Journal of Cleaner Production 388 (2023) 135819

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

Agro-waste based adsorbents as sustainable materials for effective adsorption of Bisphenol A from the environment: A review

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ARTICLE INFO

Handling Editor: Prof. Bing-Jie Ni

Keywords:
Bisphenol A
Endocrine disruptive
Adsorption and desorption
Agro-wastes
Kinetics
Isotherm and thermodynamics

ABSTRACT

Endocrine disruptive compounds (EDC) pose a great threat to the normal functioning of the human endocrine system leading to various illnesses and malfunctions. Several EDCs have been reportedly found in receiving water bodies including Bisphenol A (BPA). Bisphenol A (BPA) is a synthetic organic compound that is mainly used in the production of polymer materials polycarbonate and epoxy resin. BPA has been found all over the world due to widespread use and erroneous processing techniques, raising questions about its effects on the environment and human health. Removal strategies however are ineffective as residues of EDCs escape through various treatment plants and into drinking water. Adsorption using activated carbon from agro-waste however is an economical and sustainable substitute to the utilization of expensive commercial activated carbon for the sequestering of BPA. This review aims to provide a comprehensive overview of the use of agro-wastes for the uptake of BPA and operational parameters for its biosorption. Most adsorption of BPA took place at acidic pH mostly at pH 3 and the prominent mechanism was the π- π interactions. The isotherm, kinetics and thermodynamics modelling of BPA adsorption was extensively discussed. Langmuir and Freundlich isotherm models were best fit to equilibrium data, pseudo-second-order mostly described the kinetic studies with pore diffusion mechanism dominance. Most acid-functionalized sustainable agro-waste adsorbents had better percentage removal efficiency (%RE) for BPA uptake having %RE > 90% This study also covers the reusability of agro-waste for the uptake of BPA. This study will therefore enable upcoming researchers to explore means of applying and modifying agro-waste for the removal of BPA thereby remediating the environment. A research gap has been identified for researchers to explore more utilization of nanoparticles, composite nanomaterials, polymeric materials, and other mesoporous and microporous materials in the future to remove BPA. These future studies should be conducted on a laboratory, pilot, and industrial scale. The information on the disposal of spent agro-waste adsorbents once they have lost their BPA adsorption performance should be reported.

1. Introduction

As a result of expanding urbanization and industrial advancement, chemical manufacturing has risen day by day since the beginning of the industrial revolution (Gonzales-Garcia, 2017; Mpatani et al., 2021). Chemical products such as insecticides, detergents, disinfectants,

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https://doi.org/10.1016/j.jclepro.2022.135819
Received 25 August 2022; Received in revised form 7 December 2022; Accepted 29 December 2022
Available online 10 January 2023

plastics, pharmaceuticals, and personal care items have increased in production as a result of this expanding demand, all of which are hazardous to the environment if not adequately controlled (Gmurek et al., 2017). Several investigations have shown that considerable volumes of untreated micropollutants are generated and discharged into the aquatic environment (Mpatani et al., 2021). Urbanization, population growth, climatic change, and industrialization all have the potential to contaminate water systems, which could increase the possibility of future freshwater shortages (Park et al., 2014; Zbair et al., 2017).

The prevalence of Endocrine Disruptive Chemicals (EDCs) in surface and groundwater bodies has raised concerns and received considerable attention in recent times. As stipulated by the European Commission (1996), endocrine disruptors are also referred to as exogenous substances which obstruct the typical functioning of the endocrine system, leading to detrimental health effects" (Gmurek et al., 2017) (Onyekwere et al., 2019). Endocrine disruptors vary widely and include but are not limited to pharmaceuticals including paracetamol, aspirin, indomethacin (Fauzan et al., 2016), ibuprofen, (Olcer et al., 2017), precursors for the production of plastics such as bisphenol A (BPA) (Jiang et al., 2018), persistent organochlorine pesticides and herbicides (Combarnous, 2018), vinclozolin (Krishnan et al., 2018), heavy metals including nickel, mercury, cadmium, lead, uranium and arsenic (Sajjadi et al., 2020; Obayomi et al., 2022), various compounds found in products used for personal care including parabens (Gomes et al., 2017) and dyes (Zhao et al., 2018). Production demands for items including packaging, food and beverage, medical equipment, adhesives, electronics, vehicles flame retardants, building materials, and paper coatings rise as countries urbanize and develop (Ndagijimana et al., 2022). As a result of this, during the past 58 years, BPA consumption has increased significantly. In 1957, BPA production started commercially in the United States, and a year later, in Europe (Yeon Lee et al., 2021). The annual increase in global output has generally been between 0% and 5%, with China experiencing the most recent substantial growth. In fact, the BPA market alone in Asia increased at an average rate of 13% per year between 2000 and 2006 (Geens et al., 2012). Around 1 million tons (2.3 billion pounds) of BPA were reportedly generated in the United States in 2004, and in 2005 and 2006, little over 1 million tons were also produced in Western Europe (European Commission Joint Research Center, 2008; U. S. National Toxicology Program, 2008). BPA is therefore categorized in the United States as a chemical with a large production volume. (Selvakumar et al., 2019). However, in most countries in Africa, regulations guiding endocrine-disrupting compounds are not fully established. In Nigeria, several studies have been reported on the risk of exposure of humans to EDC through various sources and their results have shown the dire need for regulatory bodies that will enforce laws to aid the reduction of EDC exposure in our environment in urban and rural settlements (Onyekwere et al., 2019).

2,2-bis (4-hydroxyphenyl) propane most often referred to as Bisphenol A is an EDC of public concern (Nguyen et al., 2019). Its major application is as a common chemical applied industrially in the production process of polycarbonate plastics like baby bottles, toys, thermal receipts, medical devices, and electronic equipment (Antunes et al., 2013). Similarly, the production of epoxy resins which finds application in coating materials of food cans, dental sealants and various products as a result of their good physio-chemical properties (Ali et al., 2020), has grown progressively over the last 58 years (Liu et al., 2009). The worldwide use of BPA was recorded at approximately 5.5 million tons in the year 2011 (Okereke et al., 2016; Zhu et al., 2018). The sales and consumption of BPA increased by an average of 13% between 2000 and 2006 in Asia (Selvakumar et al., 2019). Between 2004 and 2006, in both the united states and Europe, about 1 million tons of BPA was produced (European Commission Joint Research Center, 2008; U.S. National Toxicology Program, 2008) (Corrales et al., 2015).

A major route through which BPA enters the environment is through effluents from manufacturing industries and sewage from residential areas (Mart et al., 2020). Fig. 2 shows various BPA transmission routes and measures to avoid BPA exposure. Human exposure to BPA can also be caused by the leaching of BPA into groundwater and surface water bodies from landfills and dumpsites of solid waste (Li et al., 2018). In Nigeria, various unsorted municipal waste products ranging from pharmaceuticals and personal care products (PPCPs), plastics, paints, alkylphenol polyethoxylate (APEs), batteries, various persistent organic pollutants (POPs) such as perfluoroalkyl substances (PFASs), bisphenol-A (BPA), phthalates polycyclic aromatic hydrocarbons (PAHs) and electrical/electronic gadgets find their home in dumpsites and landfills all around the country (Zhu et al., 2018).

BPA has been shown to have various negative effects on humans including disruptions in the endocrine system, cancer and thyroid hormones. Its estrogen-like and endocrine-disruptive effect makes BPA an EDC of concern (Zhu et al., 2018; Ndagijimana et al., 2019). Exposures of children and infants to BPA have been reported to have health effects on their brain and prostate (Kessler et al., 2019; Metz, 2016). Other negative effects include cancer, infertility, low sperm count, headaches, dizziness, etc. BPA removal had been a serious concern among researchers due to its continued use. Various methods have been explored for the removal of BPA such as ozone treatment, nano filtration, reverse osmosis. However, the adsorption process has proved to be a cost-effective technique for the adsorption of BPA from the environment (Xu et al., 2022). The majority of the agrowastes and their by-products are present in the environment without being properly utilized for any purposes. These waste products can be successfully used as a raw material to develop adsorbents. These materials have the ability to regulate surface area, number of pores, shape, functional groups, better adsorption capacity, thermal strength, and antibacterial activities (Ndagijimana et al., 2022). A significant amount of agrowaste is present in the environment but is not being properly utilized. These wastes can be used as a starting point to develop an effective adsorbent that, from an economic standpoint, can replace the current adsorbents. Agrowaste based adsorbents such as argan nutshell, corn cob, palm shell, peanut shell, and so on have been explored for the uptake of BPA from the environment.

A few years ago, the use of agro-wastes as low-cost, alternative adsorbents for the uptake of BPA drew a lot of attention because of their advantages such as eco-friendliness, ease of surface modification, renewable, biodegradability, abundance in nature, low-cost, ability to be reused and regenerated after adsorption (Han et al., 2021; Yeon Lee et al., 2021). Agricultural waste materials also contain a number of components and functional groups that are involved in the uptake of contaminants (Balci and Erkurt, 2016).

Although review articles exist that describe using various adsorbents such as agricultural waste materials, clays, nanomaterials, graphene, and activated carbons to remove BPA from aqueous solutions (Li et al., 2018), this review will concentrate on the most recent advances in the use of agro-waste for BPA adsorption ranging from 2013 to 2022. To the best of our knowledge, no review article covers the isotherms, kinetics and thermodynamics of the adsorption of BPA onto agro-waste-based adsorbents, additionally, the operational parameters governing BPA adsorption were reported.

In addition, this review covers the Eco-toxicological impacts of BPA as well as the most common technology for removing BPA from wastewater. Adsorption isotherms, kinetics, and thermodynamics investigations governing BPA adsorption onto agro-waste materials from aqueous matrices, as well as regeneration/desorption studies of spent BPA-loaded agro-waste-adsorbents, were also presented. This analysis also highlights the potentials and constraints of agro-waste adsorbents as ecologically friendly BPA uptake material.

2. Sources and mechanism of BPA released

A large range of commercial BPA-based items are available for purchase and are widely used in the industry. The physicochemical properties and chemical structure of BPA are presented in Table 1 and Fig. 1.

