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REVIEW ARTICLE

The removal of pharmaceutical pollutants from aqueous solution by Agro-waste

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Abstract Pharmaceuticals are a unique class of emerging contaminants owing to their intrinsic ability to induce physiological effects on man and animals at low concentrations. Pharmaceuticals are released into the environment via diverse routes; human and animal wastes are the major sources. The persistence and mode of action of pharmaceuticals in the environment make them a major concern. Among methods available for wastewater treatment, the adsorption technique is found to be effective and easy to operate. The expensive nature of commercial activated carbons, however, created a limitation to the adsorption technique; hence the exploration for low-cost and sustainable adsorbents for the removal of different categories of water contaminants. Agricultural wastes offer such advantages as low-cost, abundance and eco-friendly materials in adsorbent preparation. Herein presented are the category and classes of pharmaceuticals cum the risks associated with pharmaceuticals released into the environment. The chemistry of activated carbon/agro wastes viz-a-viz suitability and potency in adsorption of different pharmaceutical waste removal were reviewed; the benefits associated with agricultural wastes usage in pharmaceutical removal have also been presented. Various challenges, gaps cum research prospects in the current field of discussion are herein presented. This work will serve as a tool for public education and enlightenment, help environmentalists make plans for envisaged threats and serve as a guide for policy makers.

1. Introduction

The environment is daily loaded with emerging contaminants through various anthropogenic activities including agricultural and industrial practices, healthcare delivery as well as domestic cleaning amongst others (Dimpe and Nomngongo 2016; Martín-Pozo et al., 2019; Ramírez-Malule et al., 2020). The occurrence of this group of contaminants has been a source of concern in the last two decades due to their great adverse effects (Dimpe and Nomngongo 2016; Taheran et al., 2018). Prominent classes of emerging contaminants are pharmaceuti-

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cals, flame retardants, personal care products and endocrine-disrupting chemicals (Martín-Pozo et al., 2019; Ramírez-Malule et al., 2020).

Pharmaceuticals are crucial for public health care and quality living. Keeping a healthy society calls for advanced therapeutic drugs and timely availability (Barra Caracciolo et al., 2015). A huge rise in the use of pharmaceuticals to combat different diseases has been experienced across the globe (Thomas 2017). Unfortunately, this use of medication has mostly been inappropriate (Holloway 2011; Thomas 2017). Pharmaceuticals have found great use in the prevention of man and animal diseases and therapeutics; their residue is directly or indirectly discharged into the environment (Al-Farsi et al., 2017). The direct injection of pharmaceuticals into the soil, as antibacterial agents for plant protection, may also greatly contribute to pharmaceuticals' release into water systems through surface run-off. The bulk of the consumed dose which is not absorbed by the body system, is released into the environment via various human waste discharges. Hotspots of pharmaceutical discharge into the environment include wastewater treatment plants (Wang et al., 2020; Wöhler et al., 2020), hospital effluents, septic tanks, surface waters (Wang and Wang 2018), landfills, sweat, urine and faeces (Baccar et al., 2012a; Ramos-Payán et al., 2020; Wang et al., 2021). The presence of pharmaceuticals in the environment can lead to the degradation of surface and subsurface water quality, consequently impacting the health of living organisms. The evidence of chronic long-term and sub-lethal effects of pharmaceuticals on aquatic populations and non-target organisms have been reported (Barra Caracciolo et al., 2015; Jureczko & Przystaś, 2019).

Several conventional water techniques have been employed for the elimination of pollutants and are reported to be accompanied by many drawbacks (Inyinbor et al., 2022; Moradi and Sharma, 2021; Rajabi et al., 2019). These techniques include chemical coagulation accompanied by the formation of sludge with high content of salts used as coagulants (Kooijman et al., 2020; Qian et al., 2020), ion exchange disadvantaged by high operational costs, advanced oxidation process which requires a large quantity of reagents for its operation (Wang, 2016), reverse osmosis is known to be expensive (Anis et al., 2019), electrocoagulation produces sludge (Zaied et al., 2020), constructed wetland process requires a large area of land (de Oliveira et al., 2019; Lancheros et al., 2019; Yan et al., 2018) and biological treatment process slowly progresses (Bhatia et al., 2018; Gholizadeh et al., 2020). In contrast, adsorption processes are inexpensive and efficient (Dada et al., 2013; Inyinbor et al., 2019a, 2019b, 2019c) and have become the most preferred technique due to their ease of operation, adaptability and simple design (Anijiofor et al., 2018). Also, developing cheap and effective adsorbents will make adsorption globally accessible. Hence, a huge quest for natural, readily available, eco-friendly and low-cost materials as adsorbents (Bai et al., 2021; Ronda et al., 2015; Wang and Chen 2014; Xu and Wang 2017).

Agricultural wastes are of low or no economic importance (Adeniyi et al., 2020; Adeniyi and Ighalo 2019), and liters the environment. Therefore, their clean-up is necessary. Agricultural wastes are lignocellulosic and carbonaceous in nature with abundant surface functional groups, which qualifies them as alternatives to commercial activated carbon (Inyinbor et al., 2019a, 2019b, 2019c). Many adsorbents have been produced from different waste entities such as rice husks (Li and Xiao 2019; Ng et al., 2019; Reddy et al., 2017), avocado peels (Palma et al., 2016; Salomón-Negrete et al., 2018), orange peels (Ahmed et al., 2020), neem husk (Mandal et al., 2020; Marichelvam and Azhagurajan 2018), cow faeces (Kaur et al., 2016; Mohd Nasir et al., 2019), tamarind fruit shell (Ashok et al., 2020), cotton seed hull (Yahya et al., 2020), banana fronds (Ali 2017; Ali et al., 2016) and many others (Anijiofor et al., 2018). These waste products may emanate from, industrial, domestic and/or agricultural operations.

This review, therefore aims at summarizing the occurrence, the environmental impacts of pharmaceuticals and the exploration of different agricultural wastes for the adsorptive removal of different pharmaceutical residues from wastewater. Factors that influence agrowastes potential in contaminants uptakes viz-aviz the chemistry of pharmaceutical uptake has been succinctly discussed. A review of the literature covering over one decade of study carefully highlighted the gaps, challenges, and future prospects in the field of discuss. The novelty of this work further lies in the fact that, the adsorption of chloroquine (CQ) and its counterpart hydroxychloroquine (HCQ) is an emerging field of research and currently calling for attention. Hence, this review tried to establish the possibility of agrowaste in the uptake of CQ and HCQ. A look ahead into preserving the environment from the threat of emerging contaminants and further conclusions were drawn from facts and figures.

2. Classifications and usage of pharmaceuticals

Pharmaceuticals are natural or synthetic chemicals that can be found in over-the-counter therapeutic drugs, prescription and veterinary medicine. Pharmaceuticals have designed pharmacological effects that provide the society with significant benefits (Khan et al., 2020).

2.1. Antibiotics

Antibiotics refer to any drug that has selective lethal action on the growth of microorganisms such as fungi, bacteria, and viruses. Antibiotics are used by man and animals for the treatment of infectious diseases (Inyinbor et al., 2021). Currently, there are about 250 different types of antibiotics registered for human and veterinary treatments (Kümmerer 2009). These drugs are usually classified based on the type of organisms on which they act. Antibacterial drugs such as tetracycline, penicillin, macrolide, sulfonamide and quinolone classes are used to treat bacterial infections. Antifungal drugs such as polyenes, echinocandins, allylamines and azole classes are used to treat fungal infections (Thompson et al., 2009). Natural and synthetic antibiotics were introduced in the late 1930s and their usage has increased both for man and animals (Li 2014). There are emerging concerns about the widespread of antibiotics through agriculture and wastewater effluents, which may promote antibiotic resistance (Bottoni et al., 2010; Inyinbor et al., 2021; Wang et al., 2020).

Antibiotics production increases regularly as the total usage per annum has reached 200,000 from 100,000 tons, across the globe (Gelband et al., 2015). The defined daily dose, in 76 countries between the years 2000 and 2015 has increased by about 65 %, to 42 billion defined daily doses in 2015 (Klein et al., 2018). There has been a prediction of a 200 % increase in global antibiotic consumption in the year 2030, emanating from the middle and low-income countries (Cycoń et al., 2019; Klein et al., 2018). Regardless of their health benefits, the regular release into the environment and potential health risks on living creatures are of serious concern (Barra Caracciolo et al., 2015; Brandt et al., 2015; Inyinbor et al., 2021).

2.2. Analgesics/anti-inflammatory

Analgesics are medications used for pain relief. Analgesics such as non-steroidal anti-inflammatory drugs (NSAID) and non-narcotic analgesics act on the central and peripheral nervous systems in several ways and are generally used to ease pain in virtually all diseases. Commonly used NSAIDs include ibuprofen, diclofenac, ketoprofen, fenoprofen, naproxen, and mefenamic. Non-narcotic analgesics include aspirin and acetaminophen (paracetamol). Narcotic analgesics include morphine, codeine, oxycodone and methadone (Li 2014). Diclofenac is one of the common pharmaceuticals detected in European rivers and groundwater at a concentration of 4 μg/L. Paracetamol was detected in groundwater at a concentration of 120 μg/L (Barra Caracciolo et al., 2015). Another literature reported the concentration of diclofenac and paracetamol to be 2770 ng/L and 0.17 μg/L in groundwater (Ślósarczyk et al., 2021). This indicated that the concentrations vary among different countries, ranging from several nanograms to micrograms.

