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Removal of emerging pollutants from aqueous matrices

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ABSTRACT

Water pollution is a growing problem and causes rising concern among researchers. As a result of increased consumption of pharmaceuticals and, as a consequence, the growth of the pharmaceutical industry, the pollution of substances harmful to human health in water matrices is gradually increasing every year. The lack of satisfactory methods for wastewater treatment from emerging pollutants exacerbates the situation. That is why many researchers have directed their efforts to the study of the removal processes and the development of new water treatment methods. Of considerable interest is the possibility of using organic waste to prepare an effective adsorbent and its use in the removal of pharmaceuticals.

In this work some knowledge of recent years studies is gathered together on purpose to study preparation and application of organic wastes based activated carbon for removal pharmaceutical compounds from aqueous matrices. Methods of adsorbent preparation and adsorption providing are described. Factors influencing adsorption efficiency were also analyzed.

Keywords: Water Pollution; Emerging Pollutants; PPCP; Pharmaceuticals; Removal Processes; Adsorption; Activated Carbon; Organic Waste.

RESUMO

A poluição da água é um problema crescente que causa preocupação progressiva entre os investigadores científicos. Como resultado do aumento do consumo de produtos farmacêuticos e, como consequência, do crescimento da indústria farmacêutica, a poluição de substâncias nocivas à saúde humana nas matrizes hídricas vem aumentando gradualmente a cada ano. A falta de métodos satisfatórios para o tratamento de águas residuais relativamente à remoção de poluentes emergentes agrava a situação. Por essa razão, muitos investigadores têm direcionado seus esforços para o estudo dos processos de remoção e o desenvolvimento de novos métodos de tratamento de água. Neste contexto, é de considerável interesse a possibilidade de usar resíduos orgânicos para a preparaçãode adsorventes eficazes na remoção de produtos farmacêuticos de matrizes aquosas.

Neste trabalho, alguns conhecimentos referentes a estudos científicos recentes são reunidos com o objetivo de estabelecer um resumo do estado atual do conhecimento referenteà aplicação de materiais de carbono ativadobaseados em resíduos orgânicos para a remoção de compostos farmacêuticos de matrizes aquosas. Os métodos de preparação dos adsorventes, assimcomoos processos de adsorção são descritos. Analisam-se igualmente os fatores que influenciam a eficiência da adsorção.

Palavras-chave: Poluição da água; Poluentes Emergentes; PPCP; Produtos farmacêuticos; Processos de remoção; Adsorção; Carbono ativado; Resíduos Orgânicos.

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List of Abbreviations

AC	Activated Carbon
BET	Brunauer – Emmett – Teller
CVD	Cardiovascular Disease
EC	Emerging Compound
EDC	Endocrine Disrupting Chemicals
EP	Emerging Pollutant
EPA	Environmental Protection Agency
CAC	Chemically Activated Carbon
CPHAC	Cocoa Pod Husk Activated Carbon
GAC	Granular Activated Carbon
HPLC	High-Performance Liquid Chromatography
HSDM	Homogeneous Surface Diffusion Model
MRI	Magnetic Resonance Imaging
NSAID	Non-Steroidal Anti-Inflammatory Drug
OSAC	Olive Stone Activated Carbon
PAC	Powdered Activated Carbon
PCP	Personal Care Product
POP	Persistent Organic Pollutants
PPCP	Pharmaceuticals and Personal Care Products
SCAB	Sugarcane Chemically Activated Biochar
SPAB	Sugarcane Physically Activated Biochar
UV	Ultraviolet
WHO	World Health Organization
WWTP	Wastewater treatment plant

1. Motivation and objectives

1.1Introduction

Water is the most valuable source in human life. Water has a crucial role in all metabolic processes in the human organism. At the same time, it is an indispensable resource in any direction of human needs: domestic sphere, medicine, agriculture, light and heavy industry, electric power production, pharmacology, etc…Huge consumption of natural water sources leads to serious consequences. As a result, humanity must to tend water resources and maintain it in satisfactory condition to avoid noxious impact to environment and human health [1].

Fresh water represents only 3% of total water amount of planet. Moreover, approximately 85-90% of fresh water is contained in ice. Freshwater pollution is the ingress of various pollutants into the waters of rivers, lakes, and groundwater. This occurs by direct or indirect dumping of pollutants into the water in the absence of quality measures for the treatment and removal of harmful substances. Thousands of chemicals, with unpredictable effects, are present in aqueous matrices, among which compounds described as 'emerging pollutants'. Growing concentrations of toxic heavy metals (e.g. cadmium, mercury, lead, and chromium), pesticides, nitrates and phosphates, petroleum products, surfactants, drugs and hormones can be found in water, and some of them are detected in drinking water [2]. The discharge of untreated wastewater into water sources leads to microbiological pollution of the water. According to the World Health Organization (WHO), 80% of the world's diseases are caused by inappropriate quality and unsanitary conditions of water [2, 3].

Despite appearing in very low concentrations, some compounds can induce significant damage to human health. These are substances whose effects have not yet been fully studied, but their presence in aqueous matrices causes considerable concern. Emerging pollutants occur normally in range of concentrations from nanograms to micrograms per litter. These circumstances lead to a need to develop specific analysis and treatment methods [2].

1.2 Objectives

The main objective of this work is to review current methods of pharmaceutical removal from aquatic matrices with focus on application of organic waste based activated carbons as a source of appropriate adsorbent due to availability and low cost.

The specific objectives include:

- Review of the research materials of recent years regarding existing methods for removing pharmaceuticals from aqueous matrices;
- Bibliographic research of recent studies considering adsorption of pharmaceuticals using organic waste based activated carbon;
- Description of methodologies applied for adsorbent preparation and adsorption processes; to analyze factors influencing adsorption efficiency.

2. Water pollution

2.1 Classifications of water pollution

The most common water pollution is based on chemical and bacterial contamination. Radioactive, mechanical and thermal pollution is much less commonly observed [4].

Microbiological pollution is expressed in the appearance in the water of pathogenic bacteria, viruses (up to 700 species), protozoa, fungi, etc. This type of pollution is temporary due to the lifespan of the microorganisms [4].

The presence in water, even at very low concentrations, of radioactive substances causing radioactive contamination is very dangerous. The most harmful are “long-lived” radioactive elements that have an increased ability to move in water (strontium-90, uranium, radium-226, cesium, etc.).Radioactive elements fall into surface water bodies when radioactive waste is dumped in them, waste is buried at the bottom, etc. Uranium, strontium, and other elements enter groundwater both as a result of their precipitation on the earth's surface in the form of radioactive products and wastes and subsequent seepage into the earth along with atmospheric waters, and as a result of the interaction of groundwater with radioactive rocks [2, 5].

Mechanical pollution is characterized by the ingress of various mechanical impurities into the water (sand, sludge, sludge, etc.). Mechanical impurities can significantly impair the organoleptic characteristics of water. In relation to surface waters, their pollution (more precisely, clogging) with solid waste (garbage), residues of timber rafting, industrial and household waste, which degrade water quality, adversely affect the living conditions of fish, and the state of ecosystems are also distinguished [4].

Thermal pollution is associated with an increase in water temperature as a result of their mixing with warmer surface or process waters. With increasing temperature, there is a change in the gas and chemical composition in the waters, which leads to the multiplication of anaerobic bacteria, an increase in the number of hydrobionts and the release of toxic gases such as hydrogen sulphide and methane. At the same time, algal blooms occur as well as the accelerated development of microflora and microfauna, which contributes to the development of other types of pollution. According to existing

sanitary standards, the temperature of the water body should not increase by more than 3 °C in the summer and 5 °C in the winter, and the heat load on the reservoir should not exceed 12 to17 kJ / m^3 [4].

Chemical pollution is the most prevalent, persistent and far-reaching. It can be organic (phenols, naphthenic acids, pesticides, etc.) and inorganic (salts, acids, alkalis), toxic (arsenic compounds of mercury, lead, cadmium, etc.) and non-toxic. During sedimentation at the bottom of water bodies or during filtration in a formation, harmful chemicals are adsorbed by particles, oxidized and reduced, precipitate, etc., however, as a rule, complete self-purification of polluted waters does not occur. The focus of chemical pollution of groundwater in highly permeable soils can spread up to 10 km or more [6].

2.2 Pollutants

Chemical pollution is a change in the natural chemical properties of water due to an increase in the content of harmful impurities in it, both inorganic (mineral salts, acids, alkalis, clay particles) and organic nature (oil and oil products, organic residues, surfactants, pesticides) [4].

Inorganic pollution

The main inorganic (mineral) pollutants of fresh and marine waters are a variety of chemical compounds that are toxic to the inhabitants of the aquatic environment. These are compounds of arsenic, lead, cadmium, mercury, chromium, copper, fluorine. Most of them get into water as a result of human activity. Heavy metals are absorbed by phytoplankton and then passed along the food chain to more highly organized organisms [4].

Wastes containing mercury, lead, copper are localized in certain areas off the coast, but some of them are carried far beyond the territorial waters. Mercury pollution significantly reduces the primary production of marine ecosystems, inhibiting the development of phytoplankton. Wastes containing mercury typically accumulate in the bottom sediments of bays or river estuaries [7].

Its further migration is accompanied by the accumulation of methyl mercury and its inclusion in the trophic chains of aquatic organisms.

So, the Minamata disease, first discovered by Japanese scientists in people who ate fish caught in the Minamata Bay, into which industrial waste with technogenic mercury was uncontrolled, gained notoriety [8].

Organic pollution

Among the soluble substances introduced into the ocean from land, not only mineral, nutrient elements, but also organic residues are of great importance to the inhabitants of the aquatic environment. The removal of organic matter into the ocean is estimated at 300 to 380 million tons/year.

Wastewater containing suspensions of organic origin or dissolved organic matter adversely affects the state of water bodies. Precipitating, suspensions fill the bottom and retard the development or completely stop the activity of these microorganisms involved in the process of water self-purification. When decaying these sediments, harmful compounds and toxic substances, such as hydrogen sulphide, can form, which lead to pollution of all the water in the river. The presence of suspensions also avoids the penetration of light into the water and slows down the processes of photosynthesis [8].

One of the basic sanitary requirements for water quality is the content of the required amount of oxygen in it. All contaminants that somehow contribute to lowering the oxygen content in the water have a harmful effect. Surfactants - fats, oils, lubricants - form a film on the surface of the water, which prevents gas exchange between water and the atmosphere, reduces the degree of oxygen saturation of the water. A significant amount of organic matter, most of which is not characteristic of natural waters, is discharged into rivers along with industrial and domestic wastewater. Increasing pollution of water bodies and drains is observed in all industrial countries [4].

Due to the rapid pace of urbanization and the somewhat delayed construction of wastewater treatment plants or their unsatisfactory operation, water basins and soil are polluted with household waste. Particularly noticeable is pollution in bodies of water with a slowed flow or a stagnant one (reservoirs, lakes).

