Techniques of Agro Wastes Materials as Viable Adsorbents - A Review

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Abstract

Nigeria and the world, by extension, generate enormous amounts of agricultural waste and residue. These wastes, which are inappropriately deposed off either by unplanned landfilling, burning or indiscriminate dumping, are a menace to society. In an effort to reduce the degradation and pollution load of these wastes on the environment, they are being geared towards recycling and reuse as a potential resource in meeting the increasing demand for easily attainable, cost-effective, efficient and environmentally friendly wastewater treatment alternatives. This study reviews the various adsorbent types and recent use of agricultural wastes as viable adsorbents in the society. The study therefore serves as a blueprint for the elimination of various contaminants from wastes.

Keywords
Adsorbents, Rice-hull, Coconut-Shell, Kaolin, Peanut-Hull.

1. Introduction
Environmental pollution all over the globe is gradually reaching an alarming stage with several countries beginning to develop technologies to tackle this menance (Ogbonna and Mafimisebi, 2016). Pollution can be defined as the introduction of solid, liquid or gaseous materials into the surrounding at a faster rate than it can decompose, dilute, be recycled, or stored in a harmless form (Ajibade et al., 2021). One of such technologies developed is adsorption. The rapid separation of an adsorbate (the substance that is adsorbed) from liquid to a surface (also known as Adsorption Technology), is the most preferred method for pollutants removal from effluent water via an adsorbent (the solid whose surface adsorbs the substance) (Hu and Xu, 2019). This study was therefore an attempt to review various adsorbent types and recent use of agricultural wastes as viable adsorbents in the society.

2. Literature Review

2.1 Adsorption

Adsorption technology is regarded as one of the most significant technologies applied in wastewater treatment because of its simplicity of design, ease of operation and convenience (Hu and Xu, 2019). Compared to other technologies, adsorption has demonstrated its efficiency and economic feasibility and has gained importance in industrial applications (El-Araby *et al.*, 2017). Absorption differs from Adsorption because it is said to occur when a fluid permeates through the entire volume of a material. However, Adsorption which is an exothermic process can be defined as a surface phenomenon where materials (adsorbates) such as ions, atoms or molecules in solution attach to an adsorbent's outer surface by adhesion from physicochemical forces (Tien, 2019; Fanourakis et al., 2020, Zarrouk and MacLean, 2019). Adsorption is categorised as a physical or chemical process in accordance with the different adsorption forces (see Table 1). Physical adsorption (physisorption) is a reversible process that occurs when adsorbates adhere to the surface of an adsorbent through weak bonds such as van der Waals force, electrostatic force, hydrogen bonding and hydrophobic interactions (Sandhyarani, 2019; Zhang et al., 2016). Conversely, if chemical bonding binds adsorbates to the adsorbent's surface, it is called chemical adsorption (chemisorption), and it is a non-reversible process (Bakhtyari et al., 2020; Siyal et al., 2020). The efficiency of adsorption is dependent on the chemical and physical properties of the adsorbates and adsorbent surface (Cossu et al., 2018). The best way to improve or tailor adsorption is to select a solid or composite matrix that offers chemical and physical functionalisation (Fernández-Reyes, et al., 2019). An adsorbate is a material that gets adsorbed unto the surface of the solid (Cossu et al., 2018), while an adsorbent is the solid whose surface adsorbs the material in a solution and is considered economical if it is copious or a by-product gotten from industries or needs little to no processing (Zarrouk and MacLean, 2019). There exists a direct relationship between the porosity, amount of surface area, site availability and an adsorbent's effectiveness (Saleh et al., 2020). Adsorbents can also be classified based on their porosity: microporous, mesoporous and macroporous, with pore sizes of < 2 μm, $< 2 – 50$ μm, and > 50 μm, respectively (Siyal et al., 2020). Porous adsorbents can be grouped as naturally occurring and engineered. Naturally occurring adsorbents are regarded as low-cost materials compared to engineered adsorbents (Table 1).

