

Low-cost Adsorbents Derived from Agricultural By-products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review

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Received: 23 August 2016

Accepted: 6 November 2016

Abstract

A major threat to the comfort of human life has been imposed by increased industrialization and urbanization. The generation and disposal of huge amounts of toxic materials and pollutants have heavily contaminated our environment. Some Organics such as synthetic dyes (SD) and heavy metals (HM) are becoming increasingly prevalent as the most dangerous pollutants in soil and surface water environments. They are causing great concern worldwide due to their toxicity to many life forms.

Environmentally friendly utilization of agricultural by-products/waste materials either as raw materials or in production of so-called activated carbons (AC) is an important issue. Because it is apparent from our literature review that the main factors characterizing these materials are their affordability, local availability, and efficiencies in removing many unwanted toxics and pollutants, they therefore could be utilized instead of more conventional but expensive adsorbent materials, particularly in developing countries where many industries lack appropriate individual sewage treatment systems; even where they exist, they lack satisfactory functioning and maintenance because of the lack of good budgets.

A number of case studies are supplied in this review. These case studies have pointed to the efficient removal of SD/HM ions from aqueous solutions by the agricultural by-products/wastes in the form of a raw material, signifying spent tea leaves (STL) as a good example. Besides, the efficient removal of such ions by AC produced from these agricultural by-products/wastes has also been given in detail, suggesting a variety of AC agricultural by-products/wastes sources. Both kinds are widely used adsorbents in the treatment of wastewaters. Our review has shown that these adsorbents are characterized by many exceptional physical and chemical features that make them widely used adsorbents in the treatment of wastewaters. The adsorption efficiencies by these substances were also affected by the characteristics of AC, which depend on the physical and chemical properties of the precursor (i.e., agricultural by-products/wastes) as well as on the activation method applied, which is either chemical or physical. The structural properties of the resulting

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AC can be affected by a number of factors such as time of activation, temperature of activation, and the oxidizing agent used in addition to the starting precursor.

Keywords: activated carbon, agricultural by-products/waste, adsorption, heavy metals, synthetic dyes

Introduction

In the past few decades, urban and industrial activities have contributed enormously to the pollution of the environment, which has become a major problem that needs to be solved or at least controlled. The excessive release of colored effluent and the dyestuff wastewaters produced by the textile, paper board, wood pulp, paper, fertilizer, paint, and pigment industries comprises one source. The released dye in water streams represents a risk of ecotoxicity and a potential danger of bioaccumulation. The transport of these contaminants through the food chain could even affect human health [1].

Synthetic dyes (SD) and heavy metals (HM) are usually found as part of their constituents and can be two examples posing a global problem. This fact implies the need to conduct treatment processes to the SD and HM containing water before discharging to the environment. According to the United Nations World Water Development Report, 2 million tons of waste are discharged to water bodies daily, including industrial wastes, dyes and chemicals, and human and agricultural wastes (fertilizers or pesticides) [2], about 10,000 various commercial dyes and pigments exist and over 700,000 tons are produced annually worldwide [3]. More than 600 organic and inorganic pollutants have been reported in water along with microbial populations. Among these pollutants, heavy metal ions are very dangerous due to their toxic and carcinogenic nature. Moreover, some metal

ions are not biodegradable or bio-transformable and, hence, exist in the environment for a long time. In general, water pollutants have been categorized into four groups: organic, inorganic, miscellaneous, and biological. Water pollution accounts for the deaths of more than 14,000 people daily [2]. Fig. 1 shows a classification of water pollutants.

According to the U.S. EPA (2007), the top toxins release inventory emitters to surface water by industry are shown in Figure 2 [4-5]. From an environmental point of view, the environmental benefits of reducing U.S. office paper use by 540,000 tons can protect about 11 billion gallons of wastewater – enough to fill 16,000 Olympic-Sized swimming pools. While 1.9 million tons of wood use, whose annual equivalent is 13 million typical trees [5-6].