Decomposing in the aquatic environment, organic waste can become an environment for pathogenic organisms. Water contaminated with organic waste becomes practically unsuitable for drinking and other necessities. Household waste is dangerous not only because it is the source of certain human diseases (typhoid fever, dysentery, cholera), but also because it requires a lot of oxygen for its decomposition [9, 10].

If domestic wastewater enters the reservoir in very large quantities, then the content of soluble oxygen may fall below the level necessary for the life of marine and freshwater organisms [10].

2.3 Emerging pollutants

Emerging pollutants in domestic water are a growing problem for the environment and public health organizations around the world. Emerging pollutants, which include pharmaceuticals, personal care products, and pesticides, are on the U.S. Environmental Protection Agency's list of priority pollutants and are priorities for the European Environment Agency [11].

Not all substances permitted in pharmacology, agriculture and industry, as well as in domestic use, are completely biodegradable. This means that they cannot be completely removed during wastewater treatment using conventional technology. As a result, the amount of pollutants remaining in the water and reaching its consumers is constantly increasing, that is, the process of bioaccumulation occurs [10].

This process is the reason for the constant increase in the amount of harmful substances and the associated negative impacts on the aquatic environment in the future, if appropriate measures are not taken to prevent them.

Some micropollutants, such as the active components of contraceptives (ethinylestradiol), affect the hormonal system of humans and animals. Endocrine disrupting substances, EDCs, are active even in the smallest concentrations (up to µg/L) and have been described by scientists as especially dangerous [10]. Due to the negative

impact on the environment and living organisms, these compounds are considered as priority:

- There is a negative effect on the reproductive function of some fish species, including feminization (the acquisition of female traits) of males.
- The deterioration of the reproductive function of humans and animals, due to a decrease in the quality of germ cells.
- The spread of certain types of cancer, which may be due to disorders in the hormonal system [11].

Depending on the origin, emerging pollutants are divided into several types: pharmaceuticals, personal care products (PCP's), endocrine disrupting chemicals (EDCs), hormones and steroids, surfactants and surfactant metabolites, flame retardants, pesticides, industrial additives, nanomaterials and gasoline additives, industrial additives and agents, perfluoronated compounds, antiseptics [9]. The emerging contaminants are categorized relatively to their properties:

- CMR: carcinogenic, mutagenic, toxic to reproduction
- EDC: endocrine disrupting chemicals
- PBT: persistent, bioaccumulative, toxic
- vPvB: very persistent, very bioaccumulative
- POP: persistent organic pollutant
- PPCP: pharmaceuticals and personal care products
- Priority pollutants
- Xenobiotics, exotics
- Toxicants, toxins, toxics
- HPV: high production volume chemicals.

2.4 Pharmaceuticals and Personal Care Products

2.4.1 Occurrence

Pharmaceuticals are substances which consist of pharmacologically active compounds, are prescribed for the prevention, diagnosis and treatment of diseases and they can change the functional state of the body. Usually, before application in medical practice, their side effects on human and animal health were carefully studied. Nevertheless, the potential environmental influence of pharmaceuticals production and large use only recently has become a topic of scientific interest. Metabolites of pharmaceuticals are polar water-soluble substances that are formed due to physical and biochemical processes. Typically, metabolites of pharmaceuticals are not so toxic compared to their initial compounds. Nevertheless, some metabolites may be more active than the original drugs, injected into the water body [11].

Expired or not used pharmaceuticals can be found in landfills because they are disposed of with chemical or domestic waste. However, in most cases, pharmaceuticals that are excreted from the human body with urine and feces enter the wastewater, and then fall into the treatment plant. These medicines are biologically active elements in the human body. Medications can be stable in the external environment, and they are not always absorbed or completely destroyed in the body [7].

There are currently no treatment facilities that can remove the metabolites of drugs or other unregulated contaminants, such as personal care products. Chemical reactions in the aquatic ecosystem associated with metabolites are still not fully understood. It should be borne in mind that drugs are initially developed with high biological activity, and, as a rule, they have high stability in the environment. Since in many cases they are not biodegradable, even at very low concentrations, pharmaceutical drugs and their metabolites can accumulate in humans, animals and fish organisms [10].

In all countries there is today an intensive development of pharmaceutical products, increasing the risk of producing a large amount of fake, low-quality, expired products. Moreover, there may be risks of non-compliance or violation of storage

conditions, non-compliance of the equipment of most medical enterprises with modern environmental safety requirements. Unlike other toxic environmental pollutants, such as heavy metals, pesticides, etc., drugs are specialized for individual use, and their release into the environment has no geographical, climatic and other restrictions. There are a countless of ways in which drugs enter surface water. The main of them are: wastewater from pharmaceutical plants, urban wastewater treatment plants, hospitals and landfills. Incorrect disposal of pharmaceuticals leads to the emergence of invulnerable mutant viruses. Microparticles of even the newest antibiotics or antiviral drugs can be found in soil, water and even food after some time. From there, microdoses of drugs inevitably enter human body and make bacteria and viruses more resistant. The sad result is the appearance of an invulnerable superbacterium or mutant virus, which are absolutely resistant to a wide variety of antibiotics and antiviral drugs [8].

The Boston Adaptation Genetics Center found that the concentration of antibiotics in groundwater is thousands of times higher than the minimum level at which resistance to drugs begins to develop in bacteria. Laboratory staff in the German city of Wiesbaden tested German groundwater for 60 of the most common drugs in Europe. The result of the research is worrisome - in each sample of water more than 30 of the tested drugs in concentrations harmful to health were detected. Among them are soporific, cardiovascular, contraceptive and antiepileptic drugs [9].

When chemicals are consumed together, an enhanced effect occurs, which is known as synergism. Moreover, consequences of this effect are not clearly studied. If serious measures will not be taken, the harm from pharmaceuticals can exceed their benefits. It is mandatory to improve water treatment methods and technology [3].

2.4.2 Characteristics and classification

Depending on application, pharmaceuticals are divided into several groups. The most common are antibiotics, anti-inflammatories, analgesics, antiepileptics, hormones, and central system stimulating, which have huge interest among researchers [9].

2.4.2.1 Anti-inflammatories

Anti-inflammatories represent the most used group of pharmaceuticals drugs and include huge range of compounds. For better understanding of the extent of the problem of environmental pollution, side effects and risks of each prevalent medicine of the group are introduced bellow.

Diclofenac is a non-steroidal anti-inflammatory drug from the group of phenylacetic acid derivatives. In dosage forms is used in the form of sodium salt [12].

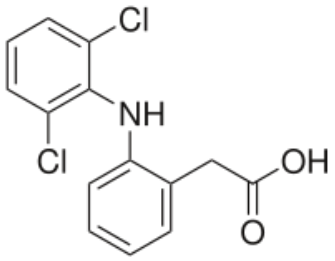

Figure 1. Diclofenac chemical structure.

Diclofenac is included in the list of vital and essential medicines. However, experts can completely ban it due to an increase (about 40%) in the risk of heart attacks and other cardiovascular diseases (CVD) with prolonged use. Danish researchers conducted a large study, the results of which showed that among patients taking diclofenac, cases of primary heart attack, atrial fibrillation or death from CVD are 20-30% more likely than among those who use ibuprofen, naproxen or paracetamol. Moreover, in comparison with people not taking painkillers, the risk of CVD in the diclofenac group was 50% higher. According to scientists, an increased risk of CVD was observed already during the first 30 days of diclofenac therapy. In addition, this drug has been associated with increased gastrointestinal bleeding (compared with ibuprofen)[3, 4].

Ibuprofen is a non-steroidal anti-inflammatory drug from the group of propionic acid derivatives and has an analgesic and antipyretic effect. The mechanism of action and the profile of ibuprofen are well studied, its effectiveness is clinically proven, and therefore this drug is included in the list of essential medicines of the World Health Organization. However, it can increase the risk of heart, kidney, and liver failure. At low

doses, it does not increase the risk of a heart attack; however, this is possible when used in higher doses [9, 13].

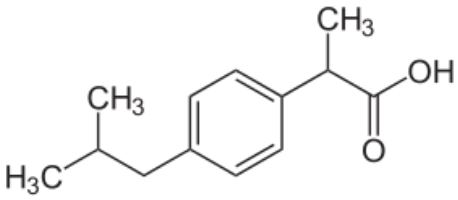

Figure 2. Ibuprofen chemical structure.

Naproxen or its sodium salt is a non-steroidal anti-inflammatory from the group of derivatives of naphthyl propionic acid. White crystalline powder, insoluble in water. It is destroyed at a temperature of 40 °C.

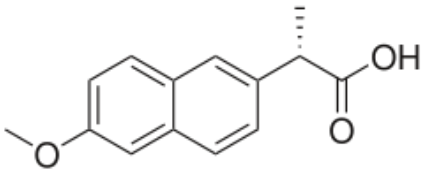

Figure 3. Naproxen chemical structure.

Common adverse effects of naproxen include central nervous system effects (e.g., dizziness and headache), blood effects (e.g., bruises), allergic reactions (e.g., rash), and gastrointestinal upsets (e.g., heartburn and stomach ulcers). It has an intermediate risk of stomach ulcers compared to other drugs in the same class. NSAIDs seems that increase the risk of serious cardiovascular events, although this risk appears to be less with naproxen compared to other NSAIDs. Serious drugs interactions may occur in combination with other drugs that affect the blood, or with drugs that also increase the risk of ulcers [14].

Ketoprofen is a non-steroidal anti-inflammatory drug from the group of derivatives of propionic acid. The empirical formula is $C_{16}H_{14}O_3$, molecular weight 254.29 g / mol. It belongs to the group of non-selective COX-1 and COX-2 inhibitors (standard or traditional NSAIDs). It has a pronounced analgesic, moderate anti-inflammatory and antipyretic effect.

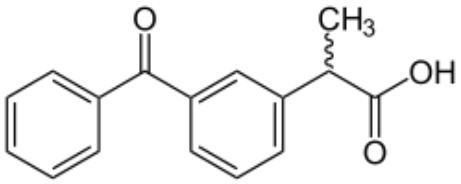

Figure 4. Ketoprofen chemical structure.

Experiments have found that ketoprofen, like diclofenac, is a veterinary medicine that causes lethal effects in Indian eared vultures. Vultures that feed on the carcasses of recently processed livestock suffer from acute renal failure for several days after eating corpses [4].

Acetylsalicylic acid (salicylic ester of acetic acid) is a drug that has analgesic, antipyretic and anti-inflammatory effects.

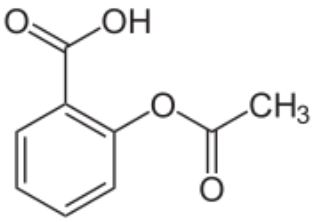

Figure 5. Acetylsalicylic acid chemical structure.

The mechanism of action and the safety of acetylsalicylic acid are well studied, its effectiveness has been clinically tested, and therefore this drug is on the list of the most important medicines of the World Health Organization.