2.3. Anti-cancer

Anticancer drugs are medications formulated to treat a wide range of cancer such as Hodgkin's and Non– Hodgkin's lymphoma, seminomas of the testis, Oesteo-sarcoma, lymphoblastic leukemia, myeloblastic leukemia, as well as breast, cervical, head, small cell lung and neck cancer. Some of the anticancer drugs approved by the Food and Drug Administration (FDA) agency between the years 2020 and 2021 include tepotinib, ripretinib, lurbinectedin, tazemetostat, pralsetinib and capmatinib (Sarfjoo et al., 2022). Generally, anticancer drugs are not completely metabolized by the human system, and tend to release via human wastes (Li et al., 2021a, 2021b). Hospitals and pharmaceutical industries are the major hotspots for the release of effluents containing anticancer drugs. This is because, cancer treatments are administered to cancer patients in the hospital, whereas effluents from industries that manufacture anticancer drugs contain high concentrations of these drugs (Cristóvão et al., 2020; Jureczko and Przystaś, 2019; Lai et al., 2018).

2.4. Anti-viral

Drugs that are specifically used for viral infection treatments are called antiviral drugs. Specific antiviral drugs are targeted towards specific viruses. These classes of drugs inhibit the development of their target pathogens rather than destroying them (Kausar et al., 2021). More than a hundred antiviral drugs for the treatment of nine human infections (Variola, Influenza, Human immunodeficiency, Hepatitis B, Respiratory syncytial, Hepatitis C, Human cytomegalovirus, and Varicella-zoster viruses) have been approved in the past decades. The release of antivirals into the environment is of substantial concern. This is because, antiviral drugs can cause antiviral resistance and can potentially cause alterations in the ecosystem (Nannou et al., 2020).

2.5. Antimalarials

Until recently, antimalarial drugs are mostly used in countries prone to malaria. Its threat to water bodies have been established; Sulphadoxine and chloroquine have been detected in well and tap water, collected from locations close to a hospital (Olaitan et al., 2016). However, the recent pandemic left the world with a search for both preventive and therapeutics for COVID-19. Chloroquine and hydroxychloroquine have been classified as virus-entry-blocker hence their potential in COVID-19 therapeutics (Srivastava and Singh, 2021).

Other classes of pharmaceuticals include antidepressants, antiepileptics and Central Nervous System (CNS) stimulants.

3. Occurrence of pharmaceuticals in the aquatic environment

More than a hundred different pharmaceuticals have been found in sewage effluents, surface waters, groundwater and even drinking water (Kim et al., 2020; Praveena et al., 2019). In the past few years, chronic pollutants of organic nature were detected in water habitats. Larsson et al. detected pharmaceuticals such as enoxacin, metoprolol, citalopram, enrofloxacin, norfloxacin, ciprofloxacin and ofloxacin in the effluent of Sewage Treatment Plant (STP) in India (Larsson et al., 2007). Raw water samples were collected from twenty drinking water supply well in Cape Cod, Massachusetts, USA and were found to contain sulfamethoxazole and phenytoin (Schaider et al., 2014). Pharmaceuticals such as acetaminophen, amoxicillin, sulphamethoxazole, carbamazepine and many more were detected in both effluent and surface water samples in Egypt (Abou-Elwafa Abdallah et al., 2019). Naproxen, diclofenac and ibuprofen have been detected in Mbokodweni river, South Africa (Amos Sibeko et al., 2019). Caffeine, a Central Nervous System stimulant was detected in the Jiulong River watershed, in southeastern, China (Hong et al., 2020).

Niemi et al, focused their research on rural hospitals' wastewater treatment plants. The crew detected pharmaceuticals such as paracetamol, carbamazepine, ibuprofen, and clarithromycin in raw water supply and hospital wastewater discharge (Niemi et al., 2020). In separate studies, Mohd Nasir et al., (2019) and Praveena et al., (2019) investigated the occurrence of nine pharmaceuticals including ciprofloxacin, chloramphenicol, amoxicillin and sulphamethoxazole in drinking water from Kajangand Putrajaya resident area, Malaysia respectively (Mohd Nasir et al., 2019; Praveena et al., 2019). Pharmaceutical wastes in various water sources are being established hence requiring easy and effective clean-up attention.

In the last 20 years, the presence of pharmaceuticals in surface waters, have become a great issue. This is due to the risks, posed by these toxic chemical substances on the environment (Gomes et al., 2017; Sivaranjanee and Kumar, 2021). Traces of pharmaceutical wastes have also been found in drinking water (Gogoi et al., 2018; Praveena et al., 2019; Kim et al., 2020), and questions have arisen regarding the expected danger, through drinking water (Chèvre 2014). The persistence of pharmaceuticals in surface water can be toxic at all levels of the biological hierarchy, which includes organisms, cells, organs, and ecosystems. A class of pharmaceuticals like antibiotics can cause resistance, even at low concentrations, leading to long-term and fatal effects on microorganism genomes (Gaso-Sokac et al., 2017).

4. Pharmaceutical effects on the environment.

Pharmaceuticals have a significant effect on the ecosystem, which includes aquatic creatures, leading to antibiotic resistance. Some pharmaceuticals can also be transferred to man, through water and food chains (Al-Farsi et al., 2017), can alter and disrupt the endocrine system (Barra Caracciolo et al., 2015; Khan et al., 2020) and inhibit the growth of some algae (leafless plant in water habitats). At a very low concentration (< 0.1 mg/L), it can affect the aquatic system balance and controls the behavior of microorganisms (Carter et al., 2014). It may also affect the reproductive organs and survival of fish, after long-term exposure (Calderón-Preciado et al., 2012; Ramesh et al., 2018). Fig. 1 presents the toxicity of pharmaceuticals and other ECs on fish; a case study of marine lives (Amelia et al., 2021).

Pharmaceuticals from treated wastewater and biosolids accumulate in the soil, which promotes their uptake in plant tissues (Cortés et al., 2013). Man can be significantly affected, when exposed to high dosages, from accumulation in fruits and vegetables (Inyinbor et al., 2021). It is important to avoid pharmaceutical consumption, other than the recommended daily dosage intake (Heise et al., 2006). The constant disposal of these contaminants into the ecosystem can provoke serious health issues.

In general, pharmaceutical products such as antibiotics are persistent, accumulative, and biologically active (De Andrade et al., 2018). Although they are found in low concentrations, the existence of several contaminants in the ambiance, possessing similar mechanisms, can cause notable environmental effects via exposure (Taoufik et al., 2020). This type of exposure may endanger the aquatic organisms, as reported (Komori et al., 2013; Kostich et al., 2014; Omo-Okoro et al., 2018).

Pharmaceutical compounds are introduced into the environment, in their unchanged, conjugate or metabolized form. This can impact adverse effects, since the physiological activities of the transformed products could be more than the impact of the original compound (De Andrade et al., 2018). Once introduced into the aquatic region, they cannot escape, because of their non-gaseous and polar nature. Medications with short half-lives are regarded as extremely persistent in aqueous solution, resulting from the consistent mixture of effluent from wastewater treatment plants (Besse and Garric 2008).

5. Major sources of pharmaceutical release into the environment

Pharmaceuticals are ingested by humans and released into the environment, through sweat, urine and faeces, either as metabolites or in their original form. Pharmaceuticals go through sewage systems into Water Treatment Plants (WTPs), and water systems because often they are not totally removed in the WTPs (Chèvre 2014). Although, human wastes constitute a major route for pharmaceutical release into the aquatic systems, contamination from veterinary, aquaculture and other agricultural activities have also been established (Gaso-Sokac et al., 2017; Ramírez-Morales et al., 2021). Like humans, animals do not use up pharmaceuticals administered to them, hence, a huge part is expelled with their dung and urine (Fig. 2). These subsequently go into the water environment through erosion. Pharmaceuticals may accumulate in soil treated with manure over time, this may also be eroded into water systems (Camotti Bastos et al., 2020; Yan et al., 2018). This exposes receiving water organisms to an unstable concentration of different compounds. Contamination of groundwater by veterinary drugs can also occur through leaching (Gaso-Sokac et al., 2017; Ibrahim et al., 2021). Pharmaceutical occurrence is at its peak in aquatic environments and predominant in some rural settlements (Chèvre 2014).

6. Fate and transformation processes of pharmaceuticals in the environment

Pharmaceuticals have been found in aquatic environments due to direct/indirect discharge of untreated wastewater. The presence of pharmaceuticals can disrupt the biological processes in non-targeted lower organisms on exposure. Biotic and abiotic processes shape the fate of pharmaceuticals in the aquatic environment (Khan et al., 2020). Weather and climate can also influence pharmaceutical concentration in water, due to heavy rainfall, leading to increased flow rate and substantial dilution of pharmaceuticals in water (Schaffer and Licha 2015).