Table 1. Comparison of physical adsorption and chemical adsorption (Hu and Xu, 2019)

AdsorptionCategories		
Parameters	**Physisorption**	**Chemisorption**
Adsorption force	Van der Waals force	Chemical bond force
Adsorption layer	Single or multiple layers	Single-layer
Adsorption heat	Low	High
Adsorption rate	Rapid	Slow
Selectivity	Non-selection adsorption	Selective adsorption
Stability	Instable	Stable

2.1.1 Carbon-Based Adsorbents

Carbon-based materials have accompanied human history, the application of which dates back more than 5,000 years when charcoal was discovered from the incomplete combustion of wood (Zhao et al., 2018; Ilyas et al., 2020; Sharma and Garg, 2019). Since then, several carbon homologues such as activated carbon, carbon fibres, carbon nanotube, graphene, carbon aerogel and biochar have been discovered and invented (Sabzehmeidani 2021). Different types of carbon-based adsorbents which are employed during adsorption are as seen in Figure 1. The adsorption capacity of a carbon-based adsorbent to adsorb a compound is largely dependent on some specific properties of the solution conditions (temperature, pH and strength ionic), adsorbent (structure, pore size and functional groups), and adsorbate (functionality, polarity, molecular weight, and size) (Sabzehmeidani 2021) (Figure 1).

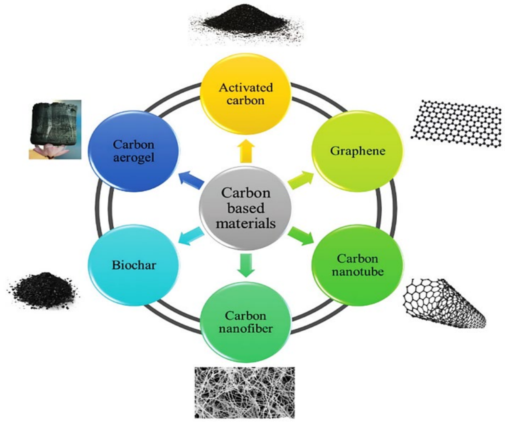

Figure 1. Various carbon-based adsorbent homologues in the adsorption process (Sabzehmeidani 2021)

2.1.2 Biochar

Biochar has gained much recognition in the last decade due to the several promising benefits of soil amendment in agriculture, which is defined as any material added to soil to improve its physical properties, such as nutrient retention and water (Padilla and Selim, 2020). However, Biochar has been extended as feedstock in water and wastewater treatment (Xiang *et al.*, 2019) (Figure 2).

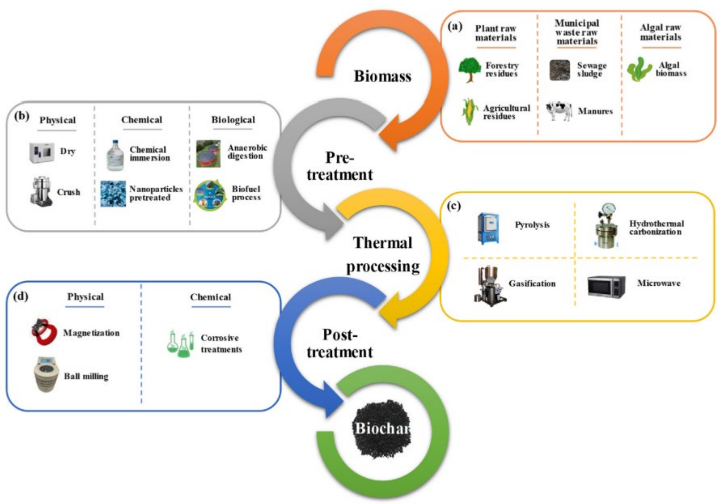

Figure 2. Biochar production technology (Xiang et al., 2020)

Biochar has been one of the most utilised adsorbents for eliminating various contaminants from waste and effluent water because of its superior properties such as adsorption capacity, specific surface area, microporosity, mineral composition, ion exchange capacity and abundant surface functional group (carbonyl, carboxyl, hydroxyl, and methyl) (Gwenzi et al., 2017), as well as it is a cheap and widespread feedstock (Yang et al.,2020).