Aspirin is used to treat several conditions, including fever, pain, rheumatic fever, and inflammatory diseases such as rheumatoid arthritis, pericarditis, and Kawasaki disease. It has been studied that lower doses of aspirin reduce the risk of death from a heart attack or the risk of stroke in some cases. However, this beneficial medicine can demonstrate its side effects. Aspirin causes an increased risk of the development of microbleeds of the brain that have an appearance during magnetic resonance imaging (MRI) scans of 5 to 10 mm or less, hypotension. Such brain microbleeds are important because they often occur before ischemic stroke or intracerebral hemorrhage, Binswanger disease and Alzheimer's disease [3].

A study of a group with an average dose of aspirin of 270 mg per day estimated the average absolute increase in the risk of intracerebral hemorrhage of 12 events per 10,000 people. For comparison, the estimated absolute reduction in the risk of myocardial infarction was 137 cases per 10,000 people and a reduction of 39 events per 10,000 people with ischemic stroke [8].

2.4.2.2 Antibiotics

Antibiotics are substances that suppress the growth of living cells, most often prokaryotic or protozoa. They are used to prevent and treat inflammatory processes caused by bacterial microflora.

Azithromycin is a semi-synthetic antibiotic, the first representative of a subclass of azalides that are slightly different in structure from classical macrolides. A broad-spectrum antibacterial agent, azalide, acts bacteriostatically. By binding to the 50S subunit of ribosomes, it inhibits the peptide translocase at the translation stage, inhibits protein synthesis, slows the growth and reproduction of bacteria, and has a bactericidal effect in high concentrations [10].

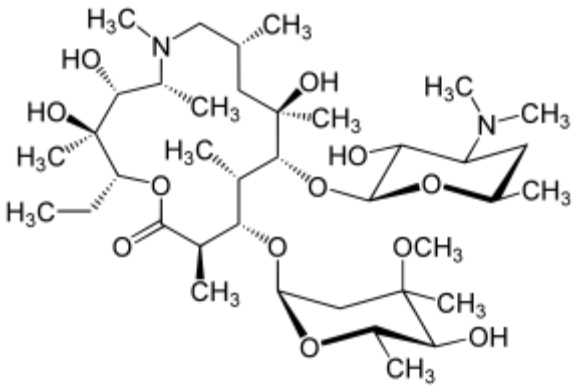

Figure 6. Azithromycin chemical structure.

Sulfamethoxazole is an antibacterial drug of the sulphonamide group. It is a chemotherapeutic agent with a wide spectrum of bactericidal action due to the blocking of

folate biosynthesis in microbial cells: sulfamethoxazole disrupts the synthesis of dihydrofolate acid.

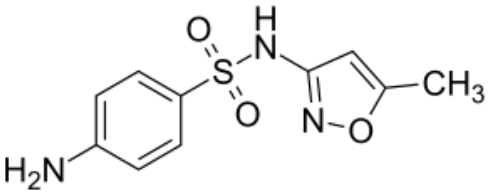

Figure 7. Sulfamethoxazole chemical structure.

In connection with the undesirable effects of sulfamethoxazole, a special public committee was created in the UK, according to which 130 deaths associated with the use of the drug were recorded. The most dangerous are serious, potentially fatal skin reactions (mucocutaneous febrile syndromes) - toxic epidermal necrolysis syndrome (Lyell syndrome) and Stevens-Johnson syndrome [10].

Summing up, one can conclude that any drug is beneficial only when used as directed. The accumulation of drugs in aqueous matrices and a gradual increase in their concentration can lead to unpredictable consequences.

3. Removal processes

One way or another, all water treatment processes on purpose to remove emerging pollutants lead to following results: the removal of pollutants using adsorption by a specific component (adsorbent), or the decomposition of pollutants in order to obtain a less complex substance with the loss of the properties of the original pollutant. Based on this pattern, removal processes can be divided into degradation and adsorption processes. Each method demonstrates unequal efficiency with various types of compounds and conditions of treatment. This needs the analysis of existing studies to select the appropriate process and reagents to develop a way of removal, taking into account the state of the aquatic environment of a particular region [12].

3.1 Degradation processes

Several studies refer that different methods can be applied to accomplish PPCPs degradation, such as photocatalytic processes, ozonation and biodegradation [12]. Comparative data of recent pharmaceuticals removal using degradation processes is represented in Table 1.

According to Lancheros *et al.*(2019), application of ozonation combined with biodegradation allows to achieve high removal efficiency for ibuprofen and naproxen contained even in fairly low concentration ($32\text{-}42*10^{-3}$mg/L of IBP, $22\text{-}67*10^{-3}$of NPX) [23].

Biodegradation is a decomposition of organic matter by microorganisms, such as bacteria, algae or fungi. This mechanism takes place in natural water basins. However, this process has insignificant effect in environment. Application of bred microorganisms in artificial ponds allows achieving satisfactory PPCPs removal efficiency at low cost and mild conditions. In some cases microorganisms cooperate increasing degradation effects [25].

Francini *et al.*, in 2018 has provided biodegradation by *Phragmites australis* and *Salix matsudana* with multiple PPCPs and determined different indicators, from 8.4 up to 100%, with the higher removal efficiency for triclosan [15].

Methods based on photolysis using various catalysts are also of interest. Photocatalysis is the acceleration of a chemical reaction due to the combined action of a catalyst and light exposure. Photocatalytic degradation can be provided using UV-light and TiO_2 or hydrogen peroxide. Moreover, last researches demonstrate possibility of application nanocomposites such as Ag-BiOBr-rGO (Xu *et al*., 2019) or ZrO_2/Ag@TNR (Naragintia *et al*., 2019) [18, 25]. Sonocatalytic processes can be applied to achieve higher degradation rate. UV-degradation using ZnO nanoparticles and hydrogen peroxide, according to Yazdani *et al*.,2018, led to high removal efficiency up to 98.4% for azithromycin, compared to research of Shokri *et al*., in 2019 [16].

Table 1. Literature review of degradation methods for pharmaceuticals removal.

Pollutant	Initial concentration (mg/L)	Method description	Removal efficiency (%)	Reference
Atenolol, Diclofenac, Ketoprofen, Triclosan	13.6 2.3 3.2 0.5	Using *Phragmites australis* and *Salix matsudana*	8.4 -100	Francini *et al*., 2018, [15]
Azithromycin	2	UV activation of hydrogen peroxide	76	Shokri *et al*., 2019, [16]
	20	Sonocatalytic process using ZnO nanoparticles and hydrogen peroxide	98.40	Yazdani *et al*., 2018, [17]
	20	Visible light and ZrO_2/Ag@TiO_2nanorod composite	90	Naragintia *et al*., 2019, [18]
Carbamazepine, Ibuprofen, Sulfadiazine, Sulfamethoxazole Sulfamethazone Triclosan	0.8-10	Using *Eichhornia crassipe* and *Pistia stratiotes*	34.3-99.8	Lin *et al*., 2016, [19]
Diclofenac	20	Direct photolysis and TiO_2 -assisted photodegradation	99. 7	Ardila *et al*., 2019, [20]
Ibuprofen	10	Using bacterium *Serratia marcescens BL1*	93.47	Xu *et al*., 2018 [13]
	20	UsingTiO_2 Film photodegradation	87	Cerrato *et al*., 2019, [21]
Ibuprofen, Triclosan	3;0.12; 0.05; 0.01: 0.002for IBP, 0,05; 0,01; 0.002for triclosan	Aerated solid-phase denitrification system	66 -79	Sun *et al*., 2019, [22]
Ibuprofen, Naproxen	$32\text{-}42*10^{-3}$ $22\text{-}67*10^{-3}$	Using ozonation combined with horizontal subsurface constructed wetlandincluding *Cyperus ligularis* plants	97	Lancheros *et al*., 2019, [23]
Ketoprofen	10	Using Ag-BiOBr-rGO photocatalyst	95	Xu *et al*., 2019 [24]

Considering TiO_2 photodegradation, some recent works demonstrate it relative efficiency to specific compounds. According to Cerrato *et al.*, in 2019, TiO_2-coated Raschig rings were used to perform ibuprofen degradation. A value of 87% of degradation was reached with 25.5% of mineralization. Batch photodegradation of ibuprofen was also investigated and it has been concluded that the use of photocatalyst is necessary to avoid increasing of toxicity and reach higher mineralization level [21].

However, the same catalysts may behave differently in certain particular cases. In Ardila *et al.*, 2019, two methods of photodegradation were compared: TiO_2-assisted photodegradation and direct photolysis. It was found that 87.9% of diclofenac removal was achieved in first ten minutes and 99.8% in 30 min with initial concentration 20 mg/L. Using direct photolysis 99.7% of diclofenac was degraded during first 8 minutes. In this case direct photolysis proved its higher efficiency as well as lower cost of process. Ecotoxicity of by-products acquired by both methods was determined as lower then diclofenac itself [20].

3.2 Adsorption processes

Adsorption is a treatment process based on accumulation of the adsorbate (pollutant) on the adsorbent surface.

3.2.1 Adsorbents

Activated carbon

Activated carbon (AC) is a porous substance that is produced on an industrial scale from various carbon-containing materials of organic origin: charcoal, coal coke, petroleum coke, coconut shell and other materials. Various organic wastes (such as nutshells, bamboo, algae, sugarcane, and bark) can be processed to obtain adsorbents. AC is a commonly used adsorbent in water treatment and found application for PPCPs removal. It can be obtained in powdered (PAC) and granular (GAC) forms [12].

There are several ways of adsorbent activation including physical and chemical processes. Chemical activation involves the interaction of organic matter with activating agents such as H_3PO_4, $ZnCl_2$, NaOH, KOH, NH_4Cl, K_2CO_3, etc. The essence of activation consists in opening pores in the closed carbon material. This is done either thermochemically (pre-impregnated with a solution of zinc chloride, potassium carbonate or some other

compounds, and heated without air), or by treatment with superheated steam or carbon dioxide or a mixture of them at a temperature of 800-850 °C. In the last case, it is technically difficult to obtain an agent having such a temperature. Mixing saturated vapour with limited amount of air can provide necessary conditions. Part of the carbon burns out, and the required temperature is reached in the reaction space. The yield of activated carbon in this process variant is markedly reduced. The specific surface area of the best brands of activated carbon can reach 1800–2200 m² per 1 g of carbon. Macro, meso and micropores can be obtained. Depending on the size of the molecules that need to be kept on the surface, the carbon must be made with different ratios of pore sizes [12, 26].

In addition to activated carbon, there are alternative adsorbents such as graphene oxide, water-soluble protein, biopolymer nanofibers, carbon magnetic composites, etc. Comparative removal efficiency of various adsorbents is presented in the Table 2.

Graphene oxide

According to Ninwiwek *et al*., 2019, graphene oxide (GO) was obtained by oxidation of natural graphite. To obtain magnetite particles (mGO), GO and Fe_3O_4were both dissolved in ethylene glycol. The solutions were mixed and glutaraldehyde was added. The mixture was stirred for 10 h, at ambient temperature. The product was obtained after centrifugation and elution with deionised water, and it was dried in oven at 105 °C for 24 h to remove residual water. To obtain silica-magnetic graphene oxide nanocomposite (mGO-Si) mGO was mixed with tetraethyl orthosilicate [37].