In the last few years, many different conventional technologies have been applied to the removal of heavy metals and dyes from wastewater. These techniques include chemical precipitation, membrane filtration, ion-exchange, electrolysis, coagulation, solvent extraction, reverse osmosis, and electrocoagulation [7]. However, most of these mentioned techniques have their own advantages and limitations in application [8]. Most of them suffer from some defects such as incomplete removal of contaminants and are characterized by low selectivity, applications of high reagent, chemical and energy requirements, the generation of other toxic wastes that need to be handled carefully, and – even more important – high cost [9]. Conversely, biosorption was defined as the

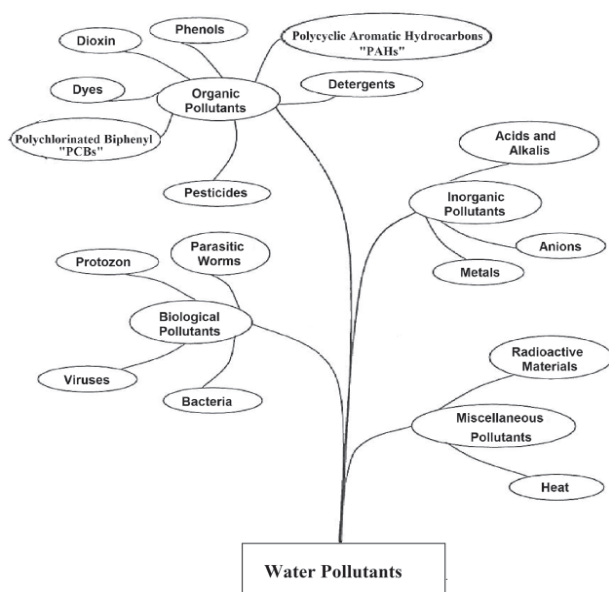
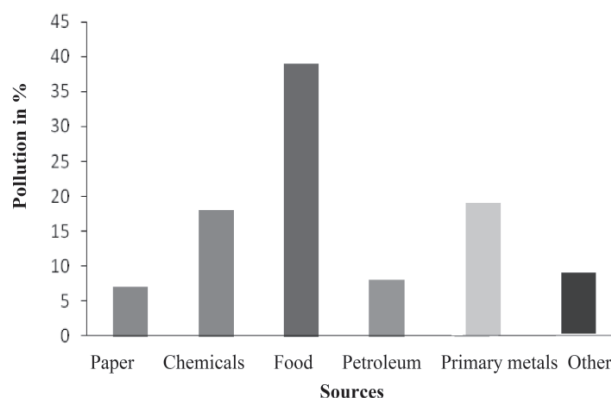


Fig. 1. Classification of water pollutants on the basis of their chemical nature [2].



removal of materials such as HM ions and SD molecules by inactive, non-living material or biological origin and has arisen as an effective alternative, a fine eco-friendly technology, and at low cost [10].

Fig. 2. Top toxins release inventory emitters to surface water by industry, 2005 [6].

Among all these mentioned techniques involving reclamation of industrial and municipal wastewater, adsorption is generally found to be a very promising one due to its high effectiveness and complete removal of metal ions even at low concentrations, and its low cost and easy adaptation and sorbent material separation from the aqueous phase after finishing treatment [11].

From an economical point of view, an economic sorbent is known as a sorbent that is abundant in nature and can be easily available, or is a by-product or waste from industry, has little or no economic value, and requires little or no processing. Agricultural residues, also called ligno-cellulosic biomass resource, are defined as a biomass by-product from the agricultural system and include stalks, leaves, seeds, shell, peels, husks, and straws. These wastes can be classified into two groups. One belonging to those residues remaining in the field after harvest or autumn season where leaves wither and fall, for example tree fronds [12] and oak tree (*L.*) dead leaves [13]. The other group can belong to by-products of industrial processing, for example date stones [14-15], olive stones [16], and tea leaves [17-18].

Carbonization of biomass has a number of advantages when compared with common biological treatments. It generally takes only hours (instead of the days or months required for biological processes), permitting a more compact reactor design. The high process temperatures can destroy pathogens and such potential organic contaminants as pharmaceutically active compounds that could be present, for example, in AR [19]. On the other hand, the preparation of activated carbon is usually conducted at relatively high temperatures in a conventional convective or conductive heating system. The thermal process may take a long processing time to reach the desired level of activation, which is also a considerable risk of overheating, leading to complete combustion of the carbon [20].