2.1.3 Activated Carbon (AC)

AC, popularly known as activated charcoal or active carbon, has been the most versatile and powerful adsorbent for the removal of contaminants in water and wastewater (Tadda e*t al.*, 2016) due to its surface reactivity (Soni *et al.*, 2020), large pore size distribution (micro- < 2 nm, meso- < 2 – 50 nm, and macroporosity> 50 nm) (Fernández-Reyes, *et al.*, 2019), chemical stability, and large surface area (500 – 1500 $m^2\ g^{-1}$) (Jackson, 2020). AC is an amorphous form of elemental carbon prepared by the destructive distillation of lignocellulosic organic materials such as coconut shells, rice hulls, cotton stalk and pine cones or other carbonaceous substances such as coal or tar pitch (Zhao, 2018).

2.2 Agro-Wastes

The increasing qualities of waste have created several environmental challenges, including soil, water and air pollution (Ilyas *et al.*, 2020; Sharma and Garg, 2019). According to the Environmental Agency, waste is any material, substance or object which a holder disposes of or intends to dispose of most likely because it has outlived its purpose. However, solid waste (municipal, industrial, and agricultural waste) when viewed in the context of sustainable development, is regarded as a useful resource in the development of improved products (Millati et al., 2019). Ramírez-García *et al.* (2018) defined agricultural wastes, otherwise called agro-waste, as unwanted wastes produced from agricultural activities. Obi *et al.* (2016) defined agricultural wastes as the set of outputs of production and processing of agricultural products that that can be useful to humanity but may possess lesser economic value than the processing and transportation cost. Agro-wastes are grouped into four categories, namely crop residues, livestock waste, fruits and vegetable wastes (FVWs), and agro-industrial wastes (AIWs) (Pattanaik et al., 2019). These wastes include leaf litter, straw, roots, fruit peels, husks, dairy products, meat and manure [(Maji et al., 2020; Sharma and Garg, 2019). Table 2 shows agro-wastes used as adsorbents.

The main structural components of agro-wastes are lignin, cellulose, hemicellulose (Dai et al., 2018; Huang and Lo, 2018), proteins, lipids and simple sugars (Alalwan *et al.*, 2020). Cellulose and hemicellulose contain oxygen functional groups, including carbonyl, and hydroxyl functional groups, while lignin (an aromatic polymer) consists of carbonyl, methyl and hydroxyl functional groups (Dai *et al.*, 2018). When these wastes are left to rot or are deposed of through unplanned landfilling, open burning and dumping, they cause environmental hazards, making the ecosystem unsustainable (Maji et al., 2020; Dai et al., 2018; Huang and Lo, 2018; Alalawan et al., 2020; Elly, 2011). The environmental impact of some of the disposal practices results in the release of carbon monoxide (CO), nitrous oxide (N_2O) and nitrogen dioxide (NO_2) (Bowan et al., 2018). However, many of these wastes are still largely under-utilised. For this, efforts have been made to convert agro-wastes into methanol, ethanol, heat steam, biodiesel, animal feed and charcoal (Harshwardhan and Upadhyay, 2017). (Table 2)

Table 2. Agro-wastes used in the removal of heavy metals from wastewater

Adsorbent	**Types of Pollutants**	**References**
Eggshell	Cu^{2+} and Cd^{2+}	(Abdullahi *et al.*, 2017)
Coconut shell	Cr^{4+}	(Ayub and Changani, 2018)
Activated coconut shell	Cu^{2+}, Fe^{2+}, Zn^{2+} and Pb^{2+}	(Bernard, *et al.*, 2013)
Walnut shell	Cr^{4+}	(Bernard, *et al.*, 2013)
Sulphur-functionalised walnut shell	Pb^{2+}	(Mwegoha, 2016)
Sesame husk	Cu^{2+}	(El-Araby *et al.*, 2017)
Activated peanut shell	Cr^{3+}	(Mwegoha, 2016)
Rice husk charcoal	Cu^{2+}	(Huang and Lo, 2018)
Modified almond shells	Cu^{2+} and Cd^{2+}	(El-Araby *et al.*, 2017)
Palm kernel shell	Zn^{2+}, Fe^{2+}, Pb^{2+} and Ni^{2+}	(Millati *et al.*, 2019)
Garlic peels	Pb^{2+}, Cu^{2+} and Ni^{2+}	(Millati *et al.*, 2019)