Table 1
Physicochemical properties of BPA (Deng et al., 2021).

Parameters	Properties
Molecular Formular	$C_{15}H_{16}O_2$
Density	1.20 gcm^{-3}
Water solubility	120–300 ppm
Molar mass	228.291 $gmol^{-1}$
Boiling Point	360 °C
Dissociation constant, pKa	10.29 1
Melting point	10.30 2–159 °C

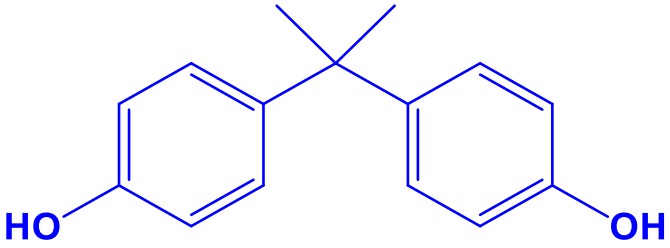

Fig. 1. Chemical structure of Bisphenol A.

Inhalation and ingestion through different media, such as air, dust, soil, and diet, maybe their exposure pathways. In summary, human exposure to BPA in the environment can come through a variety of ways, particularly the route of a water body. Table 2 below illustrates some of the sources of BPA release as well as their mechanisms of action within the last two decades.

3. Adsorption using agro-waste as A removal strategy for BPA

Adsorption has been reported to be efficient with a very simple setup hence, technically feasible, acceptable socially and finds its application in the sequestration of a wide variety of contaminants from wastewater (Tursi et al., 2018; Ndagijimana et al., 2020). Over the years, researchers have explored the development and use of activated carbon (AC), an adsorbent with low acid/base reactivity, large surface area, high porosity and pore structure, functional groups enhance the adherence of various pollutants dissolved in aqueous and even from gaseous media (Chang et al., 2012; Supong et al., 2019; Tapia-Orozco et al., 2016). The high cost of the commercially sold activated carbon precursor has placed a barrier to the level of large-scale application by industries (Gupta and Garg, 2019) Hence, the need for a cost-effective alternative has led to the growing interest to explore the suitability and feasibility of natural, low-cost and renewable materials (rice husk, plantain peel, bamboo, maize cob, tea leaves, sugarcane bagasse, chitin, chitosan, etc.) as alternatives in the removal of pollutants (Ali et al., 2020; Han et al., 2021).

Agro-wastes are by-products obtained from agricultural processes (Biswas et al., 2017). Structurally, they are comprised of three main components (hemicellulose, cellulose and lignin), hence making them lignocellulosic materials (Dada et al., 2020; Ojediran et al., 2020). The relative abundance of agro-wastes, and their availability make them a cost-effective alternative for adsorption (Mpatani et al., 2021b). The economic value of these wastes is relatively low as they are often burnt or discarded, leading to environmental problems (Tapia-Orozco et al., 2016). Many researchers, therefore, have explored the potency of these low-cost agro-wastes for the sequestration of a wide range of pollutants (Bhatnagar and Anastopoulos, 2016). The adsorption process can be described as a process where molecules (gas or liquid) adhere to the adsorbents' surfaces through the formation of chemical or physical bonds (Bello et al., 2017). Fig. 3 shows pictorial images of various agrowastes used for adsorption. Before agro wastes are applied as adsorbents, various techniques are applied for their modification to ensure their effectiveness for use as adsorbents such as acid modification (treatment with an acid such as hydrochloric acid (HCL), orthophosphoric acid (H_3PO_4) and sulphuric acid (H_2SO_4), Base activation (use of NaOH or KOH).

Golveia et al. (2021), looked at the possibility of using corncob as a low-cost adsorbent to sequester BPA from an aqueous media. Adsorption tests were conducted comprising BPA solution and ground vegetable fibre at concentrations ranging from 10 to 50 mg/L, alongside pH 3–9.

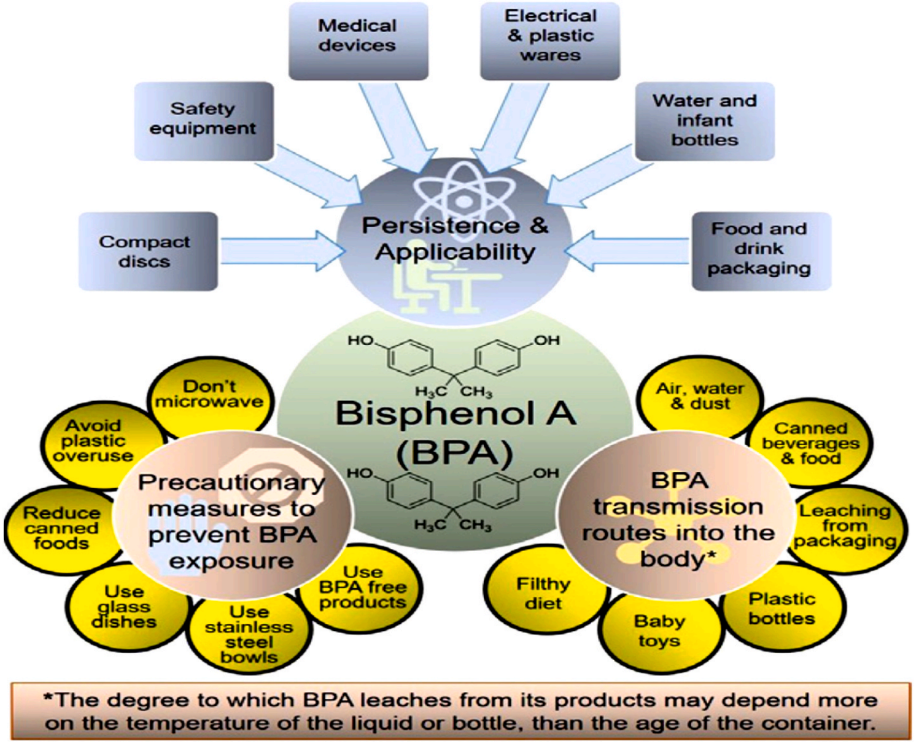

Fig. 2. Showing persistence, prevention and transmission routes of Bisphenol A. (Source (Bilal et al., 2019).

Table 2
BPA release in the last two decades, source of release and mechanism of action when released.

Source of BPA release	Mechanism of Action	Reference
BPA release via thermal degradation of BPA containing plastics.	The synthesis of free BPA and subsequent breakdown products 4-hydroxybenzoic acid and bis(4-hydroxyphenyl) methane can occur during the thermal degradation of BPA-containing polymers. BPA is released during the heating process as a result of hydrolysis/alcoholysis and chain scission of weak carbonate link bonds.	Morin et al. (2015)
BPA release from e-waste recycling and dumping sites	E-waste recycling centers, especially in underdeveloped countries, are major sources of BPA. The volume of e-waste has expanded dramatically over the last two decades due to the rapid growth of the e-industry. E-waste recycling processes can be crude, involving manual disassembly and removal of electronic components by heating in an incinerator, which releases hazardous pollutants and particles.	Huang et al. (2014)
BPA release from Micro-plastics in aquatic regions (MPs)	BPA is a common precursor in the production of polymers and resins. Micro-plastic particles made of low-density polyethylene and polycarbonate have been found to be a persistent source of bisphenol A in aquatic settings. Micro-plastics may include hazardous organic chemicals or additives that are introduced into aquatic life, enhancing their toxic effects.	Liu et al. (2019)
BPA release due to waste treatment practices	BPA is found in the hydrolytic leachates produced by plastic waste at wastewater treatment plants. Wastewater treatment plants frequently fail to entirely remove EDCs from waste water (removal efficiency ranges from 37 to 94 percent), resulting in increased release into the environment and potentially into the air. During weathering and break-down, large levels of BPA are released from plastic containing fractions. Computer printed circuit boards can also be combusted in electronic waste paint. Microbial metabolism of TBBPA under anaerobic conditions in soil and sediment can sequentially degrade TBBPA to tribromobisphenol A → dibromobisphenol A → monobromobisphenol A → BPA.	Foo and Hameed (2009); Rajasulochana and Preethy (2016)
BPA release from paper Currencies	Thermal paper has been found to have unusually high levels of BPA, up to 322 g/kg. Because BPA is sprayed on thermal sheets as a powdery layer, studies have shown that it can be absorbed into human skin when handling receipts. When a receipt is placed near currency in a cash register or wallet, or when someone handles a receipt before handling money, BPA can be transmitted from receipts to paper currencies.	Geens et al. (2012); Liao and Kannan (2011)
BPA release from canned and fresh foods	The most common way for the general public to be exposed to BPA is through food. The presence of BPA in foodstuffs is linked to BPA exposure in animals and raw plant material, as well as BPA accumulation in the environment and food contact with BPA-containing polymers. BPA is thought to be absorbed daily with food, and human exposure to BPA through the alimentary canal has been estimated to range from 0.48 to 1.6 g/kg/body weight/day. Numerous studies have shown that BPA can be introduced into food and drinking water from polycarbonates and epoxy resins.	Almeida et al. (2018); Cao et al. (2021)
BPA release from orthodontic adhesives.	BPA is employed as a raw material in the dental industry to make Bis-GMA-based orthodontic adhesives, and its estrogenic activity is limited to molecules with a double benzoic ring. Bisphenol A, a breakdown product from Bis-GMA, is frequently utilized in the fabrication of composite resin fillings and is one of the potentially dangerous bio-chemicals generated by polymers used in the oral environment. Bisphenol A is also a key component of Bis-GMA resin, accounting for up to 70% of the weight of materials used in dental fillings and enamel. BPA is a potentially physiologically damaging chemical molecule that is released in minute amounts from dental composite materials. Its action is not confined to direct induction of cytotoxicity at the cellular level. The oral environment, which is characterized by a wide range of temperature and pH fluctuations, the presence of digestive enzymes, and the regular intake of a variety of chemical substances, can facilitate the breakdown of poly-BPA molecules to bisphenol A.	Deviot et al. (2018)
BPA release due to migration from Poly carbonates.	BPA can leach from polycarbonate into liquid foods because of two different processes: diffusion of residual BPA present in polycarbonate after the manufacturing process, and hydrolysis of the polymer catalyzed by hydroxide in contact with aqueous food and simulant. The most economically important polycarbonate, also termed BPA polycarbonate is conventionally produced from the poly condensation. of BPA with phosgene. However, the raw material phosgene is known to be one of the most extremely toxic chemicals. BPA can migrate from	Hoekstra and Simoneau (2013)