In the present article, the suitability of lingo-cellulosic bio-sorbents and AC derived from agricultural byproducts/wastes and their diverse availability as to provide alternative adsorbents for wastewater treatment has been reviewed. Besides, the purpose of this article is to review the available information on the various attributes of utilization of either the raw agricultural by-product/wastes or AC in treatment wastewaters. A number of case studies concerning the application of agricultural by-products/wastes as raw material and AC by a variety of researchers in providing effective adsorbents have also been covered as part of this review to make the reader aware of the importance of such materials. The main advantages of this review are:

- 1) Extensive review for the recycling of agricultural by-product/wastes as feedstock for the production of green and potentially low-cost adsorbents in one case as raw material and in the other as an activated carbon for use in wastewater treatment.
- 2) Showing a wide range of agricultural by-product/wastes could be used as renewable sources for the production of AC.

- 3) Another main advantage is that this review showed extensive studies with the aims of finding an alternative in the form of economic adsorbents for wastewater treatment.
- 4) A comparison between results done by several studies for enhancing contaminant uptakes by raw and activated carbon of agricultural by-product/wastes.
- 5) A new proposal design of packed bed column filled with potential adsorbent for the adsorption of HMs and SD from waste liquid at laboratories of universities, colleges, and research centers.
- 6) Showing that agricultural waste materials are an environmental issue of economic value, and the best way could be to solve the disposal and pollution problem of these wastes, which is recycling technology.

Adsorbent Resources

Recently, special attention has been paid for the utilization of the available-in-nature, abundant, and eco-friendly sorbents to replace the conventional and expensive sorbents based on economic and environmental point of views [21]. In name they are called ACs. These substances are mostly synthesized and developed by the pyrolysis of carbonaceous materials of plants and agricultural residues/wastes such as coconut shells [22], walnut shells [23], palm shells [24], date stones [14, 25], almond shells [26], spent tea leaves (STL) [17-18], and cotton stalks [27], followed by either physical or chemical activation of the chars obtained from them [12]. Other more economical materials have been studied for the adsorption of SD from synthetic wastewaters, replacing the AC. For example, they are represented by clay materials (bentonite, kaolinite), siliceous materials (zeolites, alunite, perlite), and industrial waste products (i.e., waste carbon slurries, metal hydroxide sludge, coffee wastes) [28-32]. The unavailability of such materials with the desired specifications can be an obstacle detaining its utilization.

On the other hand, plant and tree leaves, most available and abundant particularly in public gardens and woods, have been proposed and reported as being economical, suitable, and simple agro-adsorbents for the study of SD and toxic HM removal [17, 33-37]. Carbonization of these high-in-carbon content plant and tree leaves can also be used in production of AC [16, 38-39].

Expanding fruit production has naturally resulted in increased amounts of waste every year [40]. It was reported that in the world several million tons of agricultural wastes are being disposed of every year. In India alone more than 400 million tons of agricultural residue is generated annually [41], and it is estimated that the production of coir pith in India is 0.5 million tons, and coir pith is disposed of as a waste and its accumulation around coir-processing centers is creating a menace [42]. And about 3.5 million tons of tea are consumed worldwide [17].

The global production of dates was 7,429,811 tons in 2009 [40, 43], while 198,000 tons of date leaf are produced

each year in Tunisia [40, 44]. The main components of date palm leaves are cellulose 38.10%, hemicellulose 22.74%, lignin 11.95%, and ash 7.71% [45]. According to the United Nations Food and Agriculture Organization (FAO), tomato is the most widely grown product in fresh vegetables around the world with a production of 145.6 million tons, and a new nonporous carbon from tomato waste as a low-cost adsorbent has been prepared by Fuat et al. (2014) [46].

While 68 million tons of orange are produced globally according to FAO, the generation of orange waste is estimated to be in the range of 15 to 25 million tons – a big volume if these wastes are still dumped every year, which causes both economic and environmental problems such as high transportation cost, lack of dumping site, and accumulation of high organic content material [47]. Rice husk is the major by-product of the rice milling industry, accounting for almost 20% of rice production [48-49]. As rice plant is the main cereal crop in Malaysia with an annual output of more than 180 million tons, the production of rice husk is over 36 million tons [49]. Generally, farmers and rice processors often burn rice husk as wastes, and this is what releases carbon dioxide (CO₂) into the atmosphere [50]. Rice husks have been reported as a good sorbent of many metals and basic dyes [51], and the main components of the rice husk are cellulose 32.24% , hemicellulose 21.43%, lignin 21.44%, and ash content 15.05% [51].