Water-soluble protein

Kebede *et al.*, in 2018 described a method of preparation of water-soluble protein obtained from *Moringa stenopetala* seeds. The seed powder was mixed with petroleum ether and stirred for 30 min. Solid seed material was separated by filtration. The recovered solid was dissolved in ultra-high purity water and stirred for 30 min to extract the water soluble protein. The filtrate was treated with ammonium sulphate to precipitate proteins from the aqueous extract; the salt was added until saturation. The precipitated protein was filtered, re-dissolved in water and then re-filtered to remove insoluble material. The protein solution was then dialyzed through cellulose membrane. Then the pure protein was freeze dried and a white powder was obtained which was stored at room temperature until ready for use. Obtained protein demonstrates significant removal efficiency (up to 86%) against a group of

pharmaceuticals (carbamazepine, ibuprofen, ketoprofen, kenoprofen, diclofenac) in initial concentration from 1 to 5 ppm [28].

Biological residues

Of great interest in environmental and economic considerations are methods using organic waste such as walnut shell, olive stones, apricot shell, bamboo waste, plant sludge and others due to its availability and low cost. All these methods are shown in Table 2 and the results of these studies demonstrate the high efficiency of removing pharmaceutical contaminants from aqueous matrices. Table 3 shows some methods of chemical activation of each of the adsorbents obtained from organic waste, as well as their characteristics, such as specific pore surface area and adsorption capacity. The choice of the activating agent can have a large effect on the adsorption capacity for the same adsorbent. This is clearly seen in the study of Boudrahem *et al*., (2019). The best properties of the adsorbent were achieved using phosphoric acid, compared with the use of zinc chloride [38]. This pattern is also evident in studies of Nazari *et al*., (2016) and Teixeira *et al*., (2019) on the use of walnut shells [29, 43].

Table 2. Literature review of pharmaceuticals removal adsorption methods.

Pollutant	Initial concentration (mg/L)	Method description	Removal efficiency (%)	Reference
Amoxicilin	25	Using activated carbon prepared by chemical activation of olive stone	93	Limousy *et al*., 2017, [27]
Carbamazepine, Ibuprofen, Ketoprofen, Kenoprofen, Diclofenac	1-5	Using water-soluble protein extracted from *Moringa stenopetala* seeds	82–86	Kebede *et al*., 2018, [28]
Cephalexin	50	Using Modified Walnut Shell	>85	Nazari *et al.*, 2016, [29]
Diclofenac	10	Using well-defined carbide-derived carbons	99	Alvarez-Tollerassa *et al*., 2018, [30]
Ibuprofen	1; 1.5; 2; 3;4 mmol/L,	Using activated carbon	91	Lach *et al*., 2018, [31]
	1–50	Using bidirectional activated biochar from sugarcane bagasse	82-91	Chakraborty *et al*., 2018, [32]
Ibuprofen, Ketoprofen	25	Using $NiFe_2O_4$/activated carbon magnetic composite (NiAC)	86	Frohlich *et al*., 2019, [33]
Ketoprofen, Aspirin	20–500	Using algae derived porous carbon	92-95	Ouasfi *et al.*, 2019, [34]
Ketoprofen, Fenoprofen, Diclofenac, Ibuprofen, Carbamazepine	0.25	Using biopolymer electrospun nanofibres	84-97	Kebede *et al*., 2019, [35]
Paracetamol, Ibuprofen, Naproxen	300	Using mesoporous carbons	95-98	Jedynak *et al*., 2019, [36]
Sulfamethoxazole	5-60	Using silica-magnetic graphene oxide nanocomposite	92	Ninwiwek *et al*., 2019, [37]
Tetracycline, Sulfamethazine, Amoxicillin	10-100	Using adsorbents prepared from olive stones	73-100	Boudrahem *et al*., 2019, [38]

Table 3. Comparison of specific surface area and adsorption capacity of different adsorbents.

Matter	Adsorbate	Activation agent	Specific surface area (m^2 /g)	Adsorption capacity (mg/g)	References
Apricot shell	Tetracycline	H_3PO_4	307	308	Marzbali *et al*., 2016 [39]
Bamboo waste	Ibuprofen	$ZnCl_2$	120	278	Reza *et al*., 2014 [40]
Laminaria digitata algae	Ketoprofen, aspirin	NaOH	799	443 970	Ouasfi *et al*., 2019 [34]
Olive stones	Tetracycline, Sulfamethazine, Amoxicillin	H_3PO_4	1254	186	Boudrahem *et al*., 2019 [38]
Olive stones	Tetracycline, Sulfamethazine, Amoxicillin	$ZnCl_2$	1194	42	Boudrahem *et al*., 2019 [38]
Olive stones	Amoxicillin	H_3PO_4	1174	68	Limousy *et al*., 2017 [27]
Plant sludge	Tetracycline	NaOH	163	672	Rivera-Utrilla *et al.*, 2013 [42]
Sugarcane	Ibuprofen	H_3PO_4	557	14	Chakraborty *et al*., 2018 [32]
Walnut shell	Cephalexin	$ZnCl_2$	1452	233	Nazari *et al*., 2016 [29]
Walnut shell	Sulfamethoxazole, Metronidazole	K_2CO_3	934	107	Teixeira *et al*., 2019 [43]

4. Experimental methodologies for PPCPs removal by adsorption

4.1 Adsorbent preparation

The adsorbent preparation consists of two steps: the first is carbonization of precursor, and the second is the carbon activation. The carbonization includes thermal decomposition of raw precursor, acquiring carbon mass with an initial pore structure. The purpose of activation is to improve pore structure by chemical or physical way. The chemical activation allows providing both steps at once using activation agents, such as phosphoric acid or zinc chloride. During chemical activation grinded precursor is physically mixed with activation chemicals, and then it is heated using furnace with a nitrogen flow. Since the activation process is carried out in an inert atmosphere, this process is called pyrolysis [44].

4.1.1 Chemical activation

Several studies describe methods of chemical activation using olive stones waste as a precursor using different conditions and activation agents. According to Boudrahem *et al*., 2019, two chemically activated carbons were obtained. A mass of 200 g of precursor was mixed with two types of activation agents: phosphoric acid and zinc chloride. The mixture was kept in furnace at 85°C for 7 hours to make activating agent permeate inside the precursor mass. The temperature was increased to 105°C to provide complete drying. Then the mixture was pyrolysed for one hour in inert atmosphere using nitrogen flow of 150 mL/min using temperature of 600°C. The obtained activated carbon was washed with hydrochloric acid and distilled water to remove remained activation agents out of the AC pores. Then AC was ground to particles with average size of 63 µm [38].

In Limousy *et al*, 2016, phosphoric acid was also used as activation agent, however conditions differed from previous study. The mass of olive stones was kept for 24 h at ambient temperature, and then the dried precursor was impregnated with phosphoric acid at ratio 1:1 at 110°C for 9 h. Pyrolysis was provided under nitrogen flow first at 170°C for 30 min, then at 380°C for 2.5 h. Activated carbon was washed with distilled water and dried at 110°C [27].

Another method of processing olive stone waste to activated carbon was described by Mansouri *et al*, 2015. Phosphoric acid was used as activation agent in ratio to precursor 3:1. Conditions of pyrolysis were following: the nitrogen flow is 300 mL/min, the temperature of process is 450°C, and the process time is 2.5 h. After this process obtained carbon was washed with distilled water and dried at 60°C overnight. The selected particle size was between 0.212 and 0.710 mm [45].

In the next two following studies KOH was applied for chemical activation of precursor to obtain olive stone waste based activated carbon. In Martinez *et al*, 2006, the precursor was dried at 100°C, and then milled to particle size of 1–3mm.Then carbonization was carried immediately in a muffle furnace at 600°C for 1h. The chemical activation was provided by using two different solutions of KOH (50 and 75%, w/w) in ratio to char 1:1. The mixture was dehydrated at 300°C for 3 h, and then pyrolyzed at 900°C in nitrogen flow. The obtained particles size of 1–2 mm was washed and dried at 100°C for 2h [46].

In Alslaibi *et al*, 2012, the precursor was washed and dried for 24 h at 105°C, and then it was ground to particle size range 1–4.75 mm. The 30 g of precursor was impregnated with KOH pellets in ratio to precursor 1.25:1. Then distilled water was added to dissolve KOH pellets. Impregnation was provided at room temperature for 24 h. After impregnation the samples were dried at sunlight for 3 days. Activation was carried out at 600°C for 3 h using nitrogen flow of 150 mL/min. Obtained activated carbon was washed by distilled water (70°C) and HCl (0.1M) solution. At the final step of adsorbent preparation, the samples were dried at 110°C for 24 h [47].

To summarize, considering the above methods, it is possible to identify common features of olive stone based adsorbent preparation process. The precursor must be processed before impregnation with activation agent. This part includes drying. According to researches, it can be provided using temperature from ambient to100–110°C. Temperature increasing influences the required process's time. Then precursor must be ground to selected particle size, which is varied from μm to mm.

The chemical activation includes impregnation with an activation agent and process of pyrolysis. The impregnation also can be sped up to 7–9 h by temperature increasing (up to 110°C). Nitrogen flow found to be 150 mL/min is required for pyrolysis and the temperature up to 600°C is needed. The time of process is varied

from 1 to 3 h. Obtained activated carbon must be washed with distilled water and hydrochloric acid solution, and dried using temperature up to 100°C for some hours [27, 38, 44–47].

4.1.2 Characterization of activated carbon

Several studies refer different analytical techniques for characterization of activated carbon. They involve application of gas sorption to characterize pore structure, scanning electron microscopy to analyze the morphology and the microscopic shape of activated carbon, Boehm titration to characterize surface functional groups, and pH_{PZC} determination.

4.1.2.1 Nitrogen adsorption measuring

According to Boudrahem *et al*, 2019, the pore structure of olive stone based prepared activated carbon was analyzed by nitrogen adsorption at -196°C using Gas Sorption Analyzer. Activated carbon was degassed at 200°C in vacuum for 24 h. Adsorption isotherms were determined over a pressure relation (P/P_0) range 0.005 – 0.985.The BET (Brunauer – Emmett – Teller) surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The total pore volume was calculated at 0.985 relative pressure. The Dubinin–Radushkevich equation represented below was applied to calculate the micropore volume (V_{mic}).

$$\log V = \log V_{mic} - D\left(\log\left(\frac{P}{P_0}\right)\right)^2 \quad (1)$$

The mesopore volume (V_{mes}) was obtained by deducting the micropore volume from the total pore volume. The average pore diameters (d_p) were estimated from the BET surface area (S_{BET}) and total pore volume ($d_p=4V_{tot}/S_{BET}$) assuming an open-ended cylindrical pore model without pore networks [38].