(continued on next page)

Table 2 (*continued*)

Source of BPA release	Mechanism of Action	Reference
	polycarbonates (PC) during polymer diffusion and hydrolysis; however, diffusion has a far smaller impact on BPA release from PC. BPA release is affected by factors such as pH levels and the presence of cations. BPA migrated faster from polycarbonate bottles (used as water containers) that had been in use for a few years (3–7) and had been subjected to higher temperatures. Furthermore, it was shown that the ratio of BPA migration from PC bottles to other solutions changed depending on the chemical features of the solutions.	
BPA Release From Epoxy Resins	Epoxy resins are epoxide-group-containing pre-polymers. The interaction of these resins with a variety of curing agents (such as anhydrides, aliphatic amines, or polyamides) produces cross-linked or thermosetting polymers in the industrial setting. The majority of commercial epoxy resins currently on the market are made from bisphenol-A diglycidyl ether (DGEBA) (15), also known as bisphenol-A diglycidylether (BADGE) (16), which is the lowest molecular weight oligomer in commercial epoxy resins and the main component in commercial liquid epoxy resins. Water-borne epoxy coatings with high solids and powder, protective coatings for food and beverage cans, adhesives, vehicle body primers, and other goods incorporating epoxy resins are among the most common. Fiber-reinforced composites, electrical laminates, castings, toolings, and adhesives are all examples of speciality goods that can be used to cover epoxy resins in structural applications.	Tsai et al. (2011)
BPA release due to corrosion protection products.	Water-borne epoxy coatings with high solids and powder, protective coatings for food and beverage cans, adhesives, vehicle body primers, and other goods incorporating epoxy resins are among the most common. Fiber-reinforced composites, electrical laminates, castings, toolings, and adhesives are all examples of speciality goods that can be used to cover epoxy resins in structural applications.	Vermeirssen et al. (2017)

Kinetic and isotherm models were tested. The findings revealed that corncob is an excellent adsorbent for BPA uptake with about 90% removal efficiency. The maximum adsorption capacity was 51.25 mg per gram of adsorbent fibre after 20 min of contact, and the pseudo-second-order kinetics and Langmuir isotherms best described the kinetic and isotherm models. Due to the presence of a significant amount of lignin, the thermogravimetric study allowed us to conclude that corn cob is a heat-resistant material.

(Choong et al., 2018) investigated the sorption ability of activated carbon covered with magnesium silicate from palm shell waste powder. The structure of the prepared adsorbent was a thin plate and mesh-like structure with 772.1 $m^2\ g^{-1}$ as the surface area. Macro- and mesopores had a surface area of 772.1 $m^2\ g^{-1}$. For binary and single modes, the Langmuir isotherm model was best fitted with an adsorption capacity of 254.7 mgg^{-1} and 168.4 mgg^{-1} respectively. The adsorbent showed good reusability after 5 cycles with heat treatment and Mg (II) solution. In a similar study, the potential of agricultural waste materials (coconut shell, coir pith and durian peel) to sequester bisphenol A (BPA) from aqueous media was reported by (Lazim et al., 2015). The treated adsorbent showed an excellent capacity to sequester BPA. Coir pith, with an adsorption capacity of 4.308 mgg^{-1}, removed 72% of BPA in 24 h, followed by durian peel with 70% removal efficiency and 4.178 mgg^{-1} adsorption capacity. Coconut shells exhibited the least removal efficiency of 69% and 4.159 mgg^{-1} adsorption capacity. The results showed that these modified agro-wastes can be used as alternative adsorbents for removing BPA from an aqueous solution.

In a similar study, the ability of argan nut shell to remove BPA was investigated by (Zbair et al., 2018). Chemical activation of the argan nut shell was carried out using sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) to yield AC-NA and AC-HP respectively. AC-HP was more effective for the uptake of BPA as a result of its higher specific surface area (1372 m^2g^{-1}) in comparison to AC-Na (798 m^2g^{-1}). The Langmuir isotherm and pseudo-second-order model (Qmax at 293 K was 1250 mg/g). corresponded well with the BPA adsorption results on AC-HP. The thermodynamic studies suggest that BPA uptake onto AC-HP was exothermic and spontaneous. After 5 cycles, the AC-HP regeneration exhibited good performance (95–93%). Similar results were reported by (Arampatzidou and Deliyanni, 2016) who investigated the adsorption of BPA using activated carbon made from potato peels in an aqueous solution. The effect of the activation agent on potato peel was tested by activating with $ZnCl_2$, H_3PO_4 and KOH. The optimum conditions for BPA uptake were pH 3 at 25 °C. The adsorption data best fit the Langmuir and Freundlich isotherms with a maximum adsorption capacity of 454.62 mgg^{-1} and the pseudo-second-order kinetics was followed. The phosphoric acid-activated carbon proved to be the best adsorbent.

4. Eco toxicological impacts of BPA

The effects of chemical exposure on an organism's state, dynamics, or at other levels of biological organization are referred to as eco toxicological effects (Santos et al., 2021). The subcellular level, the cellular level, tissues, people, populations, communities, and ecosystems, as well as landscapes, may all fall under this category (Fuzil et al., 2021). BPA has excellent chemical stability, persistence, bioaccumulative qualities, and poses a great risk for ecosystems and human health. The blood estrogen/androgen ratio, egg production, hatching rate, embryo incubation time, deformity rate, and even the ratio of males to females have all been demonstrated to vary when exposed to BPAs, which disrupts the reproductive system (Choong et al., 2018). At the same time, it causes unfavorable effects such cell malfunction, gene damage, and chromosomal abnormalities, as well as endocrine system dysfunction in terms of thyroid hormone concentration, blood parameters, and enzyme activity (Liu et al., 2021).

In different vertebrates, bisphenol A functions as an endocrine disruptor and teratogen(Gultekin and Ince, 2007). The majority of teratogenic consequences in animals happen at environmentally improbable BPA doses. BPA exposure during gonadal organogenesis can alter sex determination, exposure both during and after gonadal organogenesis can alter gonadal function, and exposure of fully organized individuals can induce the production of hepatic vitellogenin(Huang et al., 2021). These are just a few of the endocrine disrupting effects of BPA that have been found in wildlife species. The majority of research on BPA's effects has been done on rats and mice, but in recent years, investigations on BPA exposure in some invertebrates, fish, amphibians, reptiles, birds, and wild mammals have dramatically increased. At environmentally

Fig. 3. Images of agro-wastes applied for adsorption of BPA.

relevant concentrations (0.1–1000 g/L), BPA, also known as a typical endocrine-disrupting chemical (EDC), has estrogen-mimicking, hormone-like qualities that change the way the endocrine system works and have negative consequences on intact organisms (Yeon Lee et al., 2021). Low levels of BPA impair gonadal function in a number of species, but high quantities induce incorrect sex determination in some fish, amphibians, reptiles, and birds (Santos et al., 2021).

BPA has been shown to alter the timing of reproduction in wild fish in addition to lowering sperm count and thereby lowering fertilization success. In earlier research, bisphenol A showed signs of genotoxicity, reproductive toxicity, endocrine disruption, cytotoxicity, and neurotoxicity. In experimental research, BPAs have been linked to thyroid hormone disruption that could enhance the growth of organisms (Geens et al., 2012). It has been discovered that 0.5 g/L BPS and BPF at environmentally relevant levels could control the expression of genes associated to immunity during the early stages of zebrafish development (Huang et al., 2021).

5. Unique features of agrowaste-based adsorbents enhancing their suitability for the uptake of BPA

Cellulose, Lignin and hemicellulose are the major constituents of the agro-wastes (Dada et al., 2016; Tursi et al., 2018). However, many inorganic and organic elements are present in them such as potassium

(K), chlorine (Cl), nitrogen (N), phosphorus (P), magnesium (Mg), sodium (Na), calcium (Ca), oxygen (O), hydrogen (H) and carbon (C) (Balarak et al., 2019)(Chang et al., 2012). Various functional groups have been identified in these agro-wastes such as ketones, ethers, aldehydes, phenolic groups, carboxylic acid, and alcohols (Corrales et al., 2015; Foo and Hameed, 2009). These inorganic and organic constituents play significant roles in the adsorption process and as such, agro-wastes have been widely considered as adsorbents because of their efficacy in the uptake of a wide range of contaminants (Bello et al., 2017). Agro-wastes can be characterized using various analytical techniques, to identify the functional groups, morphology, elemental compositions, chemistry and surface nature. These techniques used range from pH point of zero charge (pHpzc), X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Brunner Emmett Teller (BET), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), amongst others (Dada et al., 2021, 2022). Furthermore, characterization studies in conjunction with adsorption isotherms, kinetics, mechanisms and thermodynamics can aid in understanding the nature, rate, interaction and mechanism that governs adsorbate-adsorbent interactions (Sartape et al., 2017; Tursi et al., 2018). Physicochemical characterization on these agro-wastes reveals the existence of numerous surface characteristics (such as pore size, pore volume, adsorption sites and particle sizes), shape, moisture content, ash content, bulk density and functional groups (González-García, 2018; Ojediran et al., 2020; Zbair et al., 2017). These characteristics are primarily responsible for the sequestration of BPA in aqueous solutions (Golveia et al., 2021). Changes in the adsorbent's surface characteristics, shape, and functional groups after BPA uptake indicate that they play a vital role in the adsorption process (Ao et al., 2018).