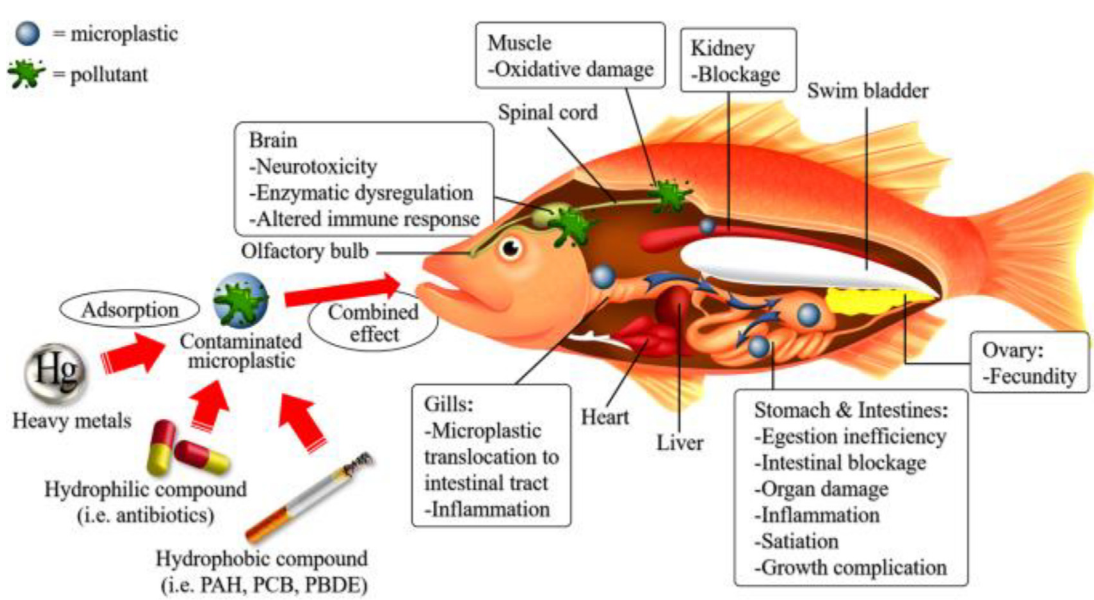

Fig. 1 Toxicity of ECs of fish (Adapted from Amelia et al. 2021).

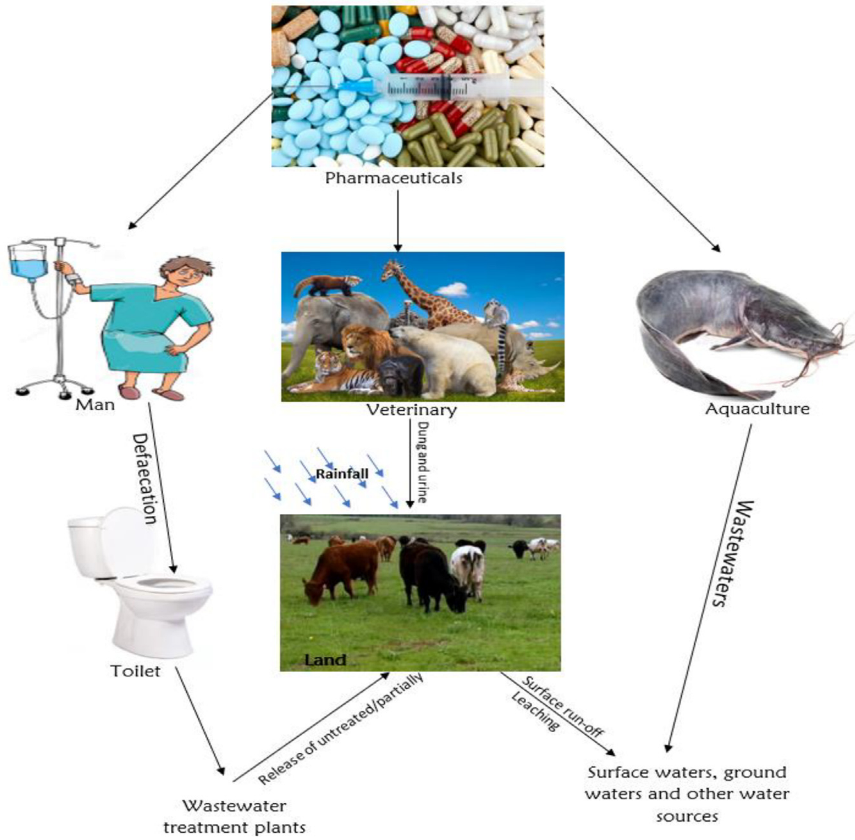

Fig. 2 Pharmaceuticals pathway into the environment.

Pharmaceuticals such as antibiotics accumulate in plants when antibiotic-polluted water are used in irrigating plants; such plant may be eaten by human hence a constituted cycle. An established cycle may also follow; animal waste containing antibiotics (which were used at preventive, prophylaxis or therapeutics at various stages of animal husbandry) in use as manure on agricultural fields. Plants grown on such fields accumulate antibiotics or their degradation product and the consumption of such crops by humans follows (Cycoń et al., 2019). Furthermore, certain bacteria can transform some antibiotics by utilizing the beta-lactamases they produce; this is especially true for beta-lactam antibiotics. This is because beta-lactams are considered to be less toxic. However, they have been reported to affect the division of plastids in lower plants.

Fluoroquinolones have a cumulative effect on the environment. These antibiotics obstruct photosynthetic pathways thereby causing morphological deformities, especially in plants. In the case of tetracyclines, plant growth can be inhibited as a result of the chromosomal abnormalities caused by the phytotoxic effects of this antibiotic. This leads to a reduction in photosynthetic chlorophyll as well as carotenoid pigments in such a plan. The concentration of oxytetracycline in certain aquatic plants has been reported. Furthermore, tetracycline and chlortetracycline can induce breakage in DNA and cause alterations in the enzymatic activities of earthworms (Polianciuc et al., 2020). The fate of pharmaceuticals in the environment is primarily determined via three processes viz degradation, sorption and migration (Khan et al., 2020; Sui et al., 2015; Yu et al., 2013). Degradation may depend on the presence or absence of oxygen in a specific environmental matrix. For instance, there is a tendency for partial degradation of pharmaceuticals in groundwater due to the diversity of microorganisms, less proliferation and reduced redox activities of same (Sui et al., 2015). Hence, the possibility of hazardous metabolite formation. Different biodegradability rate results from the physical and chemical properties of different pharmaceuticals. Paracetamol and caffeine are more susceptible to degradation during wastewater treatment in comparison to sulfamethoxazole and carbamazepine, which are more resistant to degradation (Cycoń et al., 2019; Sui et al., 2015). An important pathway for the abiotic degradation of antibiotics is hydrolysis. The class of β-lactams is more prone to hydrolytic degradation while macrolides are less prone (Cycoń et al., 2019). Antibiotics can also undergo degradation through reductive and oxidative stress.

Adsorption can also affect the fate of pharmaceuticals in the environment by altering their movement, bioavailability and plant uptake (Tiwari et al., 2017). Chemicals with weak sorption tend to permeate into groundwaters and those with strong sorption have limited leaching effects (Sui et al., 2015). The adsorption of pharmaceuticals is influenced by the content of the dissolved organic matter in the soil. The adsorption of sulfamethazine, sulfaquinoxaline and sulfadimethoxine in four Brazilian soils, shows that sulfonamide adsorption was larger in clay than in sandy soil. This phenomenon could be described by the organic content of the soil and the lipophilicity of the sulfonamides (Doretto et al., 2014).

7. Environmental risk assessment (ERA) for pharmaceuticals

As the concentration of pharmaceuticals in the environment builds up, it is important to evaluate the fate of pharmaceuticals in the environment. This can be achieved by executing a risk assessment for new and existing pharmaceuticals. The implementation of the ERA for drugs has been put in place by Europe, the United States of America, and Canada. On the contrary, Australia, China, India and other developing countries lack proper strategies for evaluating pharmaceuticals. Risk assessment, therefore, follows the guidelines for active chemical substances (Jose et al., 2020). The critical pollution of the Patancheru Bollaram area which birthed 'a mutated antibiotic resistance gene in fungi and bacteria, led the supreme court of India to mandate the "zero liquid waste" policy (Jose et al., 2020).

The (USFDA) United States Food and Drugs Administration plays an important role in commercializing safe products and assessing clinical reports. The USFDA enforced a 0.01 μg/L maximum allowable limit of pharmaceuticals released into the environment. Specific attention is given to pharmaceuticals in clinical trials and ones whose active ingredient directly or indirectly negatively impacts the environment and living organisms. Deviation from the requirements usually attracts ERA information submission (Jose et al., 2020). For instance, diclofenac, an example of NSAIDs, has been listed as a priority hazard substance in the "Water Framework Directive" by European Union regulators. Its use in veterinary greatly reduced the vulture population in India as it indirectly affects vultures' kidneys (Shore et al., 2014). Hence, the manufacturing of diclofenac became prohibited (Petrie et al., 2013).

In light of the existing laws of disposal of pharmaceuticals and other wastes into the environment, ERA should be established for emerging threats of COVID-19 therapeutics. A study tried to establish the possible impact and toxicological risk of unsystematic use of COVID-19 combination therapy [hydroxychloroquine (HCQ) and azithromycin (AZT)]. The evaluation was carried out on the drugs individually and in a combined state on a zebra fish. The administration of 2.5 μg/L each of AZT and HCQ induced a reduction in total protein level after 72 h. This symptom was accompanied by an increase in thiobarbituric acid reactive substances (hydrogen peroxide, nitrite and reaction oxygen species) level, indicating possible oxidative stress and REDOX imbalance. The administration of combined AZT and HCQ resulted in a neurotoxic effect (Mendonça-Gomes et al., 2021). Thus, an increase in AZT and HCQ, due to covid-19 pandemic can compromise the health of freshwater organisms (Dabić et al., 2019; Mendonça-Gomes et al., 2021).