Coffee fruit processing is one of the most polluting activities in agriculture due to the large amount of waste generated in the process. According to the International Coffee Organization, the production of coffee amounted to about 680 million tons in 2008 [52]. Part of the waste is used as fertilizer, but most of the coffee grounds are dumped or burned. Globally, coffee and tea as a beverage are the second most consumed by all citizens after water. In the last few years, the consumption of coffee has rapidly increased, especially by young people. According to a survey done by Sulyman (2016) [5], which included 25 cafes in the city of Tripoli, Libya, the average generation of coffee ground wastes by only the 25 cafes is estimated to be in the range of (36-45) tons annually, and a big volume of this waste is still kept in big plastic bags for disposal by conventional methods, which are burned or dumped. It is also estimated that in one of these cafes, more than 100 cups of coffee are drunk within an hour, while in the city of Gdansk, Poland, at one café that was surveyed, more than 1,600 cups of coffee are consumed daily. And the average of coffee ground wastes at the 25 cafés is estimated to be in the range of 72-90 tons annually. However, coffee grounds are carbonaceous and have the potential to be converted into an adsorbent. This conversion could contribute to reducing the volume of waste, while producing an adsorbent with a lower cost. Moreover, conversion may prevent the discharge of carbon dioxide – one of the causes of global warming [53]. It has been reported that the amount of carbon dioxide produced by the combustion of 1,000 g of coffee grounds is estimated to be 538 g [54].

On the other hand, the total primary production of sea plant *p. oceanicu* (L) in the Mediterranean basin alone has been estimated in the range of 5-50 million tons per year [55]. In the United States, about 30 million tons of oak leaves are collected and burned every year. A new activated carbon from oak l. dead leaves as low-cost adsorbent has been produced [13]. In India, national walnut production oscillates between 40,000 to 45,000 tons per year, and the process involved to obtain unshelled walnuts generates more than 25,000 tons of shell, and approximately 11,000 tons of almond shell waste every year [56].

Olive oil is nearly totally produced in the Mediterranean region. As the demand for olive oil is rapidly increasing worldwide, environmental pollution posed by olive mill wastes (OMW) such as olive cake is a growing problem. According to the International Olive Council (IOC, 2012), the provisional figures of worldwide olive oil production for 2010-11 is 3.019 million tons of olive oil – an increase of 45,000 tons (or 1.5%) over the previous season [57]. Olive mills generate a huge amount of waste accumulate around the olive mill, and it was reported that the 1,000 kg of olive fruit can produce about 350 kg of olive cake. Most of the farmers were not able to specify the quantities of olive cake generated from the extraction process, as olive cake is not stored but dumped near the olive mill facility; 93.1% of the olive husk produced is granted to farmers, who use it for heating after drying, as well as for animal feed. The remaining quantities are then dumped in open lands [57], the exhausted olive cake has a high lignin, cellulose, hemicellulose, and low content of ash, which were found to be 14.18%, 24.14%, 11.0%, and 2.36%, respectively [58].

Recycling of Agricultural By-Products/Wastes

So far in many countries all over the world, where the bulk of fruit and other food material is produced and consumed, a major proportion of their wastes are still carried to open areas for disposal by burning or dumping, and this releases a lot of toxic material and pollutants, as well as carbon dioxide (CO₂), to the environment. However, recycling such wastes as raw materials for producing activated carbon could be the better option for minimizing disposal landfills and pollution problems of agricultural by-product/wastes, and economically at the same time [5].

Sorbents such as AC can be manufactured from both agricultural by-products and wastes [16], in addition to industrial by-products and wastes [14], while sorbents in the form of unprocessed or semi-processed agricultural by-products/wastes such as dry plant leaves can be found in abundance in public gardens, national forests [13], and private farms [59] as a result of natural annual falling withered leaves in the autumn; they are also called forestry wastes. Waste or spent tea leaves are also known as low-cost biologically originated and have been recommended as novel adsorbents for the removal of toxic HMs such