The Scanning Electron Microscopy (SEM analysis gives a pictorial view and surface morphology of the adsorbents (Dada et al., 2021). The SEM contain detectors that produce a three-dimensional image of the surface of the adsorbent's surface (Bello et al., 2017). SEM works on the principle based on the bombarding of electron beams on the analyzed samples which in turn re-emits certain particles. Fig. 4(a–d) shows various SEM images of agro-wastes before and after the sorption of BPA. The SEM results reported by (Pamidimukkala and Soni, 2018), revealed that the adsorbents surface structure was irregular, rough and porous with prominent mesopores and micropores before adsorption while after adsorption, the pores were filled which showed successful adsorption of BPA (Bello et al., 2017; Dada et al., 2020; Jiang et al., 2018).

The FTIR analysis is usually carried out on all adsorbents to identify all possible functional groups present in them (Sartape et al., 2017). Major peaks at 3300-3500^{-1} could be a result of the stretching vibrations of the O–H group, while bands C═C double bonds are identified by major peaks at 1567 cm^{-1} (Dada et al., 2021; Ojediran et al., 2020). Furthermore, C–O functional groups in heterocyclic rings alongside O–H of carboxylic, phenolic or alcoholic groups can be identified by bands at 1123 cm^{-1}. Identified peaks at 2000 and 1500 cm^{-1} show the lactone group or carboxylic acid. CC stretching vibrations in alkyne groups are responsible for bands at 2325 cm^{-1} (Orimolade et al., 2018). FTIR results of various agro-wastes are shown in Fig. 5(a–c).

6. Operational parameters for the adsorption of BPA

Various operational parameters are investigated during the adsorption of BPA to ascertain the optimum conditions required for the highest percentage removal. The most common operational parameters investigated are the effects of pH, contact time, temperature and adsorbent dosage (Bello et al., 2017; Dada et al., 2021). Table 3 shows various reported operational parameters for BPA adsorption.

6.1. Contact time

The effect of contact time is an important operational parameter carried out in order to determine the exact time at which equilibrium is reached during the sorption process, thus governing the performance of the process by influencing its economic efficiency (Sartape et al., 2017). To determine the effects of contact time, the change in residual BPA at various time intervals is observed and recorded via a UV–Vis spectrophotometer until equilibrium is reached (Dada et al., 2021; Sartape et al., 2017). A shorter contact time to reach equilibrium implies a faster rate at which BPA molecules leave the bulk and gets to the inner and outer surface of the adsorbents (Sudhakar and Soni, 2018). Increased contact time increases adsorption efficiency and this could be attributed to the presence of many unoccupied active sites on the adsorbent surface (Bautista-toledo et al., 2014; Deng et al., 2021). However, an increase in contact time, decreases the availability of pores on the adsorbent surface thereby, lowering the adsorption effectiveness (Li et al., 2018). To study the effect of contact time, a plot of percentage removal (%) versus time (t) is plotted. Various researchers have reported on the effect contact time has on the ability of agro-wastes to adsorb BPA (Zbair et al., 2018). on adsorption of BPA using argan nutshell, equilibrium was reached at 60 min with a removal efficiency of 93%. Similarly, 75 min was observed by (Balarak et al., 2019) in BPA sorption onto dried rice husk. A shorter contact time of 45 min was reported by (Orimolade et al.,

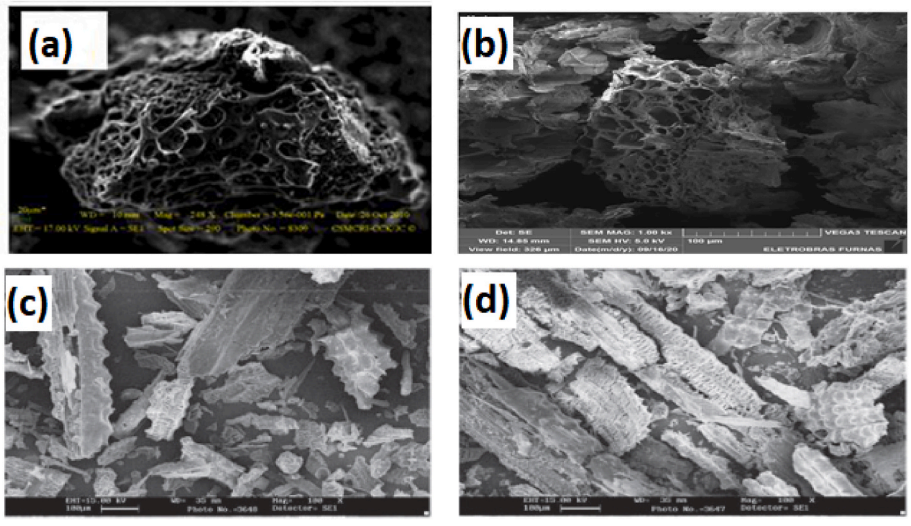

Fig. 4. (a–d): (a) Palm Shell Activated Carbon (Source: (Sudhakar and Soni, 2018); (b) c: SEM images of Corn Cob Activated carbon (Source(Golveia et al., 2021):; c–d: SEM images of rice Husk before and after loading with BPA (Source (Sudhakar et al., 2015).

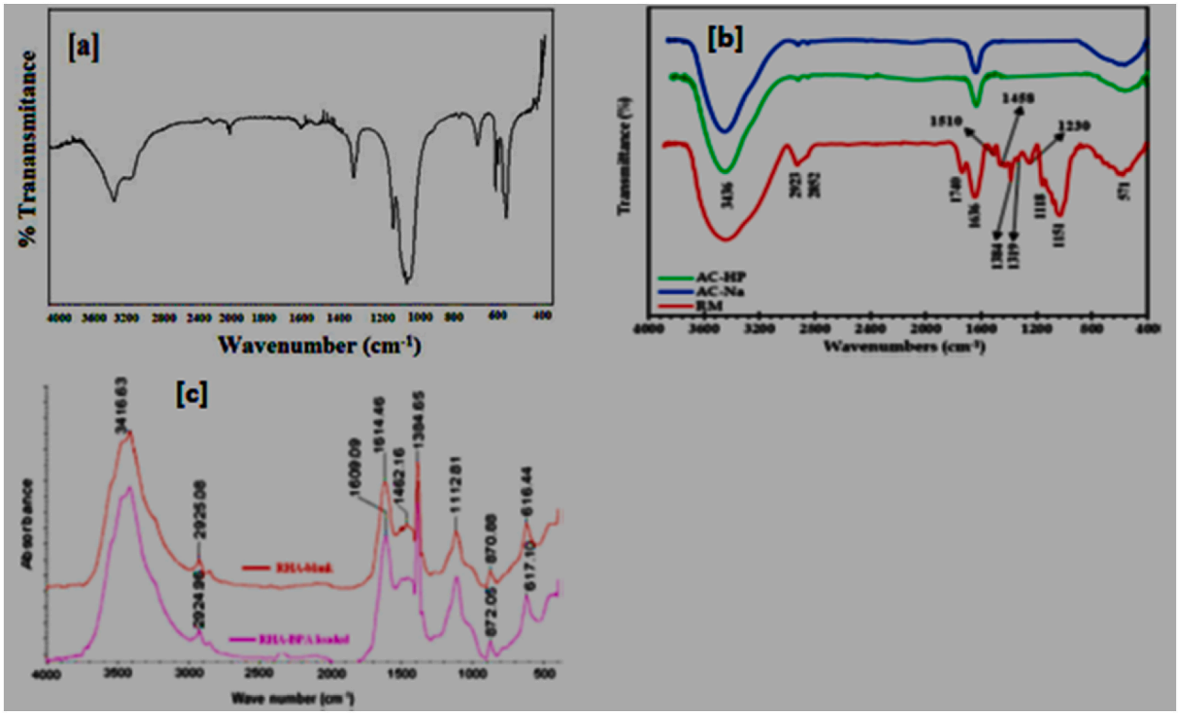

Fig. 5. (a–c) 5a: FTIR images of Palm Shell Activated Carbon (Source: (Sudhakar and Soni, 2018); (b) FTIR images of Argan Nut Activated carbon (Source: (Zbair et al., 2018); (c) FTIR of RH before and after loading with BPA Source (Sudhakar et al., 2015).

2018) for adsorption onto rice husk nanosilica while (Sudhakar et al., 2015) Sudhakar et al. (2015) reported 180 min for BPA adsorption onto rice husk ash. Table 3 shows the contact time for BPA onto various adsorbents.

6.2. Effect of temperature

The effect of temperature is an operational parameter usually investigated due to its importance in BPA adsorption system because the enlargement nature of adsorbents, solid/liquid interface and movement of ions is directly affected by the temperature of the solution (Bello et al., 2017). This adsorption parameter is important as an increase in temperature generally increases sites for adsorption and decreases the boundary layer thickness surrounding the adsorbent (Sartape et al., 2017). To monitor the effect of the temperature on BPA uptake, a plot of initial concentration (mg/L) versus percentage removal (%) can be plotted. The observed temperature for maximum BPA adsorption by various agro-wastes is shown in Table 3. (Zbair et al., 2018), on the sorption of BPA onto argan nut shell, investigated the effect of temperature from 293, 303 and 313 K. Results showed that 293 K was the temperature for optimum BPA uptake with maximum monolayer coverage of 1250 mg/g. The uptake of BPA onto rice husk was reported by (Balarak et al., 2019) where the effect of temperature was studied between 273 and 333 K with 333 K observed as the temperature optimum adsorption (Arampatzidou and Deliyanni, 2016). studied the influence varying temperatures between 25, 45 and 65 °C has on BPA uptake onto activated carbon derived from potato peel. The uptake was observed to be exothermic as maximum BPA adsorption capacity was derived at 298 K and BPA uptake decreased as temperature increased (Asada et al., 2004). The observed adsorption decreased by the increase in temperature as a result of desorption. The thermal energy increase led to a change in the adsorption-desorption equilibrium. The temperature increase may reduce the adsorptive forces between active sites on the adsorbent surface and bisphenol A species, therefore lowering adsorption effectiveness (Bello et al., 2017).