2.3 Coconut Shell

Coconut (Cocos nucifera L.) is a perennial plant that continually bears fruit for 60 to 70 years, 12 to 13 times annually, yielding between 30 to 75 fruits per annum (Gordon and Jackson, 2017). Cocos nucifera is the fruit of the coconut palm tree belonging to the Arecaceae family (Pham, 2016). It is one of the most important crops grown throughout the tropics and is ranked the seventh most crucial vegetable oil crop globally. The coconut fruit sustains the livelihood of millions of people globally, specifically in the tropics' coastal regions, providing food, fibre and wood (Siriphanich et al., 2011) and is regarded as the "tree of life" due to the versatility of its uses (Bhatnagar, 2010). Table 3 shows the proximate and ultimate analysis of coconut shell as carried out by (Windeatt et al., 2014) (table 3). Coconut palms are grown in more than 93 countries (Anwar *et al.*, 2016). The global coconut production volume for the year 2019 was estimated at 62.46 million tons according to the Food and Agriculture Organisation Corporate Statistical Database (FAOSTAT), with Indonesia, the world's leading producer of coconut accounting for about 17.13 million tons, accompanied by the Philippines, and India with 14.77, and 14.68 million tons respectively (Statista, 2021).

Table 3. Biochemical, ultimate and proximate analysis of coconut shell (Windeatt et al., 2014)

Biochemical Analysis (%)	Ultimate Analysis (%)	Proximate Analysis (%)
Cellulose 20	Carbon (C) 52.6	Moisture 5.7
Hemicellulose 49	Hydrogen (H) 6.2	Volatile matter 77.2
Lignin 30	Nitrogen (N) 2.0	Fixed carbon 22.8
	Sulphur (S) 0.0	Ash 0.6
`	Oxygen (O) 53.1	

2.3.1 Coconut Shell as an Adsorbent

Bernard, et al. (2013) studied the use of chemically AC prepared from coconut shell (ACS) as an adsorbent in the removal of heavy metals (Cu^{2+}, Fe^{2+}, Zn^{2+} and Pb^{2+}) from industrial wastewater. The carbon was activated with zinc chloride, and the effects of adsorbent dosage (0.2 – 1 g), pH (2 – 6), contact time (20, 40, 60, 80, and 120 min) and stirring rate/shaking speed (150 – 350 rpm) n the adsorption of heavy metals with a concentration of 50 mL were examined through batch experiments. SEM was used to characterize the pore structure of the developed ACS. At the end of the experiment, the authors recorded the percentage metal ion removal as the ions approached equilibrium within 40 mins for Pb (II), 60 mins for Zn (II) and 80 min for both Fe (II) and Cu (II); as Zn (II) 26.15%, Cu (II) 71.26%, Fe (II) 76.02%, and Pb (II) 100%. The optimum stirring rate, adsorbent dosage and pH were found to be at 350 rpm, pH 6 and 1g respectively. Also, the adsorption process was best described by the pseudo-second-order reaction model from the kinetic analysis. Ghosh (2013) studied the use of coconut shell (CS) for removing cation and anionic dyes from aqueous solution. Their investigation was focused on how pH affected the effectiveness of the dye adsorption to determine the maximum adsorption capacity and time of equilibrium of adsorption of two cationic dyes: Basic Violet 10 and Basic Red, and four anionic dyes: Acid Red 18, Acid Yellow 23, Reactive Black 5, and Reactive Yellow 84. At the end of the study, the authors recorded the most favourable pH for the anionic dyes and Basic Violet 10 as 3 and 6 for Basic Red. A high adsorption capacity for cationic dyes: Basic Red 46 at 68.52 mg g^{-1} and Basic Violet 10 at 28.54 mg g^{-1} compared to anionic dyes: Reactive Yellow 84 at 0.96 mg g^{-1}, Reactive Black 5 at 0.82 mg g^{-1}, Acid Red 18 at 0.66 mg g^{-1} and Acid Yellow 23 at 0.53 mg g^{-1} was also recorded. Also, it was observed that the acidic dyes: Acid Red 18, Acid Yellow 23 had the shortest equilibrium time of adsorption in the range of 18 to 45 min, whereas the alkaline dyes Basic Violet 10 and Basic Red 46 had the longest equilibrium time of adsorption from 10 to 180 min. The ability of coconut shells to remove chromium (IV) from wastewater was studied by (Ayub and Changani, 2018). It was found out that the extent of chromium (IV) removal depended on pH, contact time, adsorbent dose, particle size, and metal concentration. From the obtained results, the positive value of the thermodynamic parameter ΔH indicated the adsorption process was endothermic, the negative value of ΔG showed the feasibility and spontaneity of the process, and the positive value of entropy (ΔS) reflected the affinity of the adsorbent material. In conclusion, the authors recorded maximum adsorption of 83% at a temperature of 30℃ for an initial concentration of 50 mg L^{-1} at pH 1.5 and an adsorbent dose of 10g L^{-1}.