In Limousy *et al*, 2016, N_2 adsorption measuring procedure also was described. Characterization of the CAC pore structure was performed by the

measurement of N_2adsorption isotherms using an automatic gas sorption analyzer (ASAP). Before the experiments, the samples were outgassed under vacuum at 120°C overnight. Specific surface area was calculated from the N_2 adsorption isotherms by applying the BET equation. The t-plot method was applied to calculate the micropore surface area and the micropore volume. The external surface area was calculated by subtracting the micropore surface area from the BET surface area [27].

In Mansouri *et al*, 2015, the porosity of the samples was characterized by measuring the N_2 and CO_2 adsorption isotherms at -196°C and 0°C, respectively. Before the experiments, the samples were outgassed under vacuum at 120°C overnight. The isotherms were used to calculate the specific surface area, S_{BET}, total pore volume, V_{tot} while the micropore volumes were analyzed using the Dubinin–Radushkevich formulism to the N_2 and CO_2 adsorption data. The distribution of narrow micropore sizes was obtained from the Dubinin–Stoeckli theory applied to the CO_2 adsorption isotherms [45].

4.1.2.2 Boehm titration

In Limousy *et al*, 2016, the surface functional groups were determined by Boehm titration and described as follows: 1 g of CAC was placed in five Erlenmeyer flasks containing 50 mL of 0.1 M of HCl, NaOH, $NaHCO_3$, Na_2CO_3, and $NaOC_2H_5$ solutions, respectively. Then, the mixtures were agitated for 48 h(400 rpm, room temperature). The solutions were filtered through a 0.45-mm membrane filter, and the excess (base or acid) was titrated with 0.1 M HCl or 0.1 M NaOH, respectively. The amount of acidic groups on the activated carbon was calculated under the assumption that $NaOC_2H_5$ neutralizes carbonyl, carboxylic, lactones, and phenolic groups; NaOH neutralizes carboxylic, lactones, and phenolic groups; Na_2CO_3 neutralizes carboxylic and lactones; $NaHCO_3$ neutralizes only carboxylic group. The number of surface basic sites was calculated from the amount of HCl that reacted with the carbon [27].

4.1.2.3pH_{PZC} determination

The pH_{PZC} is the pH on zero point of charge, which is the point at which the net charge of the adsorbent is zero. This analytical method was described by Limousy *et al*., 2016. In this measurement, 50 mL of a 0.01-M NaCl solution was placed in closed Erlenmeyer flasks. Their pH values were adjusted to values between 2 and 12 with the addition of 0.01 M solution of HCl or NaOH. When the pH value got constant, 0.15 g of activated carbon sample was added to each flask and was shaken for 48 h. The intersection of the curve (($pH_{final} - pH_{initial}$) vs. ($pH_{initial}$)) and the bisector gives the pH_{PZC} value [27].

pH_{PZC} determination was also described by Boudrahem *et al.*, 2019. Aliquots with 50 mL of 0.01 M NaCl solution were prepared in different flasks. Their pH values were adjusted between 2 and 12 with the addition of 0.01 M solution of HCl or NaOH. A 0.15 g portion of AC was added to each flask and shaken for 48 h. When the pH value remained constant, the final pH was measured using a pH meter. The pH PZC value is given by the point where $pH_{initial}$=pH_{final} on the pH_{final} versus $pH_{initial}$ curve [38].

4.2 Batch sorption process

Batch sorption process using olive stone based activated carbon was described by Boudrahem *et al*, 2019. Experiments of adsorption were performed in batch reactor (3 L) placed in a temperature-controlled shaker at 25 °C. A known weight of adsorbent is introduced into 1,000 mL of solution of a given concentration (10–100 mg/L), stirred at 400 rpm for 2 h. The initial pH of the solution is adjusted with nitric acid (0.1 mol/L) or sodium hydroxide (0.1 mol/L). Small-volume liquid samples withdrawn at different time intervals are immediately filtered through a 0.45 μm syringe filter. The adsorbate amount adsorbed q_t (mg/g) at time t was determined by:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 is the initial concentration (mg/L), C_t is concentration of adsorbate (mg/L) at time t (min), V the volume of the aqueous solution (L) and m is the weight of used adsorbent (g) [38].

Similar method was described by Limousy *et al*., 2016. The adsorption experiments were conducted in a stirred batch reactor. During the adsorption test, 1 g of CAC was added to1 L of amoxicillin solution. The initial concentrations were adjusted in the range 12.5 – 100 mg/L for amoxicillin. The reactor was agitated at a rotation speed of 450 rpm. At given time intervals, 3 mL samples were taken and filtered and the amoxicillin concentration was measured on Perkin Elmer UV – visible spectrophotometer at the corresponding wave-length of 272 nm. The amount of pollutant adsorbed is calculated by equation (2) [27].

4.3 Adsorption kinetics and isotherms

4.3.1 Adsorption kinetics study of PPCPs removal

Kinetic analysis of an adsorption process provides information on the solute uptake rate, which determines the residence time required for the completion of adsorption reaction and, consequently, the scale up of an adsorption apparatus. An adsorption process generally involves three consecutive steps: (1) diffusion of adsorbate molecule across the liquid film surrounding the adsorbent particles to reach the surface of adsorbents (i.e. external diffusion), (2) diffusion of adsorbate molecule inside the adsorbent pores from the surface to sites of interior (i.e. internal diffusion), (3) adsorption and desorption between the adsorbate molecule and adsorbent active sites (i.e. reaction). Depending on the rate-limiting step of an adsorption process, different kinetic models have been developed and applied. If the rate-limiting step of an adsorption process is the external diffusion, the film diffusion model is applicable. In contrast, if the rate-limiting step of an adsorption process is the internal mass transfer, intra-particle diffusion models such as homogeneous surface diffusion model (HSDM) are more likely to be appropriate. Finally, pseudo-first- and pseudo-second-order models are the most suitable kinetic model if the interaction between the adsorbate molecule and adsorbent active sites is the rate-limiting step. Therefore,

these models may provide information to assist in elucidation of the mechanism of the adsorption process. However, there are some researches available in the literature, in which the pseudo-first- and pseudo-second-order models were used for kinetic analysis due to simplicity although the diffusional steps were the rate-limiting steps. In such cases, it is essential to combine other analytical approaches in order to explore the actual mechanism [48]. Based on the literature, the adsorption kinetics models used for the adsorption PPCPs on AC are presented in Tables 4.

Table 4. Adsorption isotherms and kinetic models applied in studies using organic waste based AC.

Adsorbent precursor	Adsorbate	Adsorption isotherm models	Adsorption kinetic models	Reference
Apricot shell	Tetracycline	Freundlich, Langmuir and Temkin	Pseudo-first-order, Pseudo-second-order models	Marzbali *et al*., 2016 [39]
Bamboo waste	Ibuprofen	Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich	Pseudo-second-order model	Reza *et al*., 2014 [40]
Laminaria digitata algae	Ketoprofen Aspirin	Freundlich, Langmuir and Liu	Pseudo-first-order, Pseudo-second-order Avrami-fractional-order models, Intra-particle diffusion	Ouasfi *et al*., 2019 [34]
Olive stones	Tetracycline Sulfamethazin Amoxicillin	Freundlich, Langmuir and Redlich–Peterson	Pseudo-first-order, Pseudo-second-order	Boudrahem *et al*., 2019 [38]
Olive stones	Amoxicillin	Freundlich, Langmuir, Redlich–Peterson, Sips, Toth and Temkin	Pseudo-first-order, Pseudo-second-order models	Limousy *et al*., 2017 [27]
Olive stones	Amoxicillin Ibuprofen	Freundlich and Langmuir	Pseudo-second-order model	Mansouri *et al*., 2015
Plant sludge	Tetracycline	Freundlich and Langmuir	n/a	Rivera-Utrilla*et al.*, 2013 [42]
Sugarcane	Ibuprofen	Freundlich and Langmuir	Pseudo-first-order, Pseudo-second-order, Elovich models, Intra-particle diffusion	Chakraborty *et al*., 2018 [32]
Walnut shell	Cephalexin	Freundlich, Langmuir, Sips and Toth	Pseudo-first-order, Pseudo-second-order models	Nazari *et al*., 2016 [29]
Walnut shell	Sulfamethoxazole Metronidazole	Freundlich and Langmuir	n/a	Teixeira *et al*., 2019 [43]

4.3.1.1 Pseudo-first-order model

The pseudo-first-order model is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. It was initially presented to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal. However, it later proved to be appropriate for kinetic analysis of various adsorption applications such as adsorption of pollutants from wastewater. As Tables 4 shows, the pseudo-first-order model has often been used to describe the kinetics of adsorption of emerging pollutants on AC, and its wide application is attributed to its simplicity. The pseudo-first-order kinetic model can be presented as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

The linear form of the pseudo-first-order kinetic model is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t, \tag{4}$$

where q_e and q_t (mg/g) are the adsorption capacities (i.e. the amounts of the organic pollutant adsorbed) at equilibrium and time t (min), respectively. k_1 (min^{-1}) is the pseudo-first order rate constant, and it can be obtained from the slope of the regression line on the plot of $\log(q_e - q_t)$ against time [48, 49].

4.3.1.2 Pseudo-second-order model

Pseudo-second-order model can be expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

or in its linear form of

$$\frac{t}{q_t} = \frac{1}{V_i} + \frac{1}{q_e} t, \tag{6}$$

where V_i [mg/(g min)] is the initial adsorption rate, and it equals to $k_2 q_e^2$. The parameter k_2 (g/mg min) is the pseudo-second-order rate constant. In this model, V_i can be first obtained from the intercept of the regression line on the plot of $\frac{t}{q_t}$ against time, and $k_2$can be subsequently determined from V_i [48, 49].

4.3.1.3 Intra-particle diffusion model

Intra-particle diffusion is the process of movement of species from the bulk of the solution to the solid phase. This model is applicable for the adsorption process occurring on a porous adsorbent and can be described by the equation of intra-particle diffusion model represented bellow.

$$q_t = k_{id} t^{1/2} + C_i, \quad (7)$$

where k_{id} is a diffusion coefficient, C_i is intra-particle diffusion constant (intercept of the line). C_i is directly proportional to the boundary layer thickness [50].

4.3.2 Application of different isotherm models for PPCPs removal

Experimental adsorption isotherms are the most common way to describe adsorption phenomena. The methods for obtaining adsorption data for constructing adsorption isotherms are based on measuring the amount of gas (liquid) removed from the gas (liquid) phase during adsorption, as well as on various methods for determining the amount of adsorbate (adsorbed substance) on the surface of the adsorbent (adsorbing substance), for example, volumetric method, gravimetric method, etc. Several adsorption models can be applied to describe adsorption mechanism [51, 52]. According to studies presented in Table 4 which are related to organic waste based activated carbon application, Langmuir and Freundlich models are commonly used, besides such models as Redlich-Peterson, Temkin and others.

