity verified was 44.87 mg g−1, indicating that the adsorption performance of the material prepared was similar and superior to other adsorbents reported previously and thus could be employed as an alternative adsorbent in the removal of pharmaceutical dye from wastewater (Vitória *et al*., 2017).

Equilibrium sorption of thermally treated rice husk (TTRH) for sulfamethazine: Equilibrium sorption of TTRH for Sulfamethazine (SMT, a pharmaceutical product) adsorption was studied by Balarak *et al*., (2020a). The Physico-chemical properties of the modified rice husk were determined in the study. Balarak *et al.*, (2020a) showed that the sorption data fitted into Langmuir, Freundlich, and Dubinin–Radushkevich isotherms. The Langmuir Adsorption model had the highest regression value and hence the best fit. Hence, rice husk modified with the thermal process is a potential biosorbent for the removal of SMT from its aqueous solution (Balarak *et al.*, 2020a).

Adsorption of ibuprofen, ketoprofen, naproxen, and diclofenac onto a low-cost activated carbon, prepared from olive-waste cakes: Adsorption of ibuprofen, ketoprofen, naproxen, and diclofenac onto a low-cost activated carbon, prepared at the laboratory scale from olive-waste cakes, was investigated by Baccar *et al.*, (2012). In the study, the exhausting olive-waste cake was collected from an oil factory ‘‘Agrozitex’’ located in Sfax, Tunisia, and used as raw material to produce activated carbon via chemical activation using phosphoric acid (analytical grade) as a dehydrating agent. After structural characterization of the sorbent, the thermodynamics and kinetics aspects of the adsorption were investigated. From the equilibrium study carried out, the Langmuir model provided the best fit and hence agreed with monolayer adsorption for the four considered pharmaceuticals. Time-based investigations showed that the adsorption process followed the second-order model. Large quantities of the drug were adsorbed in a mixture indicating the ability of the prepared adsorbent to adsorb multiple drugs (Baccar *et al.*, 2012). From the experimental work carried out, the percentages removal of naproxen, ketoprofen, and ibuprofen from mixture drug solution at 25^{o}C are shown in Table 4.

Table 4: Percentages removal of naproxen, ketoprofen, and ibuprofen from mixture drug solution at 25^{o}C unto olive-waste cakes

Drug	Percentage removal (%)
Naproxen	90.45
Ketoprofen	88.40
Ibuprofen	70.07

Source: Baccar et al., 2012

Adsorption of diclofenac from aqueous solution using potassium ferrate activated porous graphitic biochar: Biochar is obtained by heating organic biomass under a limited oxygen environment to obtain a material that has excellent adsorption capacity for various pollutants in wastewater due to a highly specific surface area and porous structure. Biochar and its activated derivatives, as an attractive absorbent, have been widely employed in wastewater treatment and soil remediation. It has also been reported that biochar could remove toxic contaminants such as pathogens, organic pollutants, and inorganic pollutants from wastewater (Petrie *et al.*, 2015).

There are several methods for the modification of a biochar surface, including physical or chemical activation, steam activation, and coating for the contaminants' removal from wastewater. Among them, chemical activation has gained significant scientific attention. Activated biochar materials obtained by activated chemicals have numerous advantages, such as having a wide spectrum of functional groups, high specific surface area, and porous structure. Those advantageous characteristics contribute to the increase in the adsorption capacity of activated biochar. Thi *et al.*, (2019) studied the adsorption of diclofenac from aqueous solution using potassium ferrate activated porous graphitic biochar as the adsorbent and concluded that the method was greatly simplified, cost-effective, highly efficient, strongly reproducible, and economical because of the abundance of raw material.

Porous graphitic biochar was synthesized by one-step treatment biomass using potassium ferrate (K_2FeO_4) as an activator for both carbonization and graphitization processes. The modified biochar (Fe@BC) was applied for the removal of diclofenac sodium (DCF) in an aqueous solution.

The prepared material possesses a well-developed micro/mesoporous and graphitic structure, which can strengthen its adsorption capacity towards DCF. The experimental results indicated that the maximum adsorption capacity (q_{max}) of Fe@BC for DCF obtained from Langmuir isotherm simulation was 123.45 mg_L1 and it was a remarkable value of DCF adsorption in comparison with those of other biomass-based adsorbents previously reported. Thermodynamic quality and effect of ionic strength studies demonstrated that the adsorption was an endothermic process, and higher environmental temperatures may be more favourable for the uptake of DCF onto Fe@BC surface; however, the presence of NaCl in the solution slightly obstructed DCF adsorption. The adsorption capacity was found to have decreased with an increase in the solution's pH. Besides, the possible mechanism of the DCF adsorption process on Fe@BC may involve chemical adsorption with the presence of H-bonding and π-π interaction. With high adsorption capacity and reusability, Fe@BC was found to be a promising absorbent for DCF removal from water as well as for water purification applications. Table 4 shows the DCF adsorption capacity of various adsorbents (from agricultural waste) compared to Fe@BC as reported by Thi *et al*., (2019). This vividly shows the sorption efficiency of adsorbents produced from agricultural waste in the adsorption of pharmaceutical pollutants.