8. Water clean-up

Water pollution is a global problem that is created by various human activities; for instance, the release of agriculture and industrial wastewater into water bodies. Water pollution may also occur naturally; i.e. varying range of elements and salts such as iron, arsenate, magnesium and nitrates leach into water bodies through rocks and soils (Sharma and Bhattacharya 2017). Several techniques such as biological treatment, electrocoagulation, membrane filtration, advanced oxidation, membrane fuel cell, ozonation, ion exchange, coagulation and adsorption processes, have been successfully employed for the removal of water pollutants (Khasawneh and Palaniandy 2021; Taoufik et al., 2020; Taoufik et al., 2021; Wang and Wang 2016). However, most of these techniques are accompanied by several limitations as presented in Table 1. The microbial fuel cell process may require continuous cell replacement which can result in a high cost of operation and high energy consumption. Membrane fouling occurs in the membrane filtration process, electrocoagulation results in huge sludge generation, as well as numerous electrode replacements. Nutrients and pathogens are partially removed during biological treatment and hence post-treatment is required. The ozonation process usually results in the disruption of radical scavengers (Zaied et al., 2020). However, the adsorption process is an effective method for trapping impurities, odors and colors. Adsorption of pharmaceuticals from different routes of disposal is presented in Fig. 3. In adsorption processes, contaminants in the solution stick onto the surface of the adsorbent such as zeolites, silica gel, ion exchange resins, and activated carbons (Sharma and Bhattacharya 2017). Various adsorbents have been tested and found effective in the removal of various pharmaceuticals from aqueous media (Afolabi et al., 2020; Bello et al., 2020; Coimbra et al., 2019; Li et al., 2018; Topal and Topal, 2020).

9. Activated carbon

Activated carbon (AC) is a carbonaceous matter that possesses a wide surface area, a high degree of porosity and an amorphous structure. AC structure plays a vital role in the determination of its properties and performance. Within the structure of AC exist micropores, mesopores and macropores, based on the International Union of Pure and Applied Chemistry (IUPAC). Micropores are < 2 nm, mesopores are between 2 nm and 50 nm while macropores are > 50 nm (Yahya et al., 2020). AC is readily available in powder, granular and pellet forms (Bernal et al., 2017; Sun et al., 2019; Szabová et al., 2022) for the adsorption of different wastewater pollutants. A broad range of precursors can be used in the preparation of activated carbon. The major precursors for AC preparation are coal, petroleum residue, wood and lignite, which are very expensive and exhaustible. However, the expensive nature of coal has necessitated the search for alternative and cheap precursors for activated carbon preparation. Activated carbon is usually prepared from various sources, majorly biomass materials, through activation processes and carbonization at high temperatures (Ogungbenro et al., 2020).

The surface of the AC is functionalized through the availability of various elements such as; oxygen (quinines, phenolics, lactones, carbonyl) (Montes-Morán et al., 2004), nitrogen (pyrrole, amine, imine, pyridine, lactam, nitro) (Bandosz and Ania 2006; Lladó Valero 2016) and sulfur (thiophenol, sulfoxide, thioquinone, sulfide) (Bandosz and Ania 2006) (Fig. 4). The presence of these groups allows for distinctive interactions and increases the polarity of the carbon surface (Lladó Valero 2016).

10. Preparation processes of activated carbon

The two major preparation processes for activated carbon are chemical and physical activation. The efficiency of AC for the

Table 1 Highlight of technologies for wastewater clean-up.

Clean-up technology	Merits	Demerits	Reference
Adsorption process	Simple operating conditions, low energy consumption, minute sludge production and high efficiency.	Huge cost of commercial activated carbon.	(Garba et al., 2019; Zaied et al., 2020)
Membrane filtration process	Fast operation, efficient removal of salt and organic matter and can be used in large volumes of wastewater treatment.	High membrane cost and membrane fouling may occur.	(Gu et al., 2018)
Electrocoagulation process	Continual mode of operation, large volumes can be treated, very effective in the removal of colloidal and ionic matter.	Sludge production and replacement of electrodes.	(Song et al., 2017)
Advanced oxidation process	Effectively removes organic compounds in aqueous media, some heavy metals can also be removed in the form of $M(OH)_x$ precipitate.	High cost and large volume of reagents required while some of the techniques require pretreatment to aid consistent performance.	(Anjali and Shanthakumar, 2019)
Biological treatment process	Simple construction and operation of the reactors, bioenergy (methane) is produced during the process and high removal efficiency even at low temperatures.	Time consumption due to low progress rate it takes for the microbes to be active, post-treatment is required due to partial removal of nutrients and pathogen.	(Dogan et al., 2020)
Ozonation process	Effective removal of organic pollutants and oxidants assisting sterilization properties and disinfection.	Disruption of radical scavenger, high energy depletion and release of oxidative by-products	(Gomes et al., 2017; Wang and Bai 2017)
Ion exchange process	Very effective in water softening, the wastewater that is produced during the process is also used for water treatment.	The iron exchangers involve high operational cost and must be cleaned for high level of saturation.	(Ahmed and Hameed 2019)

removal of water pollutants is influenced by several factors such as pore structure and functional groups on the surface. The pore size can be manipulated by varying the activation parameters including the method of activation, temperature and activating agents (Sakhiya et al., 2021).

10.1. Physical activation method

The physical activation procedure is usually carried out in two stages. The first stage involves pyrolysis in the absence of air, at low temperatures to produce char. The produced char has a moderate surface area with low or no activity for pollutant removal (Malima et al., 2021). The second stage incorporates the activation of the char produced in the first step, under an oxidizing atmosphere, therefore increasing its surface area to a great extent. The activated char can then be used for pollutant sequestration. Some literature have successfully combined the two steps, into single-step activation. This led to high carbon yield, low operational cost, high energy saving and less processing time (Plaza et al., 2014; Yang et al., 2010). In the developed single stage, pyrolysis is performed under the flow of an oxidizing agent, such as air, steam or carbondioxide (Plaza et al., 2014).

10.2. Chemical activation method

Surface chemistry is an important factor that determines the performance of an adsorbent. Different adsorbent modification techniques are with various attendant benefits such as improved surface area, carbon content, surface functionality and hydrophobicity as elaborated in Fig. 5 (Liu et al., 2022). It is, therefore, necessary to modify the surface quality of an adsorbent, to enhance its performance during the adsorption process. This can be achieved by either physical or chemical surface modification. Chemical modification is preferable, as it directly influences the surface chemistry of the material. This method assists in the transformation of the adsorbent materials into valuable materials with high adsorption efficiency (Rostami et al., 2018).

The chemical activation procedure involves a single-stage procedure, where the carbonaceous raw material is soaked in a dehydrating agent, such as $ZnCl_2$, KOH and phosphoric

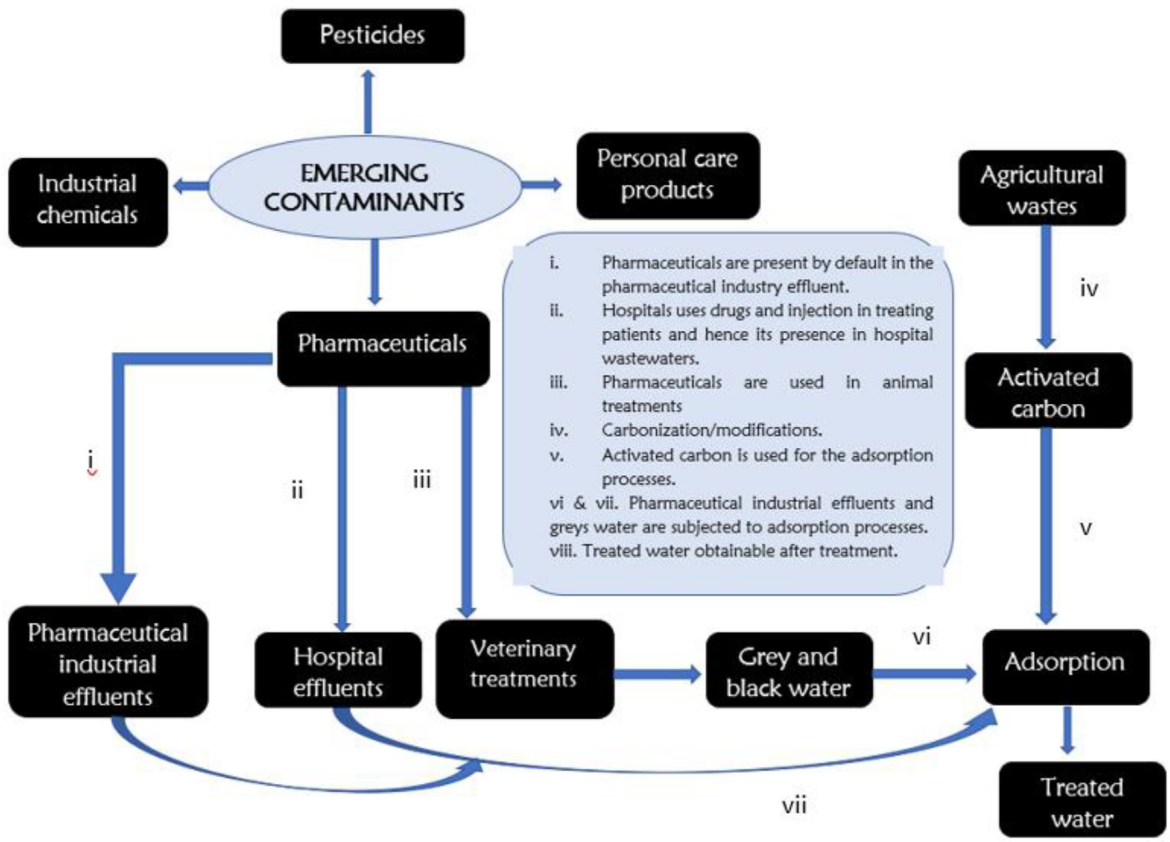

Fig. 3 Adsorption of pharmaceuticals from various possible disposal routes.