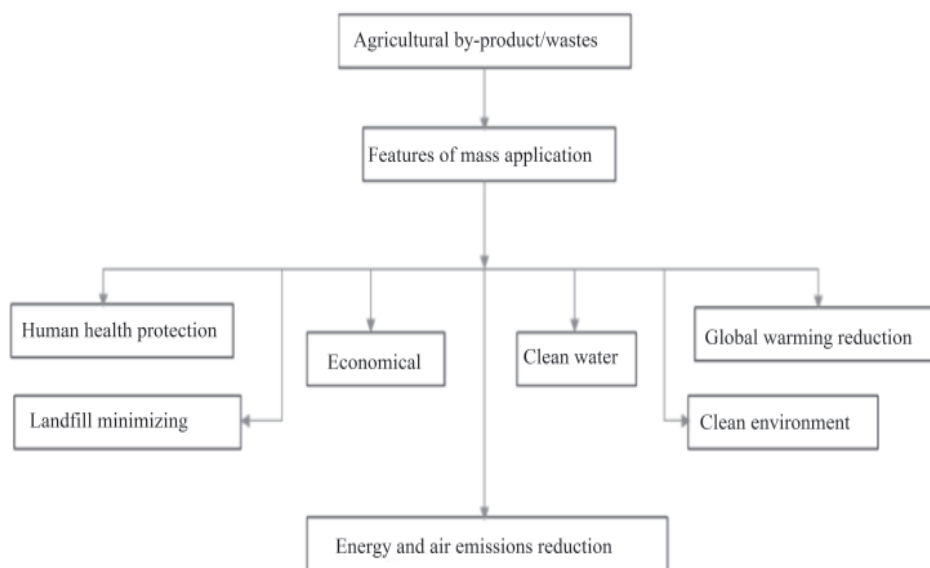


Fig. 3. Scheme representation of features of mass application derived from agricultural by-products/wastes [5].

as Pb(II) [60], Cu(II) [61], and some organic pollutants (e.g., pesticides, SD, etc.) [18, 62-66]. Fig. 3 shows the main advantage and predictable features of the mass application derived from agricultural by-products/wastes [5]. On the other hand, Figure 4 shows the possibility of recycling agricultural by-products/wastes as the main precursor to synthesize either AC through carbonization (track 1 in Fig. 4) or can be used as raw materials that need little or infrequently no processing (track 2 in Fig. 4). They afterwards can be used as adsorbents for different applications.

Applications of Agricultural By-products/wastes as Sorbents

Raw Agricultural By-products/Wastes as Sorbents

The by-products/wastes from some agricultural substances may be used as an alternative food resource for ruminant animals. There are many companies using a certain whole plant or parts of the plant for the production of a good quality usable product. However, they produce

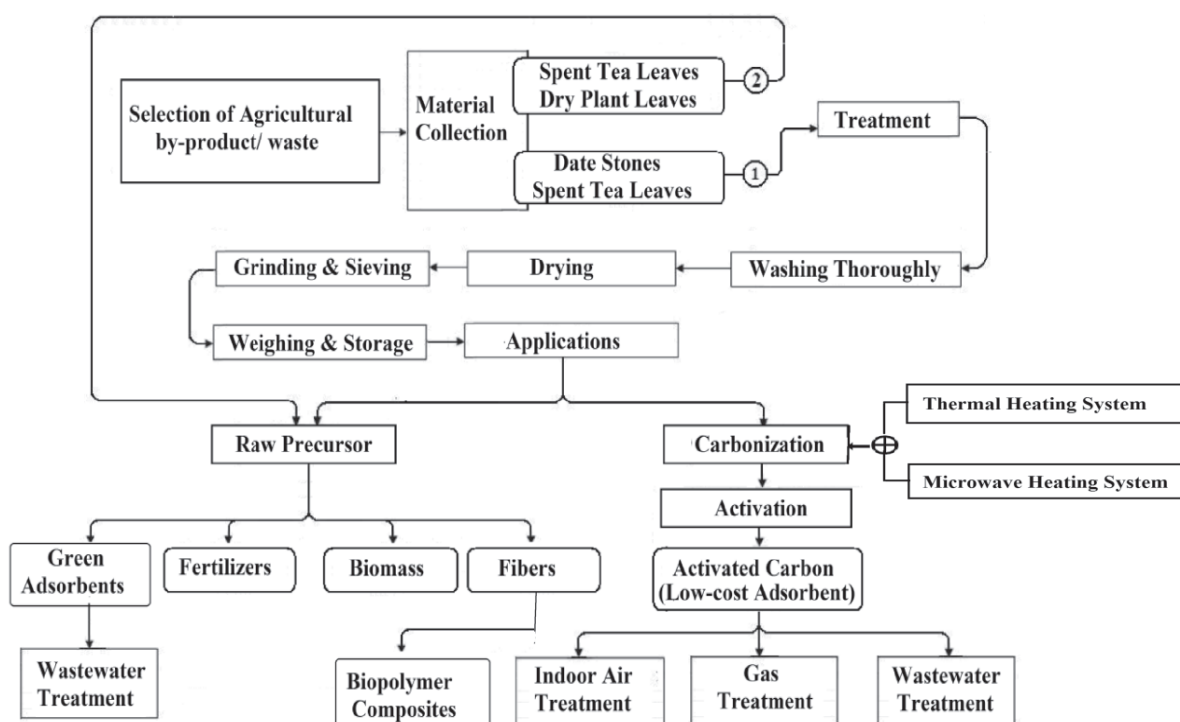


Fig. 4. Scheme of agricultural by-products/wastes recycling.