2.4 Rice Hull

Rice (Oryza sativa seed) is the staple food of more than half of the world's population (Ayub and Changani, 2018). Paddy rice cultivation produces two significant residues: rice straws and rice hulls (Huang and Lo, 2018). Rice hulls, also referred to as "rice husks", are hard protective coverings for rice grains that are separated from the grains during rice milling (Soni et al., 2020). Each kilogram of milled rice results in approximately 0.28 kg of rice hull as a by-product during rice production (Millati et al., 2019) (table 4). According to the most recent official data from FAOSTAT, the global production of milled rice for 2019 was estimated at 495.78 million tons. In 2018, China was the world's leading producer with 209.6 million tons, followed by India and Indonesia with 177.65 and 54.6 million tons, respectively (Statista, 2021). Therefore, using the aforementioned statistics, approximately 138.8 million tons of rice hulls was generated worldwide. Most of these rice hulls end up being dumped or burnt in open spaces, resulting in energy wastage and land and environmental pollution (Ghosh, 2013). Thus, efforts have been applied to utilise rice hulls as an additive in many materials and applications, such as fuel for energy production, fillers in polymers and rubbers, catalyst support, adsorbent, and manufacture of silicates and silicon materials (Shiva, 2020). Rice hulls are rich in ash and crude fibre (Wu and Xu, 2019). Chemical examination shows that rice hulls are made up of organic compounds (94.99%) and inorganic compounds (5%) (Shukla, 2020). Where the major organic compounds are cellulose (35%), hemicelluloses (25%), and lignin (20%) (Shukla, 2020), the inorganic compounds are majorly silica, and traces of metals and oxides (Siddique et al., 2019; Emanuelle et al., 2016), as presented in Table 4. Rice hulls have unique physicochemical and biochemical properties, making them a proper material to be transformed into several low-cost adsorbents, such as hydrogel, silica, activated carbon, and composite for wastewater treatment (Wu and Xu, 2019). The three significant properties that make the rice hull ideal for water treatment are its processability, high specific surface area and catalytic properties (Wu and Xu, 2019).

Table 4. Biochemical and ultimate Analysis of rice hull (Millati *et al.*, 2019)

Biochemical Analysis (%)			**Ultimate Analysis (%)**	
Cellulose	**Hemicellulose**	**Lignin**	**Organic Compound**	**Inorganic Compound**
43.3	28.6	22.0	C 39.8	SiO_2 99.50
			N 37.4	Al_2O_3 0.17
			H 5.7	P_2O_5 0.11
			O 0.5	MgO 0.02
				SO_3 0.02