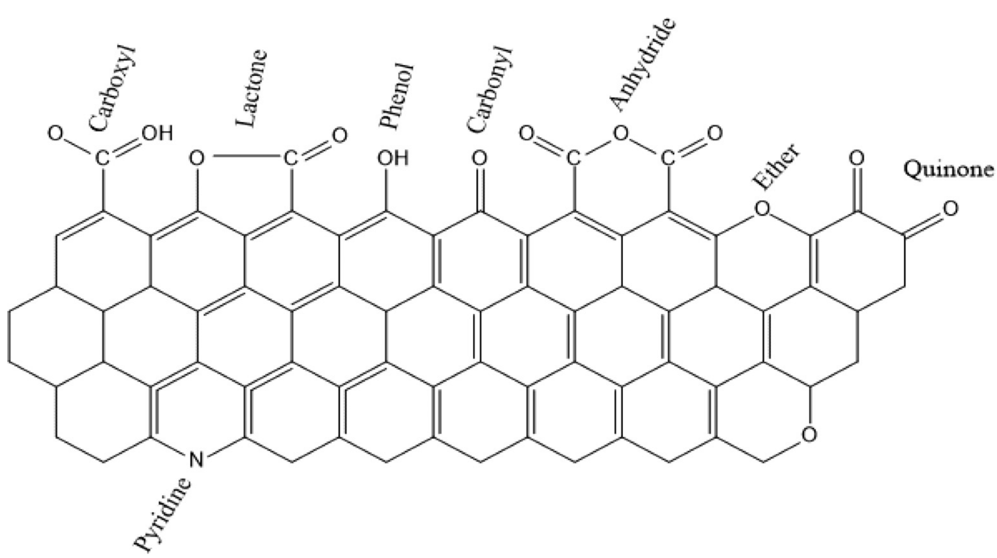

Fig. 4 Different functional groups on the surface of activated carbon.

acid. The activation is carried out at moderately high temperatures (Hadi et al., 2015). The advantages of chemical over physical activation include high carbon yield and low activation temperature, while the demerits include the need for an extra washing step and the high cost of the activating agent. It should be noted that, employing an oxidizing surrounding instead of an inert atmosphere have a significant effect on both porosity and the active functional groups (Bello et al., 2017a; Hadi et al., 2015). Several chemicals such as alkaline, acidic and neutral solutions have been explored, for tuning the properties of adsorbent materials (Abegunde et al., 2020).

10.2.1. Acid modification

Acid modification may employ oxidants or mineral acids such as H_3PO_4, $HClO_4$, HNO_3, H_2SO_4, HCl and many more.

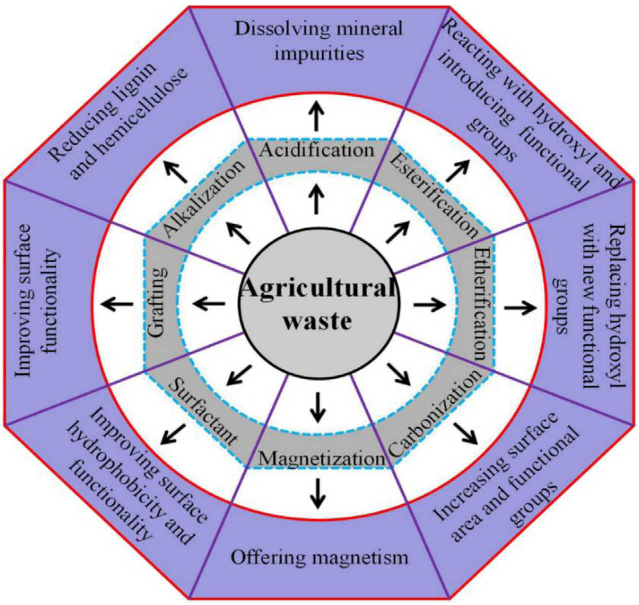

Fig. 5 Different modification techniques for agricultural wastes (adapted from Liu et al. 2022).

Organic acids such as formic acid, carboxylic acid, oxalic acid and acetic acid are seldom used due to their weak effects occasioned by their low strength (Kong et al., 2014). Acid modification of an adsorbent reduces the mineral content, thereby improving the hydrophilic nature and acidic behavior of the adsorbent. Acid activation improves the surface area, surface charge, pore volume, oxygen functional groups content, the hydrophobic and lipophilic characteristics (Rehman et al., 2019). Many researchers have used acid-modified adsorbents for wastewater sequestration (Ahmed and Theydan 2014; Azarpira and Balarak 2016).

10.2.2. Alkaline activation

Alkaline modification helps to improve the non-polar surface, and enhances the adsorption efficiency of the material as well as the relative content of alkali groups. The surface modification can be achieved by treatment with KOH and NaOH as well as other oxides. The alkaline treatment enhances the adsorption of positively charged specie on the surface of the adsorbent (Rehman et al., 2019).

Other chemical activation methods, can also be achieved by employing oxidizing agents (hydrogen peroxide and potassium permanganate), organic agents (ethanol) salts (sodium chloride and zinc chloride), and metal impregnate on (chromates, carbonates, hydroxides and nitrates) (Enaime et al., 2020). The previously detailed surface treatment processes are known to modify the surface of a material by altering the chemical, biological and physical properties of that material (Wang and Wang 2019). Surface modifications usually improve adsorbents' surface features such as surface area, reactivity and functional groups (Abegunde et al., 2020). Thermal and mechanical processes have also been greatly employed for surface modification (Malima et al., 2021; Tole et al., 2019).

10.3. Adsorption characterization techniques

10.3.1. Surface chemistry

The performance of an activated carbon depends on its structural properties. Characterization of the surface chemistry of an adsorbent is important to completely understand adsorbent-adsorbate interactions (Bläker et al., 2019). The characterization is mainly focused on the electrical charge of an adsorbent and the investigation of oxygen-containing groups. Often utilized techniques are described below.

10.3.1.1. Boehm titration. Boehm titration was designed to quantify the acidic or basic surface functional groups present on adsorbents. This technique involves selective neutralization or titration using bases that have conjugate acids (with a wide range of dissociation constants, pKa,) against surface acidic groups (Lima et al., 2019). The surface acidic groups are contacted with a base that neutralizes surface acidic oxygen-containing groups, while measuring the unreacted amount of bases, using acid-base titration. Basic reagents such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), or sodium bicarbonate ($NaHCO_3$) can be used to quantify acidic groups. $NaHCO_3$ reacts (pKa = 6.37) reacts with the strong carboxylic groups, the amount of Na_2CO_3 (pKa = 10.25) consumed is associated with the lactonic and carboxylic acids, while NaOH reacts with phenolic, carboxylic and lactonic groups. Sodium ethoxide with basic ethanol ($NaOC_2H_5$) is usually used in the quantification of weaker acids. The drawback of the use of this reagent is that the experiment is required to be performed in oxygen-free conditions and non-aqueous media. Boehm titration has been used by various researchers to quantify adsorbent oxygen-containing compounds (Agboola & Bello, 2020; Lima et al., 2019; Bello et al., 2017b). Boehm titration has recently been normalized, taking into account the agitation time, the method of CO_2 expulsion and the method of titration. It was observed that CO_2 dissolved in basic media has a substantial effect amount of functionalities detected hence, CO_2 must be removed. The removal can be achieved through heating, agitation and degassing using N_2 or Ar, before and during titration (Goertzen et al., 2010).

10.3.1.2. pH point of zero charge. The point of zero charge (pH_{pzc}) is the pH at which the adsorbent's surface is neutral, containing an equal number of negatively and positively charged surface functions (Bedia et al., 2018). At pH below pH_{pzc} the surface of an adsorbent is positively charged with affinities for anionic species, while its negatively charged at pH above pH_{pzc} with affinities for cationic molecules (Ben-Ali et al., 2017). The pH drift method was investigated by pH adjustment between 2 and 12, using 0.1 M HCl or 0.1 M NaOH in a conical flask. Activated carbon of 0.15 g each was added to each of the flasks and agitated for 4 h. The final pH was measured and the pH_{pzc} was determined from the intercept of the plot of pH_{final} versus $pH_{initial}$ minus pH_{final} (Bello, et al., 2017a, 2017b).

10.3.1.3. Fourier Transformed Infrared (FTIR) Spectroscopy. The principle of this technique is based on the radiation (infrared) transmitted or absorbed by an adsorbent material as a function of the frequency of radiation or wavelength. The functional groups on the adsorbent can then be identified based on the fact that different absorption bands signify a specific functional group (Agboola & Bello, 2020). The Fourier transformation of the signals from the interferometer is converted by the spectrometers. FTIR measurements are usually carried out by mixing the carbon sample with KBr pellets and analyzed in the wavelength range of 400–4000 cm^{-1} (Bedia et al., 2018). Prominent functional groups such as hydroxyl, methylene, carbonyl and alkene groups have been identified on adsorbents' surfaces using FTIR (Afolabi et al., 2020b; Ahmad et al., 2021; Finčur et al., 2021).