Adsorption of aspirin, paracetamol, and ibuprofen using rice husk activated carbon: Mukoko *et al*., (2015) investigated the adsorption of selected pharmaceutical waste compounds (aspirin, paracetamol, and ibuprofen) in hospital effluent using rice husk activated carbon. Rice (*Oryza glaberrima*) hulls from the Charehwa area of Mutoko North in Mashonaland East, Zimbabwe was used in the study. The activated carbon used was prepared as reported by Soleimani and Kaghazchi, (2014)

Table 5: DCF adsorption capacity of various adsorbents and Fe@BC.

Adsorbents	Adsorption Capacity qmax (mg_g^{-}1)
Fe@BC	123.5
Coca shell	63.5
Carbon xerogels	80.0
Activated carbon (Commercial)	76.0
Activated hydrochars from orange peels	52.2
Activated carbon	36.2
Activated carbon from olive-waste cakes	56.2
Granular carbon nanotubes	27.0
Tea waste derived activated carbon	62.5
Coconut shell activated carbon	103.0
Activated carbon from potato peel waste	68.5
Cyclamen persicum (herbaceous plant)	22.2

Source: *(*Thi *et al.,* 2020)

The ground rice hull particles were impregnated with phosphoric acid (85%) with a density of 1.71 g cm^{-3}, carbonized, and activated in a programmable muffle furnace. The activated carbon was dried and characterized using FTIR, SEM, and XRD. For the characterization process, the Surface morphology of the prepared activated carbon was analyzed using scanning electron microscopy Functional groups were determined using Fourier Transform Infrared Spectrophotometer. The degree of crystallinity or amorphous nature of activated carbon was determined using a Bruker D8 Discover X-ray diffractometer with a nickel filtered Cu-Kα radiation source. The result of the study showed that the adsorption isotherm of aspirin onto rice hull derived activated carbon fitted well to the Freundlich model, whereas adsorption of ibuprofen and paracetamol fitted to the Langmuir model. Adsorption of the three drugs onto activated carbon showed the best fit for the pseudo-second-order kinetic model. Langmuir maximum adsorption capacities of 169.49, 100.00, and 178.89 mg/g were obtained for paracetamol, ibuprofen, and aspirin respectively.

Also, the results from the study revealed that the removal of the studied pharmaceutical wastes was directly proportional to the adsorbent dose and contact time, while it was inversely proportional to the initial concentration. It was also observed that pH affected the structural stability of the pharmaceuticals. Adsorption of aspirin and ibuprofen was found to be in the maximum in the acidic region (pH = 4) whereas paracetamol was not affected mainly by pH changes in the pH region of 2 to 10 (Mukoko *et al*., 2015). The study concluded that Activated carbon prepared from Zimbabwean rice hull (an agriculture waste) is capable of removing ibuprofen, aspirin, and paracetamol sludge from aqueous solutions and hospital effluent (Wastewaters).

Adsorption of paracetamol, phenol, and salicylic acid by coal-based activated carbon: The degree of change undergone by a coal as it matures from peat to anthracite is known as coalification. Coalification has an important influence on the physical and chemical properties (e.g. carbon content) of the coals and is referred to as the 'rank' of the coal (peat (50%-64% of carbon content), lignite, sub-bituminous, bituminous, anthracite (92-96% of carbon) (Kural, 1994)). The emission of emerging contaminants (pharmaceuticals, pesticides, personal care products) has been causing serious environmental problems in aqueous media. These pollutants and their metabolites have been found in high concentrations in wastewater treatment plants (WWTPs) effluents, due to their resistance to biological degradation (Osorio *et al*., 2012). Coal, a carbon-rich sedimentary rock is formed from plants subjected to high pressure and heat over millions of years. During its formation and transformation, it incorporates different mineral matters including sulfur and heavy metals.