Table 1. Compilation results on the adsorption of various pollutants' raw agricultural by-product waste.

Sorbents	Pollutant sorbed	q _{max} , mg/g	Ref.
Potato peels	Ni(II)	13.09	[74]
Peanut shell	Cu(II)	25.30	[75]
Peanut shell	Cr(III)	27.86	[75]
Mango leaves	Cu(II)	15.77	[76]
Cello lignin wastes	Methylene Blue	95.2	[77]
Modified peanut shell	Hg(II)	30.72	[78]
Modified peanut shell	Cd(II)	14.17	[78]
Sunflower leaves	Cu(II)	89.37	[79]
Spent tea leaves	Zn(II)	79.76	[80]
Spent tea leaves	Methylene Blue	62.2	[39]
Raw coffee residue	Remazol Blue	232	[32]
Seaweed	Pb(II)	893	[81]
Oak sawdust	Methylene Blue	29.94	[82]
Mangrove plant leaf powder	Crystal Violet	200	[83]
Mangrove plant fruit powder	Crystal Violet	250	[83]
Mango leaf powder	Crystal Violet	200	[83]
Pine cone	Acid Blue 7	37.4	[84]
Walnut sawdust	Methylene Blue	59.17	[82]
Rice husk	Methylene Blue	40.6	[85]
Rice husk	Indigo Carmine	65.9	[86]
Spent tea leaves	Pb(II)	120.8	[80]
Spent tea leaves	Cu(II)	90	[62]
Orange peel	Pb(II)	204.50	[87]
Spent tea leaves	Cr(II)	47.98	[88]
Almond peel	Methylene Blue	77-118	[89]
Spent tea leaves	Ni(II)	18.42	[90]
Coconut bunch waste	Methylene Blue	70.92	[91]
Spent tea leaves	Methylene Blue	300.052	[65]
Spent tea leaves	Basic Violet 10	71.4	[92]
Spent tea leaves	Malachite Green	227.3	[93]
Wood apple shell	Methylene Blue	95.2	[94]

Table 1. Continued

Wood apple shell	Crystal Violet	130	[94]
Broad bean peels	Methylene Blue	192.7	[95]
Melon peel	Methylene Blue	333.33	[96]
Olive stones	Cd (II)	0.575	[97]
Olive stones	Phenol	333.3	[57]

large quantities of chaff that are eventually burnt. Apart from losing the economic value of the waste, a huge amount of capital is expended in disposing of it. In some countries, waste constitutes environmental hazards through inconvenient dumping or incineration. Leaves represent a part of the plant, and a good example of these agro-sorbents that need little (track 1 in Fig. 4) or no processing (track 2 in Fig. 4). They are attracting attention as simple and cheap methods for the removal of several metal ions [59, 67-68] and organic pollutants [12, 69]. Examples of these sorbents are *Posidonia oceanica L.* dead leaves [33], pine tree leaves [34], *Acacia nilotica L.* leaves [35], and tea leaves [17].

Some scientific reports show that a number of plant leaves (carob, cinchona, cypress, figs, guava, loquat, olive, oak, pine, pistachio, poplar, reed, sissy, walnut, and willow) can be used to remove zinc (Zn) from aqueous solution, and the maximum efficiency of Zn removal was found by walnut and poplar leaves at pH 6 with 82% [59]. Leaves of poplar were found to be effective in removing lead (Pb) [70], and copper (Cu) [71]. While removing cadmium (Cd) from aqueous solutions was found best with the use of reed leaves [72]. When a number of dry plant leaf residues (mulch) were used as adsorbents for the removal of Pb, Cd, and Cu from aqueous solutions, the efficiencies of these removals by these different dry plant leaves, at optimal conditions, were close to the efficiency of removal done by AC. However, the efficiencies of these dry leaves for the removal of the studied metals varied from one to another. The removal of metals was at maximum pH of 7.0 for Cd and 5.4 for Cu. The type of plant leaves processing also had an effect on the efficiency of metal removal, in that oven-dried leaves showed slightly higher removal efficiency of metal ions than the naturally dried leaves, based on a research study conducted by Salim and Abu El-Halawa (2002) [68].