10.3.2. Surface morphology

The changes in surface topography or morphology of an adsorbent are commonly depicted using Scanning Electron Microscopy (SEM) techniques. In SEM, a sample is projected and scanned along parallel lines, using a fine probe of energized electrons (up to 40 KeV). An image is then formed, from the various signals generated as a result of the incidence of electrons on the surface of the adsorbent. Most SEM equipment are embedded with dispersive or non-dispersive X-ray analyzers (SEM-EDX), which provide information about the elemental composition of the adsorbent materials. SEM-EDX has been used by many researchers to reveal the surface morphology and analyze the elemental composition of adsorbent materials from agricultural waste sources (Abdel-aziz et al., 2020; Thakur et al., 2020; Anijiofor et al., 2018). Transmission Electron Microscopy (TEM) imaging provides a detailed figure of crystalline, disordered and novel materials (González-García, 2018). High-resolution TEM (HRTEM) utilizes a parallel incident beam for collecting coherent signals. HRTEM has been widely implemented in the characterization of microstructures (Lin et al., 2021). TEM has previously been used in the characterization of nano-particle prepared from agricultural wastes (Mao et al., 2016; Wamba et al., 2019).

10.4. Effects of operational parameters on pharmaceuticals adsorption

Many operational parameters are involved in the uptake of pharmaceuticals using agrowaste-based adsorbents. These factors include pH effect, initial pharmaceutical concentration, adsorbent dosage, temperature and contact time effects. To optimize on an industrial scale, the in-depth study of these parameters will be of great importance (Rajabi et al., 2017; Moradi and Sharma, 2021; Bankole et al., 2022).

The effect of pH is the most important which affects an adsorbent's capacity to adsorb pharmaceuticals from aqueous media. The pH of the solution influences the adsorbate-adsorbent interactions, the degree of adsorbate ionization, functional groups and surface properties of the adsorbents. The mechanism of the interaction between the adsorbent and the adsorbate is also influenced by the pH of the solution. Many researchers have investigated the effect of pH on the removal of pharmaceuticals (Bernal et al., 2017; Ndoun et al., 2021; Bello et al., 2021; Szabová et al., 2022).

High initial concentration of an adsorbate is advantageous at an early stage of the adsorption process. This is because, a high mass transfer driving force is provided for the pharmaceutical molecules. However, as the adsorption process approaches equilibrium, the percentage removal reduces. This is attributed to the saturation of the adsorbent active sites (Rajabi et al., 2017; Agboola et al., 2021). Most thermodynamic properties are temperature dependent. An adsorption process can be moderately affected by temperatures between 20 and 35 °C and critically at higher temperatures (Adeniyi and Ighalo, 2019). An exothermic adsorption process is favored at lower temperatures (Kerkhoff et al., 2021; Ngeno et al., 2019; Wong et al., 2018) whereas an endothermic process is favored at higher temperatures Chang et al., 2020; Movasaghi et al., 2019; Quesada et al., 2019). An endothermic process may occur when there is an increase in the mobility of adsorbate molecules due to increased temperature, which can increase the adsorbate-adsorbent interaction. High temperatures could also lead to the activation of more sites on the adsorbent, for pharmaceutical adsorption (Garba et al., 2019).

The adsorbent dosage determines the availability and the number of binding sites for adsorbate molecules. High adsorbent dose can result in high pollutant removal. However, agglomeration can occur in the presence of excess adsorbent. This can lead to a reduction in the surface area and hence, decreased removal efficiency (Ahmed et al., 2015; Balarak et al., 2017a, 2017b, 2017c; Bankole et al., 2022). The contact time between the adsorbent and adsorbate molecules determines the speed at which equilibrium will be attained. Pharmaceutical removal is rapid initially, and slowly and steadily regresses as it approaches equilibrium. At equilibrium, the sorption rate is slowed down, with an insignificant adsorption rate, as most of the active sites have been occupied (Bello et al., 2021; Davoud et al., 2019; Ngeno et al., 2019).

10.5. Equilibrium isotherms, kinetics and thermodynamic studies

10.5.1. Isotherms

The distribution of molecules at the solid–liquid equilibrium phase, and the nature (multilayer or monolayer adsorption) of adsorbate-adsorbent interaction can be explained by adsorption isotherms (Aniagor et al., 2021; Moradi and Sharma, 2021). The Langmuir and Freundlich isotherms have been mostly used to investigate adsorption experimental data, by various researchers (Ahmed, 2017; Reddy et al., 2017; Sahin et al., 2020; Kerkhoff et al., 2021). The Langmuir isotherm model assumes that, reactive groups distribution on the surface of solid particles are homogeneous. The active site's ability to attract is uniform and independent of the interaction between molecules. Langmuir model was developed based on gas theory and extensively used in the description of solid adsorption of gases (Ehiomogue et al., 2021; Langmuir, 1917). Langmuir isotherm is valid when solute adsorption from a solution is a monolayer process. The non-linearized form of the Langmuir equation is presented in Eq. (1a):

$$Q_e = \frac{Q_o K_L C_E \theta}{1 + K_L C_e} \tag{1a}$$

The linearized Langmuir equation is shown in Eq. (1b):

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_o} + \frac{C_e}{K_L} \tag{1b}$$

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{2}$$

Where Q_e and C_e are the equilibrium adsorptive capacity of the adsorbent (mg/g) and adsorbate equilibrium concentration in (mg/L) respectively. K_L (L/mg) is the Langmuir constant related to the apparent energy of adsorption in L/mg, Q_o (mg/g) is the maximum monolayer adsorption capacity; these parameters are obtainable from the slope and the intercept of the plot C_e/q_e versus C_e. K_L is an important parameter in calculating R_L (Eq. (2)), which is dimensionless and explains the favorability of the adsorption process. The adsorption process is favorable when $0 < R_L < 1$, unfavorable when $R_L > 1$, linear when $R_L = 1$and irreversible when $R_L = 0$. Adsorption of metronidazole onto adsorbents prepared from canola residue was investigated. The Langmuir model was found to be the best fit for the adsorption data, with an adsorption capacity of 21.42 mg/g (Balarak & Kord Mostafapour, 2016). Adsorption of ciprofloxacin onto hazelnut shells was also investigated. The adsorption data were best described by the Langmuir model at an initial concentration of 25 – 200 mg/L (Balarak et al., 2016).

The Freundlich isothermal model describes the heterogeneity of the surface of molecules and the exponential distribution of active sites as well as their energies describe. Freundlich model assumes that the heat of adsorption may and may not be evenly dispersed on a heterogeneous surface and hence describes a multilayer adsorption system (Aniagor et al., 2021; Ehiomogue et al., 2021). The non-linearized form of the Freundlich equation is shown in Eq. (3a).

$$Q_e = K_F C_e^{1/n} \tag{3a}$$

The empirical nature and adequacy of the Freundlich model in describing non-linear processes make it suitable for data description in adsorption processes, whose adsorption sites are energetically heterogeneous (Musah et al., 2022). The linear form of the Freundlich equation is presented in Eq. (3b).

$$\log q_e = logK_F + \frac{1}{n} logC_e \tag{3b}$$

Where 1/n is the measure of the heterogeneity of the adsorption sites and the energy relative distribution. This parameter indicates favorability when $0 < 1/n < 1$, unfavorable when $1/n > 1$, and irreversible when $1/n = 1$. K_F (mg/g) is Freundlich constants. Several literature have established the Freundlich model as the best fit for the adsorption of different pharmaceuticals (Dada et al., 2021 Inyinbor et al., 2023).

10.5.2. Kinetic studies

Adsorption kinetics are very important and vital for selecting the optimum conditions for a given adsorbate-adsorbent interaction. The mechanism of adsorption can be explored via adsorption kinetic models (Aniagor et al., 2021). The pseudo-second-order (PSO), pseudo-first-order (PFO) and Intraparticle diffusion (ID) models are the commonly employed kinetic models. These models help evaluate the controlling mechanisms and the mass transfer (Moradi and Sharma, 2021). The PFO model also known as the Largergren model describes the liquid/solid adsorption system, following a first-order mechanism. The model assumes that the rate of change of adsorption at a particular time is proportional to the rate of adsorbate removal with time and the concentration difference (Musah et al., 2022). The non-linear and the linear form of the Largergren model is shown in Eqs. (4a) and (4b) respectively. Pseudo-first order model has been used in the evaluation of adsorption data on the uptake of various pharmaceuticals (Boudrahem et al., 2017; de Araújo et al., 2021).

$$q_t = q_e\left(1 - e^{-K_1 t}\right) \tag{4a}$$

$$\log(q_e - q_t) = logq_e - \frac{K_1}{2.303} t \tag{4b}$$

The Pseudo second order model assumes that the rate of solute adsorption is proportionate to the available adsorbent active sites (Dada et al., 2019). The non-linear and linear form of the PSO model is presented in Eqs. (5a) and (5b) respectively. Also, the rate-limiting step of an adsorption process, can be examined via the ID model. Adsorbate molecules adsorption involves surface diffusion, pore diffusion and film diffusion. The surface and pore diffusion may occur concurrently, whereas the film diffusion is an independent step. This mechanism can be explained by Weber and Morris, (1963), presented in Eq. (6). Several reports have however, shown that the pseudo-second-order was the best fit for most pharmaceutical adsorption onto various adsorbents (Wong et al., 2018; Agboola et al., 2021; Natarajan et al., 2021; Praveen Kumar et al., 2021).