In a study by Llado *et al*., (2016), the removal (by adsorption) of pollutants (such as paracetamol, phenol, and salicylic acid) present in pharmaceutical industry water by coal-based activated carbons was investigated. Two activated carbons; Coto Minero Narcea Activated Carbon (CNAC) and Mequinenza Activated Carbon (MAC), prepared from different evolved coals (rank): anthracite (CN) from Coto Minero Narcea, Asturias, Spain, and lignite (M) from the Mequinenza basin in Zaragoza, Spain) were used to produce the adsorbents. The precursors (CN and M) were activated by chemical activation using alkaline hydroxides (NaOH and KOH). The coals were mixed with the activated agent in a solid-state (physical mixture). Powdered alkaline hydroxides were selected as they would favour contact between the carbonaceous precursor and the activating agents. The physical mixing method is a very easy procedure that simplifies the first step in the preparation of activated carbons by chemical activation. It is widely used in the preparation of activating carbons from very different such as coals and terrestrial and marine biomass. Finally, the samples were dried at 105 ºC. The activated carbons obtained from the anthracite and lignite (<200 micrometers) were named CNAC and MAC, respectively.

Balarak *et al*., (2020b) provided an up-to-date development on the application of commercial activated carbon and various sustainable low-cost alternative adsorbents such as agricultural solid waste (Azolla, Lemna minor, canola, etc.), industrial solid waste, agricultural by-products, and biomass-based cost-effective activated carbon, and various natural materials in the removal of antibiotics from an aqueous phase in another study. Table 6 shows a comparison of the results of various reported studies on the performance of different adsorbents for the removal of antibiotics from pharmaceutical wastewater. It can be seen from the table that agricultural waste is the future of adsorbents.

Adsorption of trimethoprim from aqueous solution using both cellulose acetate polymer and attapuligate clay: Al-Bayati and Athraa, (2011) investigated the adsorption-desorption of trimethoprim antibiotic drugs from aqueous solution using two different naturally occurring adsorbents. This approach was used to prove that adsorption is an efficient method in combating drug poisoning (Al-Bayati and Athraa, 2011). Drug poisoning is a phenomenon where any substance which when swallowed, inhaled, injected, or absorbed through the skin is capable of causing death, injury, toxic reactions One of the most effective methods for emergency treatment of accidental drug poisoning is adsorption. In the study, trimethoprim (antibiotic) was used as a drug model (i.e. the adsorbate) and both cellulose acetate polymer and attapuligate clay were used as adsorbents. Adsorbents are effective in the removal of poison and it is effective, stable, easily accessible, cheap, and harmless (Al-Bayati, 2007). Results of the study showed that the adsorption isotherm of trimethoprim on both surfaces used obeyed Freundlich isotherm. The result further showed the surface heterogeneity leading to different adsorption forces from site to site and different affinities toward drug molecules. The adsorption extent of trimethoprim at pH = 1.2 on attapulgite clay surface was found to increase as compared with the neutral medium, the contact time for the maximum adsorption of the drug on attapuligate clay surface required was two hours and for cellulose acetate polymeric surface was about two and a half hours. For that reason, it was established that attapuligate clay (an agricultural waste) is a useful material for adsorption.

Table 6: The results of various reported studies of different antibiotics, adsorbents and their percentage of removal through the adsorption process

Adsorbents	Antibiotics name	% Removal range
Carbon materials	Amoxicillin	39.5-75.6
AC-vine wood	Cephalexin	44.5-87.2
Bentonite	Amoxicillin	41.8-94.6
AC-siris seed	Metronidazole	35.2- 64.2
AC	Tetracycline	44.6-78.9
Montmorillonite	penicillin G	64.8-98.2
AC-lignocellulosic	Cephalexin	21.9-92.1
NiO nanoparticle	Amoxicillin	54.3-87.9
AC- pyrolysis char	Tetracycline	71.5-91.8
AC commercial	Ibuprofen	61.4-97.4
Maize stalks	Tetracycline	54.6-94.2
Azolla filiculoides	Tetracycline	69.8-87.9
AC-macadamia shells	Tetracycline	71.4-87.2
Granular sludge	Oxytetracycline	39.8-79.8
Chestnut shell	penicillin G	28.7-81.4

Source: *(Balarak et al., 2020)*

In another study, Erki *et al.*, (2017) observed that the presence of pharmaceutical residues in the receiving water bodies of wastewater treatment plants (WWTP) and the environment has become a global concern. With the presence of metabolized in our bodies, it is certain that partially modified or unmodified pharmaceuticals will reach WWTP. In the 1990s, reports showed that the most widely known proven effect of pharmaceuticals on organisms is the major population collapse of white-backed vultures (*Gyps Africanus*) in Pakistan and India. The birds consumed the carcasses of cattle that had been treated regularly with NSAID diclofenac. For vultures, the concentration was high enough to cause kidney failure (Klatte *et al*., 2016)