6.3. The effect of pH

The pH of the solution plays a key role in BPA uptake by adsorbents because the solution pH has a direct effect on the magnitude of electrostatic charges on the surface of the adsorbent and adsorbate (Dada et al., 2021). The degree to which ionization occurs and the nature of the charge balance at the surface of the adsorbent are directly affected by the pH of the adsorption environment (Golveia et al., 2021; Lazim et al., 2015). Therefore, the pH of the adsorption system is a major factor that affects the sorption process (Dada et al., 2017). The charges at the surface of the activated carbon also depend on the solution pH value (Sartape et al., 2017; Yeon Lee et al., 2021). The charges on the surface of the adsorbent are said to be positive if the values of pH < pH_{pzc}, hence favouring the adsorption of anionic pollutants (Tapia-Orozco et al., 2016). While the uptake of cationic pollutants will be favoured if the pH > pH_{pzc}, implying that the charge at the surface of the adsorbent is negative (Bello et al., 2017). The effects of varying the initial pH on the adsorptive capacity of various adsorbents can be monitored at pH values from 3 to 11. 0.1 M NaOH and HCl are usually used to adjust the solution pH (Wang et al., 2020). A graph of pH versus efficiency removal can be plotted to study the pH effect on BPA uptake. Table 3 outlines optimum pH for BPA adsorption onto various agrowastes (Sudhakar and Soni, 2018). in observing the pH effects, values ranging from 2 to 12 were examined. The results revealed that changes in pH had little effect on adsorbents removal efficiency. Several researchers have reported optimum BPA at various ranges of pH values such as pH values 3 for BPA sorption onto dried rice husk (Balarak et al., 2019), Banana Bunch and coconut bunch (Lazim et al., 2021). pH of 8 was obtained for use of rice husk nano silica (Orimolade et al., 2018), a pH range of 2–6.5 was obtained for argan nut shell (Zbair et al., 2018) while a pH range of 1–6 was obtained for palm shell (Sudhakar and Soni, 2018).

6.4. The effect of adsorbent dose

The adsorbent dose also plays an important role in the sorption process (Huang et al., 2014) (Dada et al., 2020). Physical

Table 3
Showing operational parameters for adsorption of BPA using various agrowastes.

Adorbents	pH	Contact Time	Adsorbent Dosage	Temperature	Reusabiity Cycles	Eluting Solvents	Mechanism of adsorption	References
Coconut shell-based hydrophobic MAC modified with nanoscale zero-valent iron (NZVI@MAC)	3–10	160 $rmin^{-1}$	0.2gL^{-1}	298.15 K	8 cycles	Aqueous solution, organic solvents	strong hydrophobic interaction, π-π interaction and the weak hydrogen bonding	Xu et al. (2022)
Extract solution (ES) originating from fermented tubers and cereal wastes to enhance cross linked activated carbon and reduced graphene oxide composites	2–12	24 hrs	0.02 g	25 °C	–	90% ethyl ether and 10% methanol	Hydrophobic and electrostatic interactions are dominant between BPA, IBP molecules, and adsorbents.	Ndagijimana et al. (2022)
Corn Cob	3–7	20 min	0.2 g	–	–	–	π- π interactions, H-bonding, non-electrostatic interactions	Golveia et al. (2021)
Palm Shell	3	40 min	–	303K	3 cycles	methanol	Van der waals forces, H-bonding, π- π interactions	Sudhakar & Soni (2018)
Magnessium Silicate impregnated palm shell activated carbon	–	90 min	–	–	5 cycles	Mg(II) and thermal treatment	π- π interactions	Choong et al. (2018)
Potato peel	3	–	0.01 g	25 °C	100% BPA desorption	Diethyl ether-methanol	π- π interactions	Arampatzidou & Deliyanni (2016)
Coffee Grounds	2–4	–	–	–	–		–	Alves et al. (2019)
Dried rice husk	3	75 min	4 g/L	–	–		–	Balarak et al. (2019)
Banana bunch	3	–	100 mg	25 °C	–		–	Lazim et al. (2015)
Coconut bunch	3	–	100 mg	25 °C	–		–	Lazim et al. (2015)
Coir Pith	3	24 h	0.02 g	–	–		–	Lazim et al. (2015)
Coconut Shell	3	24 h	0.02 g	–	–		–	Lazim et al. (2015)
Durian Peel	3	24 h	0.02 g	–	–		–	Lazim et al. (2015)
Rice husk ash		3 h	30 mg/L	–	–		–	Sudhakar et al. (2015)
Rice husk nanosilica	8	45 min	50 mg/L	–	–		–	Orimolade et al. (2018)
Magnetic biochar from Banana peel	–	20 min	–	–	–		Radical reaction mechanism based on OH^{+}, $SO4^{-}$, and $O2^{\cdot-}$	Rong et al. (2019)
Pine bark	–	48 h	10 g/L	298 K	–		–	Antunes et al. (2013)
Almond shell	–	48 h	10 g/L	298 K	–		–	Antunes et al. (2013)
Argan nutshell	2–8	3 h	0.01 g	293 K	5 cycles (95% removal)		π- π interactions	Zbair et al. (2018)
Peanut shell biochar	–	–	10 mg	–	–		π- π EDA interactions, H-bonding.	Wang et al. (2019)
Activated Rice Straw	2.35	90 min	100 mg/L	30 °C	–		–	Chang et al. (2012)
Orange Albedo	2	60 min	40 mg	–	–		π- π interactions, H-bonding.	Kamgaing et al. (2017)
Chitosan immobilized nanoscale zerovalent iron nanoparticles	3	1 h	1.5 g/L		3 cycles	Methanol solution	–	Dehghani et al. (2020)
Modified Peat	7	–	0.5 g	25 °C	–		–	Zhou et al. (2012)
Eucalyptus Bark/Magnetite component	7		0.2	50 °C	–		–	Balci & Erkurt (2016)
Oil palm empty fruit bunch	2–9	48 h	1.5 g/L	–	–		π- π interactions	Wirasnita et al. (2014)
Mesoporous silica nanoparticles from sugarcane ash (MSN-CTAB)	10–11	60 min	1.0 g/L	25 °C	–		hydrophobic and electrostatic interaction	Suzimara et al. (2020)
Ficus benghalansis bark (FBB) activated carbon	6–8	24 h	1000 mg/ 50 ml BPA	–	82.05% desorption	1 N HCl,	π- π dispersion interactions	Kamaraj and Umamaheswari (2017)
Magonia pubescens fruit bark activated carbon (AC-H_2)	4–8	240 min	1.0 g/L	–	–		–	Antero et al. (2019)

characterization of various agro-wastes has revealed the presence of mesopores and macro-pores which serve as sites for adsorption (Biswas et al., 2017; Lazim et al., 2015). The active sites for adsorption on an adsorbent are said to be more if the adsorbent concentration increases. Hence, the extent of adsorption is directly proportional to the increase in the adsorbent dose (Antunes et al., 2013; Li et al., 2018). At other times, however, the adsorption efficiency may experience a decrease when the adsorbent dose is increased. This is because, the actives sites on the surface of the adsorbent may reduce because of interferences caused by the interactions between adsorbent and adsorbate (Tapia-Orozco et al., 2016). To study the effect of the adsorbent dosage, a graph of adsorbent dosage ($g{\cdot}L^{-1}$) versus removal efficiency (%) can be plotted. Table 3 shows various adsorbent doses applied for BPA uptake. In a study conducted on the removal of BPA using almond shell and pine bark reported by (Antunes et al., 2013), an adsorbent dosage of 10 g L^{-1} led to a high removal efficiency of >80%. In a similar study by (Sudhakar and Soni, 2018), an adsorbent dose of 30 g L^{-1} achieved the highest BPA uptake (Arampatzidou and Deliyanni, 2016). on the sorption capacity of potato

peel reported an adsorbent dosage of 0.5 gL^{-1} for maximum BPA adsorption. Adsorbent doses of 10 gL^{-1} for almond shell and pine bark (Antunes et al., 2013), 30 gL^{-1} for rice husk ash (Sudhakar et al., 2015), 100 mg for banana and coconut bunch (Lazim et al., 2021), 0.5 gL^{-1} for potato peel (Arampatzidou and Deliyanni, 2016). (Balarak et al., 2019) on the adsorption of BPA onto rice husk reported that an increase in adsorbent dosage from 0.5 to 4 g L^{-1} led to an increase in removal efficiency from 43 to 99.1% but however, led to a decrease in adsorption density decreased from 19.9 to 3.1 mgg^{-1}. Table 3 outlines show the various adsorbent dosage applied for BPA uptake.

7. Isotherm modeling of bio-sorption of BPA

The mechanisms controlling the sequestration of BPA onto agro-wastes can be further understood by studying the Kinetics, isotherms and mechanisms of the adsorption process (Dada et al., 2014; Mpatani et al., 2021). An adsorption isotherm is a curve used to study the adsorption process by evaluating the nature of interactions between the adsorbent and adsorbate (Kamgaing et al., 2017). The isotherm plots describe the processes involved and predict the adsorption capacity of an adsorbent. The Isotherm and kinetics graph thus explains the variations observed in the adsorbent-adsorbate interactions at a constant

Table 4
Isotherm, Kinetics and thermodynamic parameters.