2.4.1 Rice Hull as an Adsorbent

The abundance, porosity, chemical stability, insolubility in water, high mechanical strength, metal-containing and granular structure of rice hull are crucial in removing pollutants from wastewater (Shukla, 2020; Masoud et al., 2016; Ahmaruzzaman and Gupta, 2011). The decontamination of As (III) and Cu (II) metal ions from prepared aqueous samples were investigated by (Shukla, 2020) using chemically modified rice hulls as the adsorbent. The result revealed that the formation of a homogenous film adsorbent, partially crystalline, had better thermal stability, bulk density, swelling behaviour and adsorption capacity than unmodified rice hulls. In conclusion, the developed adsorbent was useful for the efficient removal of Cu (II) at 93% and As (III) at ~90%, with a removal capacity of 2g $cm^{-2,}$ and the adsorbent film was regenerated easily by washing with hot water. RHA as an adsorbent for methylene blue adsorption was studied by Kurniawati *et al.* (2015). The RHA was dissolved in HCl and calcined at 650℃ for 4hours, and the adsorption was conducted by the batch method that varied in pH (2 – 7) and time (1 – 7 hour). Characterisation of RHA by XRF spectroscopy revealed that it contained 78% silica as its highest compound. Before and after adsorption, the concentration of methylene blue was analysed using a UV-Vis spectrophotometer at a maximum wavelength of 664 nm. In conclusion, it was observed that the optimum pH for the adsorption of methylene blue on the aqueous solution was 6.14, with 64.3% percentage adsorption. While with an optimum contact time of 5 hours, the percentage adsorption was 92.6%, with an adsorption capacity of 38.8 mg g^{-1}.

2.5 Peanut Hull / Shell

Peanut (*Arachishypogaea L.*) is a leguminous crop that is nutritious and mainly grown for its oil and seed worldwide. It is either consumed as peanut butter or as a confectionary snack (Kurniawati et al., 2015). It is ranked the fourth largest vegetable oil seed produced worldwide, with China and India being the first and second-largest producers of groundnut (Duc et al., 2019; Ramgopal, 2016). The term peanut is predominantly used in North and South America, while in Africa, Asia, Australia and Europe, it is commonly referred to as groundnut (Prasad et al., 2011). Its entrance into Europe, Asia, Africa and the Pacific Islands presumably took place in the 16th and 17th centuries with the Portuguese, British, Spanish, and Dutch discovery voyages (Prasad et al., 2011). Today, the groundnut crop is grown throughout the tropics and subtropical regions, in over 108 countries on approximately 22.2 million hectares, of which Asia is the largest cultivator with 13.69 million hectares, 7.9 million hectares in Sub-Saharan African, and 0.7 million hectares in South and Central America (Madhusudhana, 2013). These shells account for roughly 20 per cent of the dried peanut pod by weight (Duc *et al.*, 2019). Table 5 shows the physical and chemical compositions of peanut shells. Peanut shells are generated in large quantities at crop processing facilities and are rarely recycled to the fields but are often mounted outside the factory. The abundance of this food-processing by-product and the richness of its shells has instigated its use in a variety of bioactive and functional components such as its utilisation as feedstock for bioethanol production, nano-sheet, fillers in fertilisers, animal feed, wet materials for water purification, insulation board and as activated carbon (Duc *et al.*, 2019). However, a significant drawback of its use in large-scale industrial processes is the higher lignin content responsible for its biodegradable resistance under normal environmental conditions (Buyukada, 2016). In an effort to limit its environmental impact, peanut hulls have been investigated as a promising adsorbent for the adsorption of dyes, heavy metals and other pollutants in wastewater (Li et al., 2018) (Table 5).