Various risk assessment methods have been developed to determine the most harmful drugs. Carlsson *et al*., (2006) assessed the ecotoxicity risks of 27 different pharmaceuticals. Based on this study, the most dangerous drugs for the environment include diclofenac, ethinylestradiol, ibuprofen, metoprolol, norethisterone, oestriol, and oxazepam. This was further confirmed in another study and an antibiotic, sulfamethoxazole was added to the list of ecotoxic pharmaceuticals (Sangion and Gramatica, 2016). Therefore, it was essential to find a treatment process that is capable of removing pharmaceutical residues, and thus the basis for the study aimed at the removal of three pharmaceuticals found in the environment, namely diclofenac (DCF), sulfamethoxazole (SMX), and levofloxacin (LFX), through the use of powdered activated carbon (PAC).

Different solutions of DCF ($C_{14}H_{10}C_{l2}NNaO_2$), SMX ($C_{10}H_{11}N_3O_3S$), and LFX ($C_{20}H_{24}O_2$) were prepared with ultrapure (ELGA) water and a known concentration of the pharmaceuticals under investigation (pH of all solutions was 7.6). The concentration was measured as total organic carbon (TOC). The results of the study showed that the three compounds were successfully removed from WWTP using a low-cost adsorbent (agricultural effluents). LFX has the best adsorption property and SMX the poorest (Carlsson *et al*., 2006).

Potato peel waste-based activated carbon for diclofenac adsorption: Bernardo *et al*., (2015) presented a report of an investigation on the use of potato peel waste-based activated carbon for diclofenac adsorption. Potato is one of the most produced and consumed carbohydrates all over the world. In 2013, the world production of potatoes was around 376 million tons. A huge amount of waste is generated as Potato Peel Waste (PPW) (Arapoglou *et al*., 2010). PPW is discarded, composted, or used as low-value animal feed. Nonetheless, the volumes of PPW are too high to be sustainable and economically disposed of through these methods.

Moreover, the potential contamination of PPW with side streams poses difficulties with disposal along with the rapid microbial spoilage of this wet waste. Hence, the conversion of PPW into added-value products such as activated carbon is a potential pathway for its valorisation, although there are very few reports concerning the use of this waste as a precursor of carbon adsorbents (Kyzas and Deliyanni, 2015). Furthermore, Diclofenac (DCF) which is one of the important and strong pharmaceutical products, is a widely used anti-inflammatory agent, frequently supplied as monosodium salt. Recently, DCF was included in the first watch list of the European Directive 2013/39/EC as a substance that may pose a significant risk to, or via, the aquatic environment. Therefore, the development of efficient and sustainable methods for the removal of DCF from water is imperative, such as adsorption processes that use activated carbon derived from biomass wastes. Bernardo *et al*., (2015) showed through the study that PPW-based activated carbon has the potential to be used as an adsorbent of DCF from an aqueous medium. Its performance was also comparable to that of a commercial activated carbon, and the biomass-derived carbon presented a higher affinity to the DCF molecule (Bernardo *et al*., 2015).

Use of sugarcane bagasse (SCB) for the adsorption of tetracycline in an aqueous medium:
Araceli *et al.,* (2014) showed in another study that sugarcane bagasse (SCB) can be used for the adsorption of tetracycline in an aqueous medium. This natural adsorbent has satisfactory maximum adsorption capacity for tetracycline. Besides, this material is more efficient than activated carbon for removing the tetracycline utilized in this study from the water supply. Therefore, this adsorbent is suggested as a possible alternative in the treatment of wastewater contaminated with tetracycline.

4.0 Conclusion

This review indicates that pharmaceuticals are useful in both human and veterinary medicine and their use is on the rise. This leads to more production and generation of pollutants in pharmaceutical wastewater which finds its way to the aquatic environment through its disposal system. Conventional methods for the removal of pollutants are seen as highly cost-effective. An alternative to this is the development of adsorbents from agricultural waste that are readily available in vast quantities. This approach will also help in getting rid of materials considered as wastes within the system. Although, this approach, i.e. the conversion of agricultural wastes into adsorbents, has been very effective and efficient, however, the use of nanoadsorbants produced from agricultural wastes as adsorbents are recommended in other to further maximise the efficiency of the process in line with the most current trend in science and technology

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