Langmuir Isotherm

This adsorption isotherm was designed to describe gas-solid phase adsorption. It also used to characterize adsorption capacity of adsorbents. The Langmuir isotherm takes into account the coverage of the surface, balancing the relative rates of

adsorption and desorption. Adsorption is proportional to the fraction of the opened surface of the adsorbent, while desorption is proportional to the fraction of the covered surface of the adsorbent [38, 44]. Langmuir isotherm has following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{8}$$

where c_e is equilibrium concentration of the adsorbate on the adsorbent, q_e is amount of the adsorbate at equilibrium (mg/g), q_m is the maximum sorption capacity, K_L is Langmuir constant [52].

Freundlich Isotherm

Freundlich isotherm is commonly used with higher concentrations. It is applicable to processes on heterogenic surfaces. The linear equation of this isotherm has the following form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{9}$$

where K_F is adsorption capacity (L/mg) and $1/n$ is adsorption intensity [44].

Redlich-Peterson Isotherm

Redlich-Peterson Isotherm is the mix of Langmuir and Freundlich models [44]. This model has the following equation:

$$q_e = \frac{AC_e}{1+BC_e^{\beta}} \tag{10}$$

where A and B are constant, β is exponent lies between 0 and 1 [52].

Temkin Isotherm

Temkin model assumed the decreasing of heat of adsorption during increasing of surface coverage. It's represented by equation:

$$q_e = \frac{Rt}{b} \ln K_T + \frac{RT}{b} \ln C_e \tag{11}$$

where b is constant related to the heat of sorption, K_T is Temkin constant [52].

Toth Isotherm

In this model, most sites have adsorption energy lower than the peak or maximum adsorption energy. This is represented by equation bellow.

$$q_e = \frac{Q C_e}{\left(\frac{1}{K} + C_e^m\right)^{1/m}}, \quad (12)$$

where Q (mg/g), K, and m are the maximum monolayer adsorption capacity parameter, Toth isotherm constant, and a dimensionless constant, respectively [52].

5. Adsorption efficiency evaluation

5.1 Raw materials processing conditions' influence on PPCP's removal efficiency

Comparative removal efficiency and adsorption capacity of various organic waste based adsorbents are presented in Table 5. To evaluate the removal efficiency and adsorption capacity it's necessary to take into account all the factors affecting adsorption process. The first one important factor is conditions of processing raw materials as temperature of carbonization.

5.1.1 Effect of raw materials carbonization temperature

Application of processed almond shell and orange peel as effective adsorbent for 2-picoline adsorption was described by Hashemian *et al*., 2014. It has been determined that the temperature of carbonization significantly affects the removal efficiency of pharmaceutical. The range of samples of pre-treated almond shell and orange peel were carbonized at different temperatures from 300 to 1200 ℃. The removal efficiency of 2-picoline was increased with increasing of activation temperature up to 700 ℃ and then decreased with higher temperatures. For example, 2-pic removal using almond shell carbon prepared at 300 ℃ was 27.6% and up to 90% using 700 °C carbonized adsorbent. Surface area of activated carbon was increased from carbonization temperature 200–700°C, but it was decreased from carbonization temperature 700–1200°C.Maximum porous structure and adsorption capacity was also obtained at 700℃ [54].

5.1.2 Effect of activation agent

In Reza *et al.,* 2014 effect of activation agent on bamboo waste microwave assisted activated carbon was described. The influence of the activating agent, such as H_3PO_4, KOH, NaOH, HCl, and $ZnCl_2$, was studied to choose the best activating agent. The activating agents, like H_3PO_4, KOH, NaOH, and HCl, were found to be less prone to volatile loss and low adsorption capacity. But $ZnCl_2$ activation develops porosity and increases the surface area of the adsorbent. Among all agents $ZnCl_2$ is a widely used activating agent as it leads to larger surface area and higher yields [40].

In Boudrahem *et al*., 2019, two activating agents $H_3PO_4$and $ZnCl_2$ were applied to produce olive stone activated carbon and properties of the obtained AC were compared. The H_3PO_4 OSAC (Olive Stone Activated Carbon) has demonstrated

significantly higher adsorption efficiency compared to $ZnCl_2$ OSAC (97.58 mg/g sorption amount against 42.01) [38].

Table 5. Comparative pharmaceuticals removal efficiency using organic waste based activated carbons

Precursor	Adsorbate	Initial concentration (mg/L)	Adsorption capacity (mg/g)	Removal efficiency (%)	Reference
Almond shell	2-picoline	100	166.7	up to 90	Hashemian *et al.*, 2014 [54]
Apricot shell	Tetracycline	100	308	99	Marzbali *et al.*, 2016 [39]
Babassu coconut mesocarp	Aspirin	50	89.9	n/a	Hoppen *et al.*, 2019 [55]
Bamboo waste	Ibuprofen	100	278	96	Reza *et al.*, 2014 [40]
Cocoa pod husk	Diclofenac	30	5.53	94	De Luna *et al.*, 2016 [56]
Cocoa shell	Diclofenac Nimesulide	n/a	63.47 74.81	n/a	Saucier *et al.*, 2015 [57]
Coconut shell	Sulfamethoxazole	1	32.97	n/a	Tonucci *et al.*, 2015 [58]
Cork bark	Paracetamol	20	0.77	76	Villaescusa *et al.*, 2011 [59]
Dende coconut mesocarp	Paracetamol	50	64.75	n/a	Ferreira *et al.*,2014 [60]
Granulated cork	Diclofenac Naproxen Ketoprofen	10	5.31	100 82 57	Mallek *et al.*, 2018 [61]
Grape stalk	Paracetamol	20	1.74	68	Villaescusa *et al.*, 2011[59]
Laminaria digitata algae	Ketoprofen Aspirin	150	443 971	86 95	Ouasfi *et al.*, 2019 [34]
Olive stone	Tetracycline Sulfamethazine Amoxicillin	100	183 190 156	up to 100	Boudrahem *et al.*, 2019 [38]

Table 5. Comparative pharmaceuticals removal efficiency using organic waste based activated carbons (continuation).

Precursor	Adsorbate	Initial concentration (mg/L)	Adsorption capacity (mg/g)	Removal efficiency (%)	Reference
Olive stone	Amoxicillin	100	68	n/a	Limousy *et al.*, 2017 [27]
Olive waste cake	Ibuprofen, Ketoprofen, Naproxen	10 20 20	10.83, 39.52, 10.83,	70 88 90	Baccar *et al.*, 2012 [62]
Onion skin	Diclofenac, Ibuprofen	200 200	134 92	82 66	Abbas *et al.*, 2017 [63]
Orange peel	2-picoline	100	288.5	up to 90	Hashemian *et al.*, 2014 [54]
Pine tree	Sulfamethoxazole	1	130.73	n/a	Tonucci *et al.*, 2015 [58]
Plant sludge	Tetracycline	700	672	n/a	Rivera-Utrilla *et al.*, 2013 [42]
Plum waste	SMX, DCF, NPX, KP, IBP	10	17.5, 17.9, 18.7, 17.8, 20.9, 22.1	n/a	Turk Sekulic *et al.*, 2019 [64]
Pomelo peel	Carbamazepine Clofibric acid Oxytetracycline	50	216.2 19.4 64.9	n/a	Prarat *et al.*, 2019 [65]
Potato peel	Diclofenac	100	68.5	70	Bernardo *et al.*, 2016 [66]
Potato peel	Dorzolamide Pramipexole	50	60 66	80 88	Kyzas *et al.*, 2014 [67]
Rice husk	Tetracycline	5	8.37	83	Chen *et al.*, 2016 [68]
Sewage sludge, Fish waste	Carbamazepine	100	37.2	96	Nielsen *et al.*, 2015 [69]

Table 5. Comparative pharmaceuticals removal efficiency using organic waste based activated carbons (continuation).

Precursor	Adsorbate	Initial concentration (mg/L)	Adsorption capacity (mg/g)	Removal efficiency (%)	Reference
Sludge and leaf	Diclofenac	10	877	89	Zhang *et al.*, 2019 [70]
Sugarcane	Ibuprofen	50	14	91	Chakraborty *et al*., 2018 [32]
Sugarcane	Diclofenac	50	315	92	Abo El Naga *et al.*, 2019 [71]
Tea waste	Caffeine	50	27	77	Keerthanan *et al.*, 2020 [72]
Vine wood	Amoxicillin Cephalexin Tetracycline Penicillin G	20	n/a	74-88	Pouretedal *et al.*,2014 [73]
Walnut shell	Sulfamethoxazole metronidazole	40	107 127	n/a	Teixeira *et al*., 2019 [43]
Walnut shell	Cephalexin	100	233	up to 100	Nazari *et al.*, 2016 [29]
Walnut shell	Sulfamethoxazole	0.5–5	n/a	up to 100	Teixeira *et al*., 2019
Yohimbe bark	Paracetamol	20	0.99	81	Villaescusa *et al.*, 2011 [59]

5.2Adsorption process conditions' influence on PPCP's removal efficiency

Experimental conditions of adsorption processes applied in studies considered using of organic waste based AC are represented in Table 6. There are several parameters affecting adsorption efficiency, such as pH, amount of adsorbent, concentration of adsorbate, contact time, temperature, and carbon particle structure [40].

Table 6. Experimental conditions for pharmaceuticals removal on activated carbon

Adsorbent	**Adsorbent Dosage (g/L)**	**Adsorbate**	**Initial Concentration (mg/L)**	**Experimental Conditions(T – process temperature (K), t – contact time (min), N – agitation rate (rpm))**	**Reference**
Almond shell	0.1	2-picoline	100	pH > 5 T=298 t=120 (150 rpm) + 10 (1000 rpm)	Hashemian *et al.*, 2014 [54]
Apricot shell	0.6	Tetracycline	100	pH=6.5 T=300 t=24 h	Marzbali *et al.*, 2016 [39]
Babassu coconut mesocarp	0.5	Aspirin	50	pH=6.4 T=298 t=24 h	Hoppen *et al.*, 2019 [55]
Bamboo waste	2	Ibuprofen	80	pH=4.9 T=298 t=120	Reza *et al*., 2014 [40]
Cocoa shell	50	Diclofenac	10	pH=7 T=298 t=223	Saucier *et al.*, 2015 [57]
Cocoa pod husk	0.25	Diclofenac	30	pH=7 T=298 t=15	De Luna *et al.*, 2016 [56]
Coconut shell	0.08	Sulfamethoxazole	1	pH=7 T=298 t=120 N=150	Tonucci *et al.*, 2015 [58]
Cork bark	0.1	Paracetamol	20	pH=7 T=293 t=120	Villaescusa *et al.*, 2011 [59]
Dende coconut mesocarp	0.05	Paracetamol	50	pH=6.5 T=318 t=120	Fereira *et al.*,2014 [60]

Table 6. Experimental conditions for pharmaceuticals removal on activated carbon (continuation).