Models	Mathematical Expression	Plot axis	Slope	Intercept	Evaluated Parameters	Description	Reference
Isotherms							
Langmuir	$\frac{Ce}{qe} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L}$ $R_L = \frac{1}{1+K_L C_o}$	C_e/q_e Vs C_e	$\frac{1}{Q_m}$	$\frac{1}{Q_m K_L}$	Q_m and K_L	q_e = amount of adsorbate adsorbed per unit mass of adsorbent(mg/g) C_e = equilibrium concentration of adsorbate (mg/L), C_0 = initial concentration of adsorbate (mg/L), K_L =Langmuir adsorption constant (L/mg), Q_m = monolayer sorption capacity of the adsorbent (mg/g)	Bello et al. (2017); Sartape et al. (2017)
Freundlich	$log\ Qe = log\ K_F + \frac{1}{n} log\ Ce$	log qe Vs log Ce	$\frac{1}{n}$	$log\ K_F$	$\frac{1}{n}$ and K_F	q_e = amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) C_e = equilibrium concentration of the adsorbate (mg/L) K_f and n = Freundlich constant affiliated to the adsorption capacity and adsorption intensity respectively. $1/n$ = intensity of adsorption 1/n = 0 irreversible; 1/n > 1 unfavorable 0 < 1/n < 1 favorable	[49], Inyinbor et al. (2016)
Temkin	$Qe = BlnA_T + Bln\ Ce$	Qe Vs ln Ce	B	$BlnA_T$	A_T and B	A_T = equilibrium binding constant (L/mg) q_e = amount of adsorbate adsorbed at equilibrium (mg/g), $B = RT/b$ = Constant related to the heat capacity (L/mg) T = absolute temperature (K), R = Universal gas constant (8.314 J/mol/K), C_e = equilibrium concentration of adsorbate (mg/L)	Balarak et al. (2019); Bello et al. (2017)
D-R	$ln\ Qe = -\beta\varepsilon^2 + \ln Q_m$ $E = \frac{1}{\sqrt{2\beta}}$	ln q_e vs ε^2	$-\beta$	$\ln Q_m$	β and Q_m	B = Dubinin-Radushkevich constant, q_e = amount of adsorbate adsorbed at equilibrium, T = absolute solution temperature R = universal gas constant, Q_m = maximum adsorption capacity, C_e = adsorbate equilibrium concentration Physiosorption if E is between 1 and 8 kJ/mol and chemisorption if E is between 9 and 16 kJ/mol.	A. O. Dada et al. (2021); Sartape et al. (2017)
Kinetics Models							
Pseudo first order	$\ln (q_e - q_t) = \ln q_e - k_1 t$	ln (q_e- q_t) Vs t	k_1	ln q_e	q_e and k_1	q_e and q_t = adsorbed BPA amounts at equilibrium and at times t, respectively. k_1: pseudo-first order rate constant.	Orimolade et al. (2018)
Pseudo second order	$\frac{t}{q_t} = \frac{1}{h_2} + \frac{t}{q_e}$ t $h_2 = k_2 qe^2$	t/qe Vs t	$1/q_e$	$1/h$	q_e, k_2, h_2	k_2: pseudo-second order rate constant, h_2 = initial adsorption rate.	Inyinbor et al. (2016); Sartape et al. (2017); Dada et al. (2020)
Elovich	$q_t = \frac{1}{\beta} lnt + \frac{1}{\beta} ln(\alpha\beta)$	q_t Vs ln t	1/β	$\frac{1}{\beta} ln(\alpha\beta)$	α, β	∝ = initial adsorption rate (mg/g-min); β = desorption constant (g/mg) during any one experiment	
Intraparticle diffusion	$q_t = K_{IPD} t^{1/2} + C$	q_t VS $t^{1/2}$	K_{IPD}	C	K_{IPD}, C	k_{id} is the intraparticle diffusion rate constant (mg. $g^{-1}min^{0.5}$) and C is the intercept indicating the thickness of the adsorbents. The q_t is the amount of solute adsorbed per unit weight of adsorbent per time, (mg/g), and $t^{0.5}$ is the half adsorption time	Bello et al. (2017); Sartape et al. (2017)
Thermodynamics							
Gibbs Free Energy	$\Delta G^\circ = -RTlnKd$				ΔG°	ΔG°: Gibbs free energy change; Kd: equilibrium constant; R: gas constant; T: temperature.	Olakunle et al. (2018); Series (2019)
Van't Hoff Plot	$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$	ln K_C versus 1/T	ΔH^o	ΔS^o	ΔH^o, ΔS^o	ΔS^o = change in standard entropy (kJ/mol K), K_L=Langmuir adsorption constant (L/mg) R = Universal gas constant (8.314 J/mol K), T = absolute solution temperature (K), ΔH^o = change in standard enthalpy (kJ/mol K).	Balarak et al. (2019); Sartape et al. (2017)
Arrhenius Equation	$\ln k_2 = \ln A - \frac{Ea}{RT}$	ln K_2 versus 1/T,	E_a	A	A, E_a,	T = absolute temperature E_a = Arrhenius energy activation for adsorption (kJ/mol), K_2 = PSO kinetic model rate constant (g/mg min). A = Arrhenius factor R = universal gas constant	Bello et al. (2017); O. A. F. A. A. Dada et al. (2019)

temperature but with varying concentrations (Foo and Hameed, 2010). The model equations for isotherm equations are presented in Table 4.

The Langmuir isotherm predicts that the maximum coverage of the adsorbate on the surface of the adsorbent is monolayer (Dada et al., 2017; Sartape et al., 2017). This implies that the layer adsorbed has a thickness of 1 mol (Dada et al., 2013). When adsorption data fit the Langmuir isotherm, it implies that chemisorption occurred on the adsorption sites with similar adsorption energies but independent of surface coverage (Arampatzidou and Deliyanni, 2016; Dada et al., 2021). It, therefore, assumes that there is a rapid decrease of intermolecular forces as distance increases. The mathematical equation for the Langmuir isotherm is shown in Table 4 with the definition of terms indicated. The Langmuir isotherm can be drawn by plotting a graph of C_e/q_e versus C_e which results in a straight line graph having $1/q_m$ as the slope alongside $1/K_Lq_m$. as the intercept (Sartape et al., 2017). A very important data parameter in the Langmuir isotherm is the R_L (separation factor) as shown in Table 4, which is a dimensionless separation factor. The R_L value of less than 1 shows the favorability of the sorption process. The favorability of the adsorptive uptake of BPA by various agro-wastes has been investigated and ascertained by the separation factor (R_L). Report from the literature has also shown that categories of adsorption could be identified with the values of R_L. Adsorption would be tagged unfavorable if the $R_L > 1$, linear adsorption process if the $R_L = 1$, and irreversible adsorption process if the $R_L = 0$. if the Various adsorption of BPA using agro waste fit the Langmuir isotherm such as Hydrochar argan nut shell (Zbair et al., 2018), palm shell (Pamidimukkala and Soni, 2018), potato peel (Arampatzidou and Deliyanni, 2016), dried rice husk (Balarak et al., 2019), coffee grounds (Alves et al., 2019), Banana Bunch, coconut bunch (Lazim et al., 2021), rice husk nano-silica (B. . Orimolade et al., 2018).

The Freundlich Isotherm usually refers to multilayer adsorption, and it assumes heterogeneous adsorption as a result of differences in sorption sites, with an uneven spread of heat of adsorption and affinities over heterogeneous surfaces (Dada et al., 2017). It is not limited to the creation of monolayers. Following this, the quantity adsorbed is the sum of sorption on all sites (each with bond energy), with the stronger binding sites being occupied first until the energy of adsorption declines exponentially at the end of the sorption process (Foo and Hameed, 2010; Sartape et al., 2017). This model suggests physical adsorption on the surface because it predicts infinite surface coverage and not the saturation of the adsorbent's surface (Arampatzidou and Deliyanni, 2016). Heterogeneous adsorption which takes place in multiple layers is assumed by the Freundlich isotherm and as concentration increases, the quantity of adsorbed adsorbate also increases infinitely. This model is applied in a single solute system (Atunwa et al., 2022; Dada et al., 2020). The mathematical equations alongside the plot axis are shown in Table 4.

Temkin equations are expressed in Table 4. Various adsorption of BPA using agro waste has fit the Temkin isotherm such as Palm shell (Choong et al., 2018), Rice husk ash (Sudhakar et al., 2015), pine bark, almond shell (Antunes et al., 2013). The Temkin isotherm is an early model that describes hydrogen adsorption on platinum electrodes in acidic conditions. The adsorbent–adsorbate interactions are explicitly considered in this model, but the extremely low and high concentration values are not. The model assumes that instead of falling logarithmically, the heat of adsorption (function of temperature) of all molecules decreases linearly with coverage (Foo and Hameed, 2010). The mathematical expression to describe the Temkin model is shown in Table 3. Different adsorption of BPA using agro waste has fit the Temkin isotherm such as Rice husk ash (Sudhakar et al., 2015).

The Dubinin-Radushkevich isotherm (D-R) with mathematical expression as depicted in Table 4 was originally developed to explain the adsorption of subcritical vapours onto micropore materials via a pore-filling mechanism. It is commonly used to express the adsorption mechanism onto a heterogeneous surface with a Gaussian energy distribution (Dada et al., 2017, 2019). With the D-R model, the mechanism of the adsorption process could be determined as either physisorption or chemisorption (Foo and Hameed, 2010) based on the magnitude of energy (E) value evaluated. If the energy value (E) is less than 8 $kJmol^{-1}$, the physisorption mechanism suffices but on the other hand, if the E value is above 8 $kJmol^{-1}$, the chemisorption mechanism suffices. Overall, Table 5 shows different agro-waste-based adsorbents used for the adsorption of BPA, the monolayer sorption capacities, Qm and their best-fit isotherm model.

8. Kinetic models modeling of bio-sorption of BPA

Kinetic studies provide valuable details on the pathway of reaction and reaction mechanism(Orimolade et al., 2018). It describes the relationship between the rate of adsorption and the adsorbate concentration as well as the effect of adsorption rate on adsorption capacity(Balarak et al., 2019; Sartape et al., 2017). The Elovich model, pseudo-first-order, Intraparticle Diffusion and pseudo-second-order models will be discussed as kinetic models for testing adsorption data as expressed in Table 4.

The Pseudo-first order (PFO) kinetic model is one of the foremost equations used to explain the rate of adsorption with respect to adsorption capacity (Pamidimukkala and Soni, 2018; Zhang et al., 2019). This model implies that the amount of solid adsorption with time and the variation in saturation concentration is proportional to the change in solute adsorption per unit of time (Ahmad et al., 2020; Dada et al., 2021). Table 4 shows its general expression (Bello et al., 2017).

The Pseudo-second order (PSO) kinetic model is however principled on the solid phase sorption capacity (Agboola et al., 2021). It is used to predict the behaviour of an adsorption process over the entire range studied (Dada et al., 2019). Its mathematical expression is shown in Table 4. Various research on BPA uptake fitted the PSO kinetics model such as sorption of BPA using palm shell (Pamidimukkala and Soni, 2018), potato peel (Arampatzidou and Deliyanni, 2016), dried rice husk (Balarak et al., 2019), Banana Bunch and coconut Bunch (Lazim et al., 2021), rice husk nano silica (Orimolade et al., 2018). It is mostly reported that most kinetics data were best fitted to PSO based on the R^2 value very close to unity as well as other prevailing supporting statistical validity models.