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{5a}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5b}$$

$$q_t = k_{id} t^{1/2} + C \tag{6}$$

Where K_1 is the rate constant of the pseudo-first-order equation (min^{-1}), K_2 (g/mg min) is the equation rate constant for the pseudo-second-order model, C is the constant (the thickness of the boundary layer surrounding the adsorbent) (mg/g), k_{id} is the rate constant of the intraparticle diffusion with dimension mg/g $min^{1/2}$, and t is time (min). Table 2 presented details of various modified adsorbents, for pharmaceuticals wastes removal. Various isotherms and kinetic models investigated by various researchers were also highlighted.

10.5.3. Thermodynamics study

Thermodynamics study is required in adsorption experiments to establish the feasibility and spontaneity of the process. The thermodynamic study is usually carried out to evaluate the influence of temperature on the adsorption system (Moradi and Sharma, 2021). Parameters such as Gibb's free energy (ΔG^o), standard entropy (ΔS^o) and standard enthalpy (ΔH^o) can be estimated. ΔG^o evaluates the feasibility and spontaneity of an adsorption process. A negative ΔG^o value confirms a spontaneous process while a positive predicts a non-spontaneous system. ΔG^o can be calculated using Eq. (7). ΔH^o is the energy supplied in the form of heat at constant pressure (Ebelegi et al., 2020). The enthalpy change proffers an insight into the mechanisms and nature of adsorption processes and can be evaluated using Van't Hoff equation as shown in Eq. (8). ΔS^o indicate the degree of randomness in an adsorption process. A positive value suggests an increased randomness while a negative value of ΔS^o indicates a decreased randomness and can be determined from Van't Hoff equation.

The adsorption of chloroquine onto plantain peel adsorbents was found to have a positive ΔS^o value, indicating increased randomness (Dada et al., 2021).

$$\Delta G^{oC} = -RTlnK_o \tag{7}$$

$$lnK_0 = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{8}$$

Where T is the temperature (K) and R is the gas constant (8.314 J/mol K). The values of $\Delta S^o and \Delta H^o$ can be obtained from the slope and intercept of the plot of $lnK_o versus \frac{1}{T}$.

11. Agricultural wastes usage as adsorbents in pharmaceutical removal: Review and mechanism

The type of starting material for AC preparation is a crucial factor in determining the properties and the effectiveness of an adsorbent (Tadda et al., 2016). The selection of raw materials for AC preparation depends on factors such as low ash content, high carbon content, low cost, high density and low degradation upon storage. Agrowastes are lignocellulosic materials composed mainly of cellulose, lignin, hemicellulose and many other functional groups capable of removing different wastewater pollutants (Abdel-aziz et al., 2020; Darryle et al., 2021; Omoboye et al., 2020). Also, the polymeric content of agrowastes is advantageous in the development of alcohol, aldehydes, ketones, ether, phenols and carboxylic functional groups. These prominent functional groups are significant in the adsorption of pharmaceuticals (Inyinbor et al., 2023; Bankole et al., 2022; Taoufik et al., 2020; Yanyan et al., 2018) Although, several agricultural wastes are still underutilized. The utilization of agrowastes in adsorption processes, however, holds great merits which include, reducing environmental pollution, building a cleaner environment and tackling a source of global warming. Various agricultural wastes have found use in adsorption processes because they are cost-effective, widely available and renewable (Bello et al., 2017b; Dai et al., 2018).

The potency of agricultural wastes in pollutants' uptake have been well established. Readily available agricultural wastes of many kinds exist including; rice husks (Goyne et al., 2005; Yi et al., 2016), palm bark (Balarak et al., 2017a, 2017b, 2017c), olive stones (Limousy et al., 2017), peach stones (Álvarez-Torrellas et al., 2016) and wood bark (Yi et al., 2016).

Activated carbon prepared from olive waste had been used in the adsorption of selected pharmaceuticals viz naproxen, diclofenac, ibuprofen and ketoprofen. Large surface area and mesoporosity characterized the prepared adsorbent. The behavior of the pharmaceuticals in varying solution pH explained their removal mechanism. The removal efficiency was reported to be highest at low pH. At pH lower than the pKa of the four pharmaceuticals, they exist in their neutral state. Hence, the possibility of hydrogen bonding or/and van der Waals' interactions between the activated carbon and pharmaceuticals (Baccar et al., 2012b).

Adsorbent pellets were produced from *Vallisneria natans* waste, and utilized in the adsorption of dimetridazole and metronidazole. The preparation conditions include a carbonization temperature of 600 °C, *V. natans* to $ZnCl_2$ mass ratio of 1: 2.4, and an adsorption time of 90 min. Characteristics of pellets produced showed uniformity in size in addition to excellent microporosity. The micropore volume, specific surface area, and total pore volume were 0.386 cm^3g^{-1}, 922.56 m^2g^{-1} and 0.421 cm^3g^{-1} respectively. The adsorption isotherms were explained using Dubinin-Radushkevic and Langmuir models, with an adsorption capacity of 82.58 mg g^{-1} and 64.23 mg g^{-1} respectively. The obtained data fitted well for the latter. The mechanism of adsorption between the adsorbents and the antibiotics was via micropore filling, π-π interaction and hydrogen bonding. The average percentage recovery was reported to be as high as 99.6 % (Sun et al., 2019).

Coconut shell wastes were employed as a cheaply sourced adsorbent. Surface modifications using HNO_3, chitosan, ozone and NaOH were investigated. The adsorbent was utilized in the uptake of acetaminophen (Ace) from wastewater via a fixed-bed experiment. The chemical modifications of the activated carbon greatly influenced its effectiveness in Ace adsorption. The ozone-treated adsorbent had about ten times better adsorption capacity than the untreated coconut waste. The chemical nature of the prepared granular activated carbon showed amphoteric characteristics hence may be effective for the adsorption of both cationic and anionic specie. Its acidic characteristics can be attributed to the existence of donor electron carrying functional groups such as the phenols and carboxyl groups. Therefore, the mechanism of Ace uptake was credited to complex donor–acceptor interactions between oxygen-containing groups and the aromatic rings of Ace (Yanyan et al., 2018).

The removal of sulphachloropyridazine and other sulfonamides, using adsorbents produced from the root of *Eichhornia crassipes* was tested. The adsorbent was analyzed using FTIR (Fourier Transformed Infrared Spectroscopy) and XPS (X-ray Photoelectron Spectroscopy) analysis. The surface of *Eichhornia crassipes* root powder was found rich in nitrogen, oxygen and carbon. Surface functional groups such as amino, carbonyl and carboxyl were thus confirmed. These functional groups played an important role in the adsorption process. The adsorption mechanism was said to proceed through the electron donor–acceptor interactions between adsorbent surface functional group(s) and sulfonamides (Liu et al., 2018).

Jia, et al prepared biochar from maize straws for the removal of oxytetracycline (OTC) from an aqueous solution. The pH effect and competing ions effects were central studies. OTC removal onto biochar was said to greatly depend on pH. Mechanisms of biochar-OTC removal was established using zeta potential measurements and FTIR. The biochar surface was reported to be very rich in phenolic and hydroxyl groups. Hence, the main mechanism of OTC removal was in a π-π interaction that occurred between functional groups in OTC and biochars graphene sheets (Jia et al., 2013).

Rice and coffee husk were prepared as natural adsorbents and utilized in the removal of norfloxacin from the aqueous media. Low surface areas and porosity were reported as part of the adsorbents' characteristics. Hydrogen bond was reported as the main mechanism of norfloxacin adsorption onto natural adsorbents prepared from rice and coffee husks (Paredes-Laverde et al., 2018).

Jing et al reported the use of raw and modified rice husk biochar in the removal of tetracycline (TC). The effect of surface modification on TC adsorption was investigated. The mechanism of TC removal was reported to be via an attraction between the basic surface of the modified biomass and the

Table 2 Some modified agricultural wastes used as adsorbent precursors for pharmaceuticals removal.