Table 5. Chemical and physical composition of peanut shells (Cook and Huffman, 2017)

Chemical Composition %		**Physical Composition**	
Parameter	**Value**	**Parameter**	**Value**
Crude fibre	60 – 70	Porosity	61.7%
Cellulose	35 – 45	Solubility in water	0.74%
Lignin	27 – 33	Bulk density	5 – 7 lb ft^{-3}
Moisture	8 – 10		
Protein	6 – 7		
Ash	2 – 4		
Fat	1		

2.5.1 Peanut Hulls as an Adsorbent

Sowmya et al. (2018) investigated the effectiveness of activated peanut shells to remove chromium Cr (III) from tannery wastewater under laboratory-scale batch experiments. The authors studied the effects of particle size (0.25, 0.4, 0.8, 1, and 1.6 mm), pH (2, 4, 7, 10, and 12), contact time (60, 120, 180, 240, and 360 min) and adsorbent dosage (3, 5, 10, 15, and 20 g) on the adsorption of Cr (III). With an initial Cr concentration of 6.643 ppm and particle size of 0.25 mm, the optimum Cr removal was obtained at a pH of 4, contact time of 180 min and adsorbent dosage of 20g per 100ml, the highest percentage removal efficiency was 98.013%, which corresponded to a final concentration of 0.132 ppm. The overall removal capacity of the activated peanut shell was found to be 2.6172 mg g^{-1}, and the Freundlich model provided the best fit to the adsorption isotherm experimental data, with R^2 being 0.9613.

In a study conducted by Sowmya et al. (2018), the efficacy of peanut shell activated carbon (PSAC) was examined to remove toxic metals from industrial wastewater. The initial pH of chromium and zinc plated water was 5.82 and 6.63, respectively, and the initial concentration range was 136 and 285, respectively. After treating the industrial water with the developed adsorbent, a final pH of 6.1 and 6.8 was recorded for chromium and zinc plated, respectively, and the final concentration range of chromium and zinc was reduced to 0.85 and 0.75, respectively. Activated carbon synthesised from three types of peanut hull as raw material were employed as an adsorbent to decolourise reactive brilliant blue X-BR dye from wastewater by Wu et al., (2019). The effects of activation state, adsorbent dosage, adsorption time, carbonisation temperature and carbonisation time during decolourisation on the performance of the adsorbents were investigated. At the end of the study, it was observed that the peanut hulls that were first activated with phosphoric acid and then carbonised at 450℃ for 3 hours offered the best performance in the decolourisation of reactive brilliant blue X-BR with an optimum dose of 4 g L^{-1} and adsorption time of 2 hours.

2.6 Kaolin

Kaolin, commonly referred to as "kaolinite clay" or "China clay", is a widely used industrial clay that is soft, lightweight, earthy and white (Yaya *et al.*, 2017; Heah *et al.*, 2011). To this effect, in 2016, the world mined production of Kaolin was estimated at 37.0 million tons (Detellier, 2018). Kaolin is derived mainly from the mineral kaolinite, which is hydrated aluminium silicate and contains other kaolin group minerals (Shaw, 2017). The stoichiometric formula $Al_2Si_2O_5(OH)_4$ represents kaolin (Hosseini and Ahmadi, 2015), which is also alternatively represented by the formula Al_2O_3 $2SiO_2.2H_2O$. According to the arrangement of their layer structure, kaolinite is categorised as a 1:1 clay mineral (Awad *et al.*, 2017). This means that a layer is composed of two different sheets (Detellier, 2018). Other clay minerals that fall in this category are rectorite, halloysite and chrysotile (Heah et al. 2011). Hence, the structure of kaolinites (see figure 3) can be described as a repetition of units consisting of tetrahedral silica (Si–O) sheet and octahedral alumina (Al–O) sheet (Król-Morkisz and Pielichowska, 2018). The chemical composition of kaolin is presented in Table 6.

Table 6. Chemical composition of kaolin (Nabbou et al. 2019; Oluseyi et al. 2016).