Adsorbent	**Adsorbent Dosage (g/L)**	**Adsorbate**	**Initial Concentration (mg/L)**	**Experimental Conditions(T – process temperature (K), t – contact time (min), N – agitation rate (rpm))**	**Reference**
Granulated cork	0.25	Diclofenac Naproxen Ketoprofen	10	pH=6 T=298 t=30	Mallek *et al.*, 2018 [61]
Grape stalk	0.1	Paracetamol	20	pH=6 T=293 t=120	Villaescusa *et al.*, 2011 [59]
Laminaria digitata algae	0.2	Ketoprofen, aspirin	150	pH=3.4 T=298 t=60	Ouasfi *et al.*, 2019 [34]
Olive stone	0.4	Tetracycline	10-100	pH=6 T=298 t=120	Boudrahem *et al.*, 2019 [38]
Olive stone	0.3	Amoxicillin, Ibuprofen	100	pH=4.3 T=298 t=60	Mansouri *et al.*, 2015 [44]
Olive stone	1	Amoxicillin	100	pH=3.6 T=298 t=4000 N=450	Limousy *et al.*, 2017 [27]
Olive waste cake	0.9	Ibuprofen, Ketoprofen, Naproxen	10 20 20	pH=4.1 T=298 t=26 h N=200	Baccar *et al.*, 2012 [62]
Pine tree	0,03	Sulfamethoxazole	1	pH=7 T=298 t=120 N=150	Tonucci *et al.*, 2015 [58]

Table 6. Experimental conditions for pharmaceuticals removal on activated carbon (continuation).

Adsorbent	**Adsorbent Dosage (g/L)**	**Adsorbate**	**Initial Concentration (mg/L)**	**Experimental Conditions(T – process temperature (K), t – contact time (min), N – agitation rate (rpm))**	**Reference**
Plant sludge	1	Tetracycline	100	pH=6 T=298 t=8 days	Rivera-Utrilla *et al.*, 2013 [42]
Plum waste	2	SMX, DCF, NPX, KP, IBP	10	pH=6 T=295 t=120 N=140	Turk Sekulic *et al.*, 2019 [64]
Pomelo peel	0.57	Carbamazepine Clofibric acid Oxytetracycline	50	pH=5 T=298 t=480 N=200	Prarat *et al.*, 2019 [65]
Potato peel	1	Dorzolamide Pramipexole	50	pH=2 T=298 t=24 h N=160	Bernardo *et al.*, 2016 [66]
Potato peel	2	Diclofenac	100	pH=5 T=298 t=24 h N=150	Chen *et al.*, 2016 [68]
Rice husk	2	Tetracycline	5	pH>7 T=313 t=600	Kyzas *et al.*, 2014 [67]
Sludge and leaf	0.625	Diclofenac	10	T=298 t=240 N=45	Zhang *et al.*, 2019 [70]

Table 6. Experimental conditions for pharmaceuticals removal on activated carbon (continuation).

Adsorbent	**Adsorbent Dosage (g/L)**	**Adsorbate**	**Initial Concentration (mg/L)**	**Experimental Conditions(T – process temperature (K), t – contact time (min), N – agitation rate (rpm))**	**Reference**
Sugarcane	1.66	Ibuprofen	10	pH=2 T=298 t=6 h	Chakraborty *et al*., 2018 [32]
Sugarcane	0.4	Diclofenac	50	pH=2 T=298 t=15 N=150 rpm	Abo El Naga*et al.*, 2019 [71]
Tea waste	1	Caffeine	50	pH=3.5 T=298 t=24 h	Keerthanan *et al*., 2020 [72]
Vine wood	0.4	Amoxicillin Cephalexin Tetracycline Penicillin G	20	pH=2 T=318 t=8 h	Pouretedal *et al.*,2014 [73]
Walnut shell	0.2	Sulfamethoxazole	40	pH=5.5 T=303 t=48 h	Teixeira *et al*., 2019 [43]
Walnut shell	0.3	Cephalexin	200	pH=6 T=303 t=20 h	Nazari *et al*., 2016 [29]
Yohimbe bark	0.1	Paracetamol	20	pH=8 T=293 t=120	Villaescusa *et al*., 2011 [59]

5.2.1 Effect pH

As pH affects the charge of the AC surface groups as well as the dissociation of organic molecule, pH plays a critical role in the capacity of adsorption process. pH values higher than point of zero charge (pH_{PZC}) make the surface of AC negatively charged. Meanwhile, the organic pollutant is simultaneously deprotonated once the solution pH values exceeded its pK_a (the negative log of the acid dissociation constant or K_a value) [40].

According Reza et al, 2014, in case of acidic pharmaceuticals such as ibuprofen, the maximum adsorption varied from pH 2 to 5. This depends on the nature of the surface functional groups on the adsorbent at different pH values and also the ionic state of IBP at these pH values. The pH values higher than the pK_a value of the IBP (4.91) molecule will be deprotonated. Consequently, as the pH increases for values higher than 5, the adsorption of IBP will be less favorable due to electrostatic repulsion between the anionic IBP and the surface of activated carbon that gradually becomes more negatively charged. In contrast, at acidic pH levels (solution $pH < pK_a$), adsorption was enhanced because the AC surface was neutral and organic pollutant (i.e. ibuprofen) was non-dissociated, and therefore, repulsive electrostatic interactions were minimized [40].

In case of ketoprofen and aspirin removal, which was investigated by Ouasfi *et al*., 2019, a pH_{ZPC} of adsorbent was found of 6.7. This means that the surface of AC is positively charged at pH < 6.7 and negatively charges at pH > 6.7. Initial pH of pharmaceutical solutions (150 mg/L) was 3.2. The high aspirin uptake of 95% was reported at pH3.4 relative to 10.84 at pH 12.0. Similarly, the high ketoprofen removal (92%) was observed at pH 3.4 and 27.16% at pH 12.During the adsorption at pH 3, the aspirin and ketoprofen molecules are in their neutral forms. They can form strong H-bonds with oxygen-containing surface functional groups present in adsorbent and be not repelled by the surface positive charge. Accordingly, they presented their highest aspirin adsorption at pH 3.4, which was close to the original pH of the aspirin solution. As the solution pH increased from 3.4 to 12.0, aspirin and ketoprofen were progressively transformed to its carboxylate conjugate bases, which were repelled from the increasingly negatively charged AC surfaces. For that reason, the removal of aspirin and ketoprofen in molecular form was favorable to the AC, while the removal

of the anionic state of aspirin and ketoprofen were unfavorable. Duplicate remarks were stated in the literature for the adsorption of aspirin and ketoprofen [34].

Initial pH influence on tetracycline adsorption using apricot shell activated carbon was studied by Marzbali *et al*., 2016. Initial pH value of solution is an important parameter for effective interaction between adsorbent and adsorbate. TC exists in three pKa of 3.3, 7.7 and 9.7; therefore due to protonation or deprotonation reactions, it shows different ionic species in different pH values. Up to pH 3.3, the adsorbent and adsorbate have opposite charges. Negative charges on adsorbent surface increase gradually and cause potent π–π electrostatic interaction. This interaction together with intermolecular hydrogen bond forces would increase adsorption capacity. After pH 3.3, TC positive charges are neutralized gradually and cease π–π electrostatic interaction. In these pH values, hydrogen bonds probably form between TC molecules and result a bigger size of molecule with complex structure. This new form of TC molecules cannot pass through the adsorbent pores and consequently decreases adsorption capacity. At pH 5 or more, the effect of hydrogen bond is negligible. Intermolecular electron donor–acceptor interaction, between TC molecule and surface of activated carbon, is possibly the main reason of increasing adsorption capacity. Benzene rings in TC molecular structure interact with the polarized aromatic rings (π electron rich surfaces) of activated carbon via the π–π electron-donor-acceptor interaction. This kind of interaction is one of the most important nonhydrophobic adsorption driving forces for antibiotics adsorption on carbonaceous materials. TC molecule can have 64 possible tautomers considering the effect of medium and variations of pH. This makes keto-enol tautomer to change the chemical properties of molecule and affecton interactions and the number of hydrogen bonds which eventually impacts adsorption capacity. At basic pH values, both TC molecule and adsorbent surface have negative charges and therefore adsorption decreases due to electrostatic repulsion [39].

5.2.2 Effect of adsorbent dosage

The effect of olive stone prepared adsorbent dose was studied by Boudrahem *et al.,* 2019. The conditions of study were following: pH=6, tetracycline initial concentration of 100 mg/L and a temperature of 25°C. When the amount of adsorbent dose increases from 0.1 to 0.2 g/250 mL of solution, the amount of adsorbed TC

increases due to the increase of active sites number. Beyond 0.2 g/250 mL, there is no significant variation in the amount of adsorbed TC which is probably due to an agglomeration of the AC particles [38].

Similar behaviour has been observed by lot of studies. For example, effect of bamboo waste AC dosage on removal efficiency of ibuprofen was investigated in Reza et al., 2014. The dependence of adsorbent dosages on the adsorption of IBP was carried out by using different adsorbent dosages which are varied from 10 to 50 mg/20 mL at 298 K temperature and fixed adsorbate concentration (100 mg/L). It has been observed that percentage of IBP removal increases from 73.45% to 97.00% with increase in adsorbent dose from 10 to 40 mg/L. The further increasing of AC affects removal efficiency insignificantly [40].

Cocoa pod husk activated carbon (CPHAC) adsorbent dosage influence was investigated by De Luna *et al.*, 2016. Sodium diclofenac (SD) removal increased from 89.8% to 91.4% when CPHAC dosage was raised from 0.25 to 0.5 g/250 mL. The improvement in SD removal at higher CPHAC dosage can be attributed to the additional active sites available for adsorption. Meanwhile, a 7.2% reduction in SD removal was observed from 0.5 to 1.0 g/ 250 mL CPHAC indicating a reversible adsorption mechanism. Beyond 1.0 g/250 mL adsorbent dosage, SD removal appeared to stabilize, suggesting chemical equilibrium between the adsorbent and the adsorbate [56].

Investigations have shown that percentage removal of pharmaceuticals increased as a function of adsorbent dosage. This increase was often attributed to the extra availability of vacant sites at higher dosages. It has been reported that adsorption of pharmaceuticals rarely reached a saturation value; therefore, further increase in adsorbent dosage may not be of measureable significance. It is true that increase in dosage level leads to extra removal of pharmaceuticals. However, amount of pharmaceutical adsorbed per unit mass of dosage gives better indication of adsorption capacity for any specific adsorbent. In fact, it was observed that ratio amount of pharmaceutical adsorbed to dosage decreased as a function of adsorbent dose [29, 32, 34, 38–40, 42–44].

5.2.3 Effect of pharmaceuticals concentration

Adsorption capacity and rate of adsorption are very much dependent upon initial concentration of pharmaceuticals. Initial concentration minimizes mass transfer resistance by supplying necessary driving force. In general, initial concentration boosts adsorption of pharmaceuticals irrespective of the nature of adsorbent surface such as microporous, mesoporous, negatively or positively charge surface. The concentration increases the accessibility of pores for adsorbate molecules and increases interactions at solid–liquid interface [29, 32, 34, 38–40, 42–44].