The Elovich kinetic model suitably explains the kinetics of the adsorption of heterogeneous adsorbents (Gündüz and Bayrak, 2017), although, this model does not predict any definite mechanism (Dada et al., 2016). The Elovich model is expressed as shown in Table 4. Adsorption of BPA using Palm shell as investigated by (Pamidimukkala and Soni, 2018) fitted the Elovich kinetic model. The Intraparticle diffusion model (IPD). The adsorption process usually consists of several processes, including the movement of adsorbate to the adsorbent external surface from the boundary layer, adsorbate at a site on the surface and adsorbate intraparticle diffusion of molecules of the adsorbate. The overall rate of adsorption is controlled by the slowest of the three steps.

In the Intraparticle Diffusion (IPD) model, the adsorbate uptake varies nearly proportional to $t^{1/2}$. (Ojediran et al., 2020). It can be expressed as shown in Table 4. If the linear graph passes through the origin, then only the IPD model can be said to be the rate-controlling step (Gündüz and Bayrak, 2017; Gupta et al., 2016), otherwise, other mechanisms may be involved alongside the intraparticle diffusion model (Dada et al., 2021). However, in most cases, the adsorption mechanism is pore-diffusion-dominated. Overall, from Table 5, it is vividly shown that most kinetics data were best fitted and described by PSO.

9. Thermodynamics modeling of bio-sorption of BPA

Thermodynamic studies are carried out in order to study the nature, feasibility and spontaneity of the sorption process (Orimolade et al., 2018; Sartape et al., 2017). Various parameters monitored in thermodynamic studies are used to disclose the various energy changes that

Table 5
Showing adsorption isotherms, maximum adsorption and surface area of agro-wastes used for adsorption.

Adsorbents	Modifying agent	Surface area ($^{-1}_{m2g}$)	Q_{max} (mg/g)	Removal Efficiency	Isotherm Model	Kinetic Model	Thermodynamics	References
Coconut shell-based hydrophobic MAC modified with nanoscale zero-valent iron (NZVI@MAC)	Ferric Solution ($Fe(NO_3)$ $3{\cdot}9H_2O$)	933.12	327.60	–	Temkin	PSO	–	Xu et al. (2022)
Extract solution (ES) originating from fermented tubers and cereal wastes to enhance cross linked activated carbon and reduced graphene oxide composites	–	–	–	–	Freudlich	PSO	–	Ndagijimana et al. (2022)
Corn Cob	HCl	–	51.25	90%	Langmuir	PSO	–	Golveia et al. (2021)
Palm shell	Conc H_2SO_4	770	45.45	–	Langmuir	PSO, Elovich	–	Sudhakar & Soni (2018)
Magnessium silicate impregnated Palm shell activated carbon	KOH, MgO. SiO_2	772.1	254.7	–	Freundlich	PSO	–	Choong et al. (2018)
Potato peel	H_3PO_4, 400 °C	120.35	454.6	–	Langmuir	PSO	Exothermic, spontaneous, feasible	Arampatzidou & Deliyanni (2016)
Coffee grounds	$ZnCl_2$	1039.0	123.2	–	Langmuir	PSO	–	Alves et al. (2019)
Dried rice husk	HCl	94.5	27.12	99.1%	Langmuir	PSO	Feasible, spontaneous, exothermic	Balarak et al. (2019)
Banana bunch		5.83	4.532	28%	Langmuir	PSO	–	Lazim et al. (2015)
Coconut bunch		3.8	4.662	–	Langmuir	PSO	–	Lazim et al. (2015)
Coir Pith	98% H_2SO_4	–	4.308	72%	–	–	–	Lazim et al. (2015)
Coconut Shell	98% H_2SO_4	–	4.159	69%	–	–	–	Lazim et al. (2015)
Durian Peel	98% H_2SO_4	–	4.178	70%	–	–	–	Lazim et al. (2015)
Rice husk ash	Thermal treatment	21.; 6	3.16	73.2%	Freundlich	PSO	Endothermic, physiosorption	Sudhakar et al. (2015)
Rice husk nanosilica	HCl	–	4.267	–	Langmuir	PSO	Exothermic, spontaneous	Orimolade et al. (2018)
Magnetic biochar from Banana peel	$FeSO_4$, hydrothermal treatment	504	20	90%	Langmuir	PSO	–	Rong et al. (2019)
Pine Bark	Formaldehyde, H_2SO_4	3.86	–	95%	Freundlich	PSO	–	Antunes et al. (2013)
Almond shell	Formaldehyde, H_2SO_4	2.02	–	87%	Freundlich	PSO	–	Antunes et al. (2013)
Argan Nutshell	H_3PO_4	1372	1250	94.9%	Langmuir	PSO	Spontaneous, exothermic	Zbair et al. (2018)
Porous Carbon from Bamboo	Carbonized at 1000 °C	–	56.5	–	Freundlich	–	–	Asada et al. (2004)
Peanut shell biochar	Carbonized at 700 °C	–	–	–	Freundlich	–	–	Wang et al. (2019)
Activated Rice Straw	KOH	1304.8	181.19		Langmuir	PSO	–	Chang et al. (2012)
Orange Albedo	–	1.46	82.36	–	Freundlich	PSO	Exothermic, spontaneous	Kamgaing et al. (2017)
Chitosan immobilized nanoscale zerovalent iron nanoparticles	Ferric Iron	–	65.16	95%	Langmuir	PFO, PSO	Favorable, spontaneous	Dehghani et al. (2020)
Modified Peat	Ion exchange between HTAB Cations and polar functional groups in peat matrix	1.02	1.71	–	Freundlich	PSO	–	Zhou et al. (2012)
Almond Shell	Carbonized in the presence of nitrogen gas	–	188.9	–	Langmuir	–	–	Bautista-toledo et al. (2014)
Olive mill waste	KOH	–	2.58	–	Langmuir	–	–	Bautista-toledo et al. (2014)
Eucalyptus Bark/Magnetite component	Co-precipitation technique	–	290.6	79.4%	Freundlich	–	–	Balci & Erkurt (2016)
Oil palm empty fruit bunch	10% $ZnCl_2$	86.62	41.98	–	Langmuir	PSO	–	Wirasnita et al. (2014)
Mesoporous silica nanoparticles from sugarcane ash (MSN-CTAB)	–	131	155.78	90%	Langmuir	PFO	–	Suzimara et al. (2020)
Ficus benghalansis bark (FBB) activated carbon	$ZnCl_2$	256	2.99	97.27%	Langmuir, Freundlich	PSO, Elovich	–	Kamaraj and Umamaheswari (2017)
Magonia pubescens fruit bark activated carbon (AC-H_2)	Water vapour	360	21.26	80%	Langmuir	PFO	–	Antero et al. (2019)

took place in the course of adsorption. Hence, three parameters are assessed which are the Standard free energy change (ΔG^o), Standard change in enthalpy (ΔH^o), and Standard change in entropy (ΔS^o) (Dada et al., 2017). Thermodynamic parameters can be evaluated using the equation in Table 4. A positive ΔS^o value suggests increased randomness or disorderliness at the adsorbent-adsorbate interface in the sorption process (Bello et al., 2017). If the ΔH^o value is positive, it suggests that an endothermic adsorption process took place (Anastopoulos and Kyzas, 2015; Chen et al., 2016). when a negative ΔH^o value is obtained (Dada et al., 2020). Furthermore, a negative ΔG^o value signifies the

spontaneity of the adsorption process at the studied temperature. Free energy change can be evaluated using the equation: The activation energy E_a, is used to determine the nature of and the Arrhenius equation is applied to determine if the process of adsorption is by chemisorption or physisorption (Li et al., 2018). Activation energy ranging between 5 and 40 kJ/mol suggests physisorption and at higher values of $E_{a\ a}$, between 40 and 800 kJ/mol, the adsorption is said to be by chemisorption (Dada et al., 2017; Park et al., 2014). From Table 5, it is obvious that not all studies investigated the thermodynamics of the system, however, in most cases, the thermodynamics of the system was always spontaneous and feasible and they could be either exothermic or endothermic in nature.

10. Mechanism of BPA adsorption

The physicochemical properties of the adsorbent give an insight into the adsorption mechanisms and the general outcome of the sorption study (Al-Ghouti and Da'ana, 2020; Mpatani et al., 2021). The major processes for the sequestration of BPA onto agro-wastes adsorbents are hydrogen bonding (H-bonding), electrostatic interaction, pore-diffusion effect, n-interaction, hydrophobic interaction, and host-guest interaction (Al-Ghouti and Da'ana, 2020; Mudyawabikwa et al., 2017; Supong et al., 2019). The surface form of the adsorbent and the physicochemical testing conditions dictate the majority of these mechanisms (Rong et al., 2019). In the adsorption process, a well-designed adsorbent can also play an essential role (Chang et al., 2012; Gomes et al., 2017). BPA interacts with the carbon surface's functional groups in a variety of ways.

Choong et al. (2018), reported that the carboxylic (COO-) and OH groups on the surface of PPAC were responsible for BPA uptake. The adsorption of an organic compound with an aromatic or C═C double bond on a graphene layer of activated carbon could be dominated by intermolecular forces such as contact (Bautista-toledo et al., 2014; Coughlin and Ezra, 1968). Second, the OH group on the surface of activated carbon can create a hydrogen bond with BPA (Deng et al., 2021; Gonzales-Garcia, 2017). Overall, hydrogen bonds, intermolecular force, and co-precipitation are involved in the removal of BPA by PPAC-MS and PPAC in binary mode. Sudhakar and Soni (2018) proposed that the oxygen and carbonyl on the carbon (as proven by XSP and IR) operate as electron donors that interact with the aromatic rings of adsorbates (phenols) that act as electron acceptors, a typical "donor–acceptor process. Hydrogen bonding between the phosphate groups, –OH groups and amino groups of adsorbates and the Phenolic and carboxyl groups of carbons could be a probable interaction between monographs and PCAC. Furthermore, the polar groups on the AC surface may bind water molecules, causing a cluster of denser water molecules to form, facilitating hydrogen bonding in monographs.