Chemical Composition wt %												
S/N	SiO_2	Al_2O_3	Fe_2O_3	K_2O	LOI	SO_3	TiO_2	Na_2O	MgO	P_2O_5	CaO	TOT
1	53.83	39.81	1.15	2.39	–	< 0.01	1.27	0.67	0.46	0.18	0.15	99.92
2	63.66	24.16	4.05	2.51	1.75	1.31	0.72	0.61	0.49	0.40	0.13	–
3	59.26	24.04	3.87	0.30	9.4	–	1.46	0.74	0.14	–	0.39	–

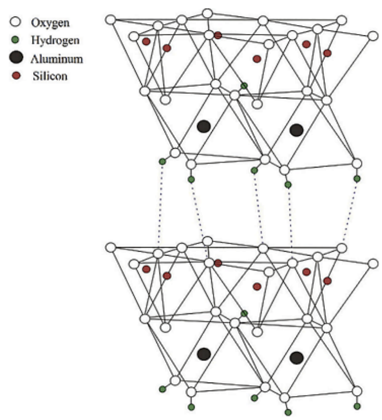

Figure 3. Schematic view of the structure of kaolinite (Cheng et al. 2019)

The unique mineralogy, morphology, electrical non-conductivity, mechanical stability, high specific gravity, heat and chemical resistivity (Figure 3), chemical purity, softness, abundance, and environmentally friendly nature of kaolin make it a versatile raw material appropriate for many different industrial applications, such as in paper, plastics, paint, ceramics, medicine, pharmaceuticals, cosmetics, refectories and low-cost adsorbents (Awad et al., 2017; Karunadasa et al., 2021; Guan and Zhao, 2020; Cheng et al., 2019). The use of kaolinite minerals as adsorbents for removing heavy metal ions, dyes and other organics from wastewater is due to its crystalline structure, which allows for a large surface area that absorbs many times its weight in water and metal binding capacity (Shaw, 2017). Kaolin can also be used as a filer to enhance the mechanical strength of the adsorbent (Chai et al., 2020).

2.6.1 Kaolin as an Adsorbent

Alasadi et al. (2019) used nano kaolinite powder as an adsorbent for the removal of Zn (II), Cu (II), and Ni (II) ions. The developed adsorbent was characterised by SEM, XRD and FT–IR techniques. Effect of initial metal ion concentration, pH, contact time, adsorbent dosage and temperature of adsorption process were examined. At the end of the study, the authors observed that the maximum percentage metal ion removal was observed at a pH ranging from 5.5 to 6, an optimum contact time of 120 min, an adsorbent dose of 1.0 g L^{-1} for an initial concentration of 40 mg L^{-1} and a temperature of 30*℃*. Also, the authors concluded that the pseudo-second-order model well described the kinetic data obtained and that the Langmuir isotherm model provided the best fit for the adsorption data. Chai *et al.* (2020) studied and compared the adsorption capacity and percentage removal efficiency of raw kaolinite versus acid-activated kaolinite for the removal of Ni (II) and Cu (II) ions by The prepared adsorbents were characterised by FTIR, XRD, SEM and zeta potential analysis. The batch adsorption studies for both adsorbents were carried out under the following optimum condition: an initial metal ion concentration of 100 mg L^{-1}, pH of 7, an adsorbent dose of 0.1 g, contact time of 60 min and temperature of 25 *℃*. At the end of the study, the acid-activated kaolinite had better adsorption capacity and percentage removal efficiency than raw kaolinite due to the increased number of metal ion binding sites upon acid treatment and the number of negative charges on the adsorbent surface. The adsorption data was an excellent fit for Freundlich and Langmuir adsorption models, while the kinetic data was found to be consistent with the pseudo-second-order model. The recorded adsorption capacities of KPC and KPA were 113.8 and 105.3 µg L^{-1}, respectively.

3. Conclusion

The use of various agricultural wastes as adsorbents for pollution reduction has been largely researched with major findings reviewed by this study. Particularly, the use of Rice Hull, peanut hull, coconut shell and Kaolin as adsorbents. Their adsorption capacities have been carefully surveyed and even though all three agrowaste materials possess excellent adsorbent capacities, rice hull was the best of the three with over 95% adsorbent capacity. It can however be safely concluded that the use these of agro-waste materials (coconut shell, rice hull, peanut hull and kaolin) as adsorbent will help reduce the pollution rate if widely adopted. Conclusively, the use of agro-wastes as alternate source of energy has been well established from past researches, yet its use as an adsorbent should be considered since it will further reduce environmental pollution especially at a reduced cost.

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