According to de Luna *et al.*, 2016 SD (sodium diclofenac) removal efficiency increased significantly as the initial SD concentration was increased from 5 to 30 mg/L. Approximately 69.8% SD removal was achieved when the initial concentration of SD was 5 mg/L and about 92.1% of SD was removed using 30 mg/L SD initial concentration [56].

Chakraborty *et al.*, 2018 found that for chemically activated biochar (SCAB), gradual increase in IBP concentration from 1to 15 mg/L led to a simultaneous increase in percentage removal of IBP from 23.20 to 78.18 and in case of steam activated biochar (SPAB), the percentage removal increased from 18.73 to 71.70% when the IBP concentration varied from 1 to 20 mg/L. The maximum removal for chemically activated biochar (SCAB) and steam activated biochar (SPAB) being observed at an initial IBP concentration of 15 mg/L and20 mg/L respectively. This increase in percentage removal of IBP may have resulted from a concentration gradient based driving force. Moreover, an increase in IBP concentration in solution may have led to a higher number of IBP molecules which are neighbouring the active sites of sugarcane bagasse resulting in higher percentage removal of IBP. However a further increase in IBP concentration beyond 15 mg/L for SCAB and 20 mg/L for SPAB resulted in a decrease in IBP removal %. This might be due to exhaustion of all available active sites of sugarcane bagasse by adjacent IBP moieties [32].

Boudrahem *et al.*, 2019 has studied tetracycline (TC) initial concentration effect on adsorption using olive stone waste AC. Experimental studies was carried out at 25 °C with varying initial concentrations of TC from10 to 100 mg/L, at pH 6 using 0.1 g of adsorbent dose in 250 mL of solution. The adsorption equilibrium is reached after 5 minutes for low TC concentrations (10 and 40 mg/L) and in 60 minutes for TC

concentrations above 40 mg/L. According to these results, the contact time solution adsorbent is fixed to 120 min to make sure that equilibrium is attained. The equilibrium time is one of the most important parameters from an economic point of view. The shorter the time, the more interesting the process is for a given application. The adsorbed amount of TC is found to be 24.99 (≈ 100%) and 183.11 mg/g (73%) at 10 and 100 mg/L initial concentration, respectively [38].

5.2.4 Effect of temperature

Since adsorption is a spontaneous process and it has an exothermic nature, it was found that an increase in temperature leads to a decrease in the adsorption capacity of the adsorbent. According to studies, the optimum temperature of the adsorption process varies from 15 to 30 and is determined empirically for each specific process.

According to Chakraborty et al., 2018, adsorption on sugarcane bagase were studied at seven different temperatures with experimental conditions of IBP initial concentration10 mg/l, dose 1.66 g/L, temperature 25 °C, agitation speed 130 rpm and time 6 h. The increase in temperature results in decrease in adsorption of IBP from the aqueous solution. The optimum temperatures were found to be 15 °C and 20 °C for SCAB (sugarcane chemically activated biochar) and SPAB (sugarcane physically activated biochar) respectively. Maximum removal percentage was found 82% for SCAB and 71% for SPAB. It was found that at lower temperature the percentage removal of IBP was high and further increase of temperature the removal was decreased due to weak interaction forces (van der wall forces and hydrogen bonding) are involved during adsorption process and increase in temperature results in breakdown of adsorptive forces thereby resulting in decrease of IBP removal at higher temperatures [32].

Baccar *et al*., 2012 has studied the temperature influence on ibuprofen, ketoprofen, naproxen and diclofenac adsorption. To mitigate the effect of this parameter, adsorption experiments were conducted for different contact time at three temperatures: 4, 25and 37 °C. The results did not reveal a perceptible effect of the studied parameter on the adsorption process in the considered temperature range for

the four studied drugs. The results showed that temperatures (25–40 °C) had no significant influence on ibuprofen adsorption process onto powder activated carbon [62].

Villaescusa *et al*., 2011 also observed the negligible influence of temperature on paracetamol sorption onto grape stalk between 5 and 30 °C and indicated that this sorption is almost athermic. One possible explanation of this athermicity is that the molecule drugs are well solvated in their aqueous solution. In order for the drugs molecules to be adsorbed, they have to lose part of their hydration sheath. This dehydration phenomenon requires energy (endothermic phenomenon).This endothermicity practically equals the exothermicity of the molecules getting attached to the surface. Consequently, the overall adsorption process is nearly athermic [59].

5.2.5 Effect of contact time

The adsorption of trace organic compounds was usually increased with an increase in contact time. However, the change could be significant or negligible depending on the kinetics of adsorption. It was observed that the increase of contact time led to limited increase in the elimination of low molecular weight organic pollutants due to fast adsorption kinetic. In contrast, the removals notably increased with the contact time for other organic pollutants with high molecular weight due to slower adsorption kinetics [29, 32, 34, 38–40, 42–44].

Limousy *et al*., 2016 has described the effect of contact time on amoxicillin removal by CAC from synthetic aqueous solutions at 25 °C. The adsorbed amounts increased with the increase of contact time. The adsorption of amoxicillin was very fast in the first 20 min and then declined slowly with time until reaching the equilibrium. This phenomenon may be attributed by the strong interaction between the surface of CAC and amoxicillin molecules during the first 20 min (electrostatic forces), and then to the physisorption of amoxicillin until equilibrium (van der Waals forces) [27].

According to Chakraborty *et al.,* 2018, the effect of contact time on uptake of ibuprofen is also a significant factor for both SCAB and SPAB. When the initial concentration, pH, adsorbent dosage, temperature, agitation speed were fixed at 10 mg/L, 3, 1.66 g/L, 25 °C and 130 rpm respectively, maximum ibuprofen removal was

obtained at 12 h of contact time when SCAB was used as adsorbent and at 18 h of contact time when SPAB was used as adsorbent. After that, the removal percentage decreased a little bit and remained constant with increasing contact time. Initially rapid adsorption was noticed due to the active free site on external surface of adsorbents. Adsorbate molecules enter into the internal surface of the SPAB and SCAB which is slow process. After occupying by all the adsorbate molecules into active site of adsorbents the removal is decreased with time. The percentage removals of IBP at 12 h for SCAB and at 18 h for SPAB were 91.9% and82.15% respectively. As the SCAB contains more fixed carbon content than SPAB, it gives more maximum removal of ibuprofen in less time [32].

5.2.6 Effect of particle size

Effect of particle size of olive stone based activated carbon on surface area and yield was investigated by Alslaibi *et al*, 2012. According to the investigation for different particle size of olive stone activated carbon, the particle size ranges from 2mm to 4.75mm is more attractive for activated carbon production which resulted in 38.67% of yield and 886.72 m^2/g of a surface area. Whereas, the produced activated carbon from the finer particle size is more fragile and for the use of olive stone in its original form leads to make most of the cavitation and pores in the outer shell of the activated carbon only with little internal pores [53].

5.2.7 Effect of agitation speed

Agitation speed is one of most important parameter for adsorption batch study. It was found by Chakraborty *et al*., 2018 that the percentage removal of ibuprofen increased with increase in agitation speed up to 160 rpm for SPAB and SCAB respectively. Again, further increase in agitation speedup to 200 rpm, IBP uptake deceased for both the adsorbents. pH, adsorbent dose, temperature and contact time were fixed at 3, 1.66 g/L,25 °C and 6 h respectively, SCAB and SPAB showed maximum removal of ibuprofen as 76% and 63% at 160 rpm respectively. It can be justified by the fact that adsorbents were agglomerate even if dispersion in the solution at lower speed in consequences many active sites were covered by the top layers of sorbents. Thus adsorption occurs only at the top layers of sorbent at lower agitation speed. But with further increase after 160 rpm, removal efficiency decreased; this may be due to the unsystematic collision between three different

combinations of adsorbate-adsorbent pair which decreases in contact time or residence time beyond 160 rpm for attachment of bond formation between IBP molecules and SCAB and SPAB [32].

5.2.8 Effect of water matrix

Mansouri *et al.*, 2015 has investigated the influence of the water matrix on the adsorption capacity of the carbons towards a binary mixture of IBU and AMX on treated water from a wastewater treatment plant located in their region (concentrations of individual compounds are 1:1 ratio). The wastewater has an alkaline pH with a moderate ionic content. Compared to the adsorption capacities obtained from synthetic solutions in distilled water, the uptake of IBU remained rather constant (slightly enhanced) whereas that of AMX was reduced, being the effect more pronounced for the oxidized carbon. An enhanced performance of adsorption on activated carbons on real wastewaters has been reported for some other compounds; this has been attributed to the changes in the solubility as the wastewater presents higher salinity and alkalinity and to the modification of the surface charge and ionization state of the compounds leading to electrostatic interactions. The fall in AMX uptake is more pronounced for the oxidized carbon, due to its higher density of negative surface charges, as at the basic pH of the treated water AMX is also negatively charged (amine groups are neutral but carboxyl moieties are deprotonated), hence electrostatic repulsions become important. For the same reason, the salinity of the treated water after the adsorption of IBU and AMX on carbon OPox decreased significantly, indicating that along with the aromatics the ions are also adsorbed on the negatively charged surface of this functionalized carbon at the pH of the real wastewater. The effect is minimized in OP and OC carbons that present a higher density of positive surface charges [44]. .

6. Conclusions

Recent studies considering adsorption of pharmaceuricals removal on activated carbon were investigated to analyze adsorption proccesses using organic waste based adsorbents.

The process of adsorption of pharmaceuticals from aqueous matrices involves several sequential steps. The first step is preparation of adsorbent. Organic waste based precursors have proved themself as the cheapest and effective source for preparation of activated carbon. According to studies, they show their high comparative efficiency. As well as others organic waste adsorbents, olive stone based activated carbon have sufficient properties to provide high removal of pharmaceutical compounds. Proccessing of olive stones to activated carbon involves chemecal activation. According to Boudrahem *et al.,* 2019, in this case phosphoric acid allowed to obtain AC with the highest specific surface area and adsorption capacity. Carbonization can be carried out by pyrolysis both before the interaction with the activation agent and after, and depends on applied methodology.

The characterization of adsorbent includes several analytical techniques. The nitrogen adsorption is applied to determine characteristics of AC, such as the BET surface area, total pore volume and average pore diameter. Boehm titration is needed to analyze surface functional groups of adsorbent. It's also important to determine the pH of zero point of charge.

To describe the course of the sorption process, it is necessary to use suitable kinetic models and adsorption isotherms. According to studies, for this purpose Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm models, and pseudo-first- and pseudo-second-order kinetic models are most used.

Another important step of adsorption providing is to adjust experimental conditions taking into account factors influence adsorption efficiency. The first important condition is solution's pH, which depends on pH of zero point of charge of adsorbent surface and pK_a value of adsorbate. Since adsorption is an isothermal process, maintaining a moderate temperature is also important. Obviously, the dose of the adsorbent and the initial concentration of the pollutant also increase the removal efficiency. The adsorption capacity is directly proportional to the characteristics of the adsorbent, such as the specific surface area and particle size of the adsorbent.

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