(Arampatzidou and Deliyanni, 2016) made a similar observation, noting that adsorbents micropores and mesopores can provide sufficient sites for uptake, resulting in a strong physical attraction of BPA molecules with a distance between two phenol hydroxyl radicals of roughly 0.94 nm. The results of the Boehm titration showed that carboxyl and phenol groups were reduced following BPA adsorption, showing that these groups were implicated in bisphenol A adsorption via hydrogen bonding. The oxygen functional surface groups on the surface of the activated carbons studied, such as hydroxyl and carboxyl groups, may also contribute to the adsorption, based on the preceding findings. More information on the mechanism of adsorption of bisphenol A was determined to sing the FTIR measurements of the carbon samples following BPA adsorption After sorption, the strength of the O–H group band at 3481 cm^{-1} rose, indicating that strong O–H interactions developed, which might be attributed to hydrogen bonding between O–H groups in both BPA and carbons. Furthermore, after BPA sorption, the bands at 1160 cm^{-1}, which correspond to the O–H bend/stretch, moved from 1160 to 1220 cm^{-1} in the carbon samples' spectra, demonstrating the interaction of these groups with the BPA's O–H groups. The π–π interactions of organic pollutants' pie (π) electrons with the π electrons of activated carbons' benzene rings could explain the adsorption of organic pollutants on activated carbons.

(Rong et al., 2019) confirmed that the radical reaction pathway based on SO_4., O_2 and OH- was responsible for BPA degradation. The OH^- was the most prevalent active species. The Biochar's multiple active adsorption sites interacted directly with persulphate, weakening the C═O bond. The charcoal matrix also acted as an efficient electron transfer support, allowing persulfate to be activated by oxidizing absorbed water to create OH.-. According to GC–MS analysis, the primary intermediates of BPA degradation in the -Fe_2O_3@BC/PS system were 4-hydroxyacetophenone, p-hydroquinone, phenol, and 4-isopropenylphenol. The radical oxidation pathway was discovered to play a prominent role in BPA degradation, with iron oxides, and doped nitrogen and oxygen functional groups all acting as catalytic active sites (Wang et al., 2017).

11. Desorption and reusability

In order to study the extent of reusability and regeneration of adsorbents for further use and the possibility of recovery of pollutants from the adsorbent surface, desorption studies are paramount (Kumar et al., 2020; Kwon and Lee, 2018). Various researchers have recovered the loaded adsorbent by washing it with water after filtration, after which eluting solvents such as NaOH, HCl, methanol or ethanol. After this, the recovered adsorbate is washed and dried before use for the next adsorption cycle and monitored (Ao et al., 2018; Liu et al., 2009). Results of reusability by various researchers have shown the potency of the reuse of agro-waste for BPA adsorption. In the selection of an adsorbent for use, desorption and adsorbents reusability plays an important role as it helps to substantiate the economic value and prolonged use of adsorbent (Han et al., 2021).

(Choong et al., 2018) investigated the reusability of palm shell waste-activated carbon impregnated with magnesium silicate. As shown in Fig. 6, the results revealed that heat treatment to PPAC-MS removed more than 80% of BPA over a 5-cycle period. As a result, utilizing Mg (II) solution and thermal treatment, PPAC-MS can be reused while maintaining its sorption capabilities. In a similar study of the uptake of BPA onto Palm shell-activated carbon (Pamidimukkala and Soni, 2018), conducted desorption studies utilizing different eluents such as hydrochloric acid, sodium hydroxide, Ethanol, acetonitrile and Methanol in comparable research of BPA adsorption onto Pam shell activated carbon. The eluents methanol and ethanol were shown to be superior. In comparison to both basic and acidic eluents, organic solvents showed to be superior eluents. Acetonitrile, Ethanol, and Methanol were the sequence of recovery. The reusability and recovery of the adsorbent were effective for up to three cycles, and after distillation, the eluent could also be reused, implying that using adsorbents could be cost-efficient. A different approach was however adopted by (Arampatzidou and Deliyanni, 2016) where potato peel-activated carbon was initially equilibrated for 24 h with water at various values of pH before filtration. The ideal pH for desorption was discovered to be 10. The organic eluents, on the other hand, achieved a desorption rate of 80% with the methanol-diethyl ether 1:9 mixture, resulting in total BPA desorption. The following was the order of BPA desorption percentages: diethyl ether–methanol 9:1 > ethanol > acetonitrile > methanol. Table 3 also shows a list of different eluent used for desorption though not all studies investigated the re-usability studies. Finally, the best eluent was a blend of diethyl ether and methanol.

12. Challenges and future prospects

Despite the fact that BPA is known to be an endocrine disruptor, it is nevertheless widely used in plastics, thermal papers, toys, food packaging, receipts, and bottles (Allard and Colaiácovo, 2011; Cao et al., 2021; Jiao and Cheng, 2010; Xu et al., 2022). BPA enters the environment primarily through human manufacture and usage, posing a serious

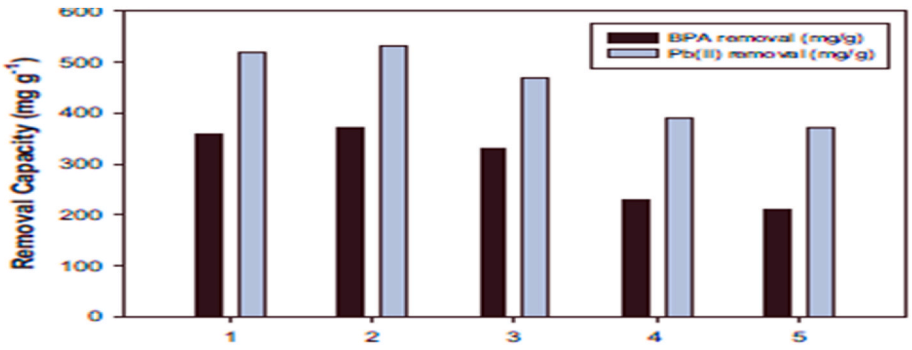

Fig. 6. Regeneration studies for BPA removal onto palm shell waste activated carbon impregnated with magnesium silicate (Choong et al., 2018).

health risk (Gmurek et al., 2017; Li et al., 2018; Ndagijimana et al., 2020, 2022). As a result, greater research into BPA removal from the environment is required. Researchers might look at agricultural waste adsorbents with improved modification techniques to boost adsorption capability (Deng et al., 2021; Shukla et al., 2021). BPA uptake is monitored on a laboratory scale, according to several publications. As a result, new industrial-scale applications using real-world effluents can be introduced to test their efficacy. These studies' potential should not be underestimated (Gonzales-Garcia, 2017; Kwon and Lee, 2018). Agricultural waste adsorbents, on the other hand, must be properly utilized in real wastewater effluents in order to be practical and financially feasible. As a result, substantial research is needed to design and manufacture agro-waste adsorbents capable of decontaminating BPA in wastewater treatment plants. The utilization of these adsorbents at the point of use (POU) can also be investigated in order to test their ability to remove BPA in a dynamic adsorption system. This could increase their use in domestic water filters and residences. Future research should focus on the design of better-modified agricultural waste adsorbents and the cost analysis for the removal of Bisphenol A should be evaluated at the laboratory, pilot, and industrial scales.

In addition, environmentally sustainable and friendly techniques for disposing of unwanted (spent) adsorbents after prolonged use, and hybridizing adsorption with other methods to achieve higher removal performance. Filling these knowledge gaps will aid in the reduction of the restrictions that prohibit most adsorbents from gaining commercial value. Future research should focus on BPA migration from consumer products to humans, as well as the possible health effects of BPA exposure in humans. It is necessary to conduct an extensive study into practical viability and cost-effective strategies for lowering and removing BPA from the environment. Future research could focus on developing safe, functional, and repeatable BPA analogues, as well as studying its breakdown products.

13. Conclusion

Bisphenol A is of growing concern as it threatens both human life and environmental health. Although various techniques have been applied and are available for the sequestering of BPA, they are however expensive. Agro-waste materials can be modified into biochar or activated carbon and applied as alternative adsorbents for use in place of commercially sold activated carbon. This review summarized the most recent research on applied agro-wastes for the uptake of BPA mostly from 2014 till date, their adsorption performances, and operational parameters monitored during the adsorption process. The review also contains adsorption isotherms, thermodynamics, mechanisms and kinetics of BPA adsorption onto various agro-wastes alongside reusability studies. The ecotoxicological effects of BPA were also presented. The finding from this review revealed that BPA adsorption took place at acidic pH mostly at pH 3 and very few at alkaline pH 8–11. Most acidic functionalized agro-waste adsorbents had better removal efficiency with the best removal efficiency of 99.1% attained using HCl as activating agent. The fastest contact time of 20 min was achieved with the use of magnetic biochar and the least contact time was 48 h. The prominent mechanism was the π- π interactions. Equilibrium data were reported to best fit Langmuir and Freundlich isotherm models while Pseudo-second-order (PSO) kinetics and pore diffusion models mostly described the rate and mechanism of the BPA adsorption process. The review concludes with the challenges and future prospects for further research on the application of agro-wastes for BPA uptake. Adsorption using activated carbon from agro-waste however is an economical and sustainable substitute to the utilization of expensive commercial activated carbon for the sequestering of BPA.

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.

Data availability

No data was used for the research described in the article.

Acknowledgement

The authors appreciate the Third World Academic of Science (TWAS) and CSIR-India Institute of Chemical Technology (CSIR-IICT), India for the award of a Postdoctoral Fellowship that gave an opportunity to the co-authors (Dr. Dada, A.O) providing enabling environment and cutting-edge research exposure under Prof. Ujjwal Pal (Senior Principal Scientist) that has put great expertise into this Review work. The Management of Landmark University is also appreciated for unwavering commitment to capacity building.

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