Class of pharmaceuticals	Pharmaceuticals adsorbed	Adsorbent material	Modifying agent	Adsorption experimental type	Adsorbent surface area (m^2/g)	q_e, mg/g	Kinetics/ Isotherm models	Desorption study		Mechanism of interaction	References
								Reagents	% desorbed		
Antibiotics	Amoxicillin	Olive stones	H_3PO_4	Batch	1174.00	67.7	PF,PS,ID/L, F,S,T,To,R-P	–	–	–	(Limousy et al., 2017)
		Palm bark biomass	–		124.36	35.9	L,F,T	–	98.10	–	(Balarak et al., 2017a, 2017b, 2017c)
		Pomegranate wood	NH_4Cl	Batch	1029	437	PF,PS,ID/L, F,D-B	–	–	Electrostatic interaction	(Moussavi et al., 2013)
	Metronidazole	Canola residues	H_2SO_4	Batch	–	21.4	L,F,T	–	–	–	(Balarak and Mostafapour 2016)
		Rice husks				4.8	L,F,T,D-R	–	–	–	(Azarpira and Balarak 2016)
	Ciprofloxacin	Date palm leaflets	H_2SO_4	Batch	24.4	133.3	L,F	HCl	83.00	Cation exchange, hydrogen bonding	(El-Shafey et al., 2012)
		Albizia lebbeck seed pods	KOH		1824.88	121.4	PF,PS,ID/L, F,T	–	–	Cation exchange	(Ahmed and Theydan 2014)
	Norfloxacin	Lotus stalk	H_3PO_4	Batch	1289.1	922.7	PF,PS/L,F,S	NaOH	60.81	Electrostatic, hydrophobic interaction	(Xie et al., 2011)
		Albizia lebbeck seed pods	KOH	Batch	1824.88	167.0	PF,PS,ID/L, F,T	–	–	Cation exchange	(Ahmed and Theydan 2014)
	Tetracycline	Rice husks	CH_3OH	Batch	65.97	95.6	PS	–	–	Hydrogen bond, π-π interaction	(Jing et al., 2014)
		Macadamia nut shells	NaOH		1524	455.3	PF,PS,E,A/L, F,T	–	–	Hydrogen bond, π-π interaction	(Martins et al., 2015)
		Rice husks	H_3PO_4	Batch	–	239.8	PF, PS, E/L, F,S,G,T	–	–	Hydrogen bond	(Álvarez-Torrellas et al., 2016)
				Fixed bed	–	99.4		NaOH	26.50		
		Peach stones			–	132.6			41.70	–	
		Beet pulp	Steam	batch	821	283.3	L,F	–	–	–	(Torres-Pérez et al., 2012)
		Peanut hulls			829	28.0		–	–	–	
	Levofloxacin	Rice husk	–	Batch	168	7.7	PF,PS,E/L,F	–	43.0	π-π interaction, pore filling	(Yi et al., 2016)
		Wood chip	–		312	5.0		–	42.0	π-π interaction, pore filling	
Analgesics	Diclofenac sodium	Isabel grape bagasse	–	Batch	2	0.13	PF,PS/L,F,S	H_2O	22.8	–	(Antunes et al., 2012)
		Cocoa shell	HCl	Batch	67	63.5	PF,PS/L,F,Li	–	–	π-π stacking, hydrogen bonds, van der waal forces	(Saucier et al., 2015)
	Ibuprofen	Peach stones	H_3PO_4	Batch	–	845.9	PF,PS,E/L,F, S,,T	–	–		(Álvarez-Torrellas et al., 2016)
		Peach stones		Fixed bed	–	55.0	–	NaOH	54.7	Hydrogen bond	
		Rice husks			–	22.7	–		70.4	–	
		Bamboo waste	$ZnCl_2$	Batch	–	278.6	L,F,D-R,T	CH_3OH	96.87	–	(Reza et al., 2014)

q_e, Adsorption capacity; K, Kinetic; I, Isotherm; A, Avrami; T, Temkin; D-B, Dubinin-Radushkevich; Li, Liu; R-P, Redlich-Peterson; S, Sips; FO, Fractionary order; To, Toth; C, Chemisorption; ID, Intra-particle diffusion.

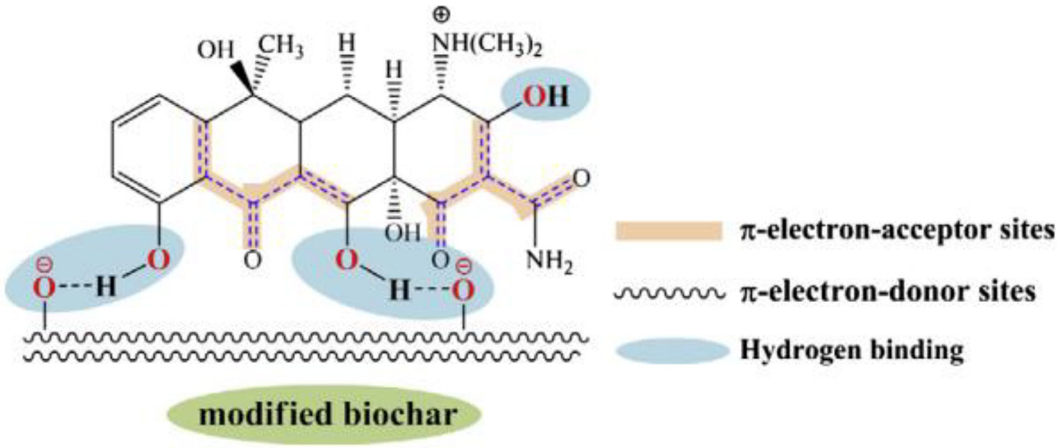

Fig. 6 Proposed mechanism for the uptake of tetracycline onto modified rice husk biochar (). Adapted from Jing et al., 2014

acidic ions in TC hence, forming hydrogen bonds (Jing et al., 2014). Fig. 6 presents a detailed proposed mechanism.

12. Would agrowastes salvage the environment from the threat of a potential Covid-19 drug?

Although researchers have greatly explored the use of agrowastes in pharmaceutical waste removal, yet many agrowastes have been neglected. In addition, some pharmaceuticals which are accessed without restrictions, hence, greatly used have not received much attention in adsorption using agricultural waste. For instance, antimalarial drugs such as chloroquine are greatly accessed in the sub-Sahara African nations and until now only very few studies exist on the adsorption of chloroquine (Dada et al., 2021). Due to the advent of the COVID-19 pandemic and efforts towards combating its menace, chloroquine and its hydroxyl counterpart may soon pose a great environmental threat globally if proper control measures are not established. The release of chloroquine and its hydroxyl counterpart currently being recommended for the treatment of COVID-19 is expected to continue to increase. This challenge may be severe for nations without a standard control strategy. Therefore, environmentalists must plan ahead to ensure a continuous sustainable and clean environment. Hydroxychloroquine is a weak base and its mode of absorption in the body follows accumulation within protonated vesicles (Schrezenmeier and Dörner 2020). Based on the foregoing, agricultural wastes with acidic surfaces may be an excellent adsorbent for the scavenging of hydroxychloroquine. The adsorption of anionic molecules onto acid-modified adsorbents has been previously reported (Chukwuemeka-Okorie et al., 2021; Hevira et al., 2020; Selambakkannu et al., 2019).

13. Challenges and future prospect

The environmental crisis arising from the release of wastewater containing pharmaceuticals from various sources is a major challenge. With the knowledge of the extent of toxicity of pharmaceuticals on the environment, it is of utmost importance that the release of pharmaceuticals' contaminated wastewater into the environment be curtailed. New drugs are been developed/produced as demand arises. Hence, it is necessary to enforce strategies to regulate the uncontrolled release of pharmaceutical wastewater. An advanced but simple technique for the detection of pharmaceuticals should be developed and necessary actions to ensure the elimination of pharmaceuticals must be established. It is also of great importance that effective, inexpensive and eco-friendly treatment technologies for pharmaceutical removal on an industrial scale be designed. The utilization of inexpensive agricultural wastes as an adsorbent precursor, for the effective removal of pharmaceuticals from wastewaters is already an endearing route. However, research on the commercialization of agrowaste-based adsorbents has not been explored. Wastewater treatment industries are faced with the challenge of massive contaminant-loaded effluents. The developing nations carelessly discharges contaminant-loaded effluents into the environment. Hence, the further application of agrowastes based adsorbent in industrial wastewater treatment processes would be a salient way out of the negative environmental impact of the aforementioned activity. A great percentage of the reported work on agrowaste-based adsorbents, focuses on batch adsorption and synthetic pharmaceutical wastewater. However, the column experiment studies present better applicability of the adsorption process in industries. A laboratory scale-up experiment is of great importance, to develop an industrial-scale adsorption experiment. In addition, while batch adsorption studies focus on operational parameters such as adsorbent dosage, initial concentration, pH, temperature and contact time, the fixed bed experiment focuses on feed flow rate, bed height, column diameter and the entire column configuration. Hence, researchers should extend efforts towards taking their studies close to industrial applications via column/fixed bed adsorption studies of real pharmaceutical effluents. The major outlook proposed for pharmaceutical remediation should include extensive awareness on the danger of releasing untreated wastewaters into the environment. and improving wastewater treatment by employing cheap, effective and sustainable approaches. Furthermore, research works looking towards establishing environmental impact assessment would be of great help to policymakers; therefore, more work in this area is encouraged.

14. Conclusion

The current review revealed the toxicity impact of pharmaceuticals to the aquatic environment and non-target organisms as well as the possible removal via adsorption. Different modification processes were illustrated. Adsorption has a great potential for wastewater decontamination which could be attributed to the presence of various surface functional groups. The negligible economic status of agrowastes makes it of advantage in wastewater treatment in the adsorption process. Agrowastes are known to possess characteristics suitable for various contaminant uptake. Various characterization techniques are employed to establish surface and internal features relevant and responsible for adsorbents potential efficiency. Surface treatment may greatly enhance the adsorption potentials of agrowastes. Adsorption operational parameters cum modeling suggests mechanisms of adsorbate uptake. Adsorption techniques utilizing agricultural wastes can serve as an environmental cleaning technology and also as an effective competitor to commercial activated carbon.

Removal of pharmaceuticals may follow different mechanisms; in most cases pharmaceuticals uptake on agrowaste enroute surface functional group leading to hydrogen bonding and/or donor–acceptor interactions. Although many reports exist for the adsorption of pharmaceuticals using agrowastes, however, very scanty report exist for some pharmaceuticals envisaged as a great upcoming threat. Hence, a call to researchers to establish a proper, feasible, effective and industrially applicable cleaning technique(s) for pharmaceuticals.

CRediT authorship contribution statement

Deborah Temitope Bankole: Writing – original draft, Writing – review & editing. **Abimbola Peter Oluyori:** Supervision, Writing – review & editing. **Adejumoke Abosede Inyinbor:** Conceptualization, Methodology, Data curation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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