In addition to the type of plant leaves and their processing method as factors effecting the removal of the polluting adsorbates (e.g., HM/SD), there are also several other factors such as pH, concentration of leaves, concentration of adsorbates, and the presence of competing ions that may affect the efficiency of removal. The effect of solution pH was evident at neutral pH for the most efficient adsorption of nickel (Ni) from polluted water using pine leaves [73], while the increase

in agitation time and the initial concentration of crystal violet (CV) and rhodamine (RHB) efficiently caused an increase in adsorption onto *Acacia nilotica* leaves [35]. An increase in temperature of adsorption reaction was very effective in the removal of CV from aqueous solution at only 60 min by STL [64]. Recently, several workers have reported that the agricultural by-products/wastes have the potential to be applied as alternative low-cost sorbents in the remediation of heavy metal contamination and dyes in wastewater. Table 1 shows applications of agricultural by-product wastes as adsorbents for wastewater treatment.

Internal Structure of an Adsorbent Derived from Raw Agricultural By-products/Wastes

It is well known that raw agricultural by-products/wastes usually contain polysaccharides of hemicellulose, cellulose, and lignin within their cellular constituents as major structural components. For this reason, they are called lignocellulosic substances. The structures of these biochemical substances in some parts are associated with a number of functional groups such as hydroxyl, methyl, and carbonyl groups. When such materials are ready as sorbents for their intended task (i.e., wastewater treatment), these functional groups become responsible for HM ion and SD molecules sorption [98-99]. For instance, plant leaves (i.e., STL) are agricultural residues and can be classified as one type of bio sorbent because they present lignocellulosic materials [98, 100-101]. The abundance of natural occurrences and the presence of large amounts of surface functional groups make various agriculture wastes good alternatives to those expensive commercial ACs [102]. It was shown that lignocellulosic substances have ion-exchange capacity and general sorptive characteristics, which both are derived from their biochemical constituent structure and polymers [103]. The polymers include extractives that are of small molecular size and available in little quantity, pectin, and protein in addition to the aforementioned components: cellulose, hemicelluloses, and lignin [98, 103].

STL represent one good example of an agricultural by-product/waste found in abundance, a low-cost adsorbent, utilized extensively in wastewater treatment, and that requires little or sometimes no processing. From this point forward in this article, STL has been chosen as a case study used and investigated as a novel sorbent for effective HM ions and SD removal from aqueous solutions/wastewaters.

Case Studies on Raw Agricultural By-product/Wastes

Spent Tea Leaves as Effective Sorbents

More than 3 million tons of tea leaves are produced worldwide annually [63] and it is consumed by a huge number of people, and only water is consumed by more people. It is estimated that somewhere between 18 and 20 billion cups of tea are drunk daily [5, 104]. After hot water is extracted from the leaves, the residual mass is of

Table 2. Some physical properties and chemical compositions of STL.

Physical properties (unit)	Value	Ref.
Moisture content (%)	12.3	[61], [64]
Pore volume (ml/g)	2.9	
Percent porosity (%)	75.0	
Specific gravity (g/ml)	0.28	
Specific surface area (m ² /g)	175.5	
Chemical compositions (%)		[106], [107]
Cell wall material	46.8	
Hot water-soluble polysaccharide-proteins	9.6	
Cellulose	37.2	
Lignin & structure proteins	14.7	
Hot water insoluble protein	12.1	
Polyphenols	25.0	
Carbon (C)	44.4	[61], [64]
Hydrogen (H)	6.4	
Nitrogen (N)	3.4	
Oxygen (O)	27.2	

no use and hence is disposed of [61]. Black tea, made from the mild oxidation of tea leaves, amounts to around 78% of the entire production, followed by green tea at 22%. Both of them, however, are obtained from basic tea leaves (*Camellia sinensis L.*) [105]. Some chemical and physical properties of spent tea leaves (STL) are shown in Table 2.

Sorption of toxic metals and organics on STL has been studied extensively in recent years due to their aforementioned advantageous properties. Among many studies published in scientific journals, the followings represent some examples of metal ions and SD removal.

Orhan and Buekguengoer (1992) [108] have investigated the removal of some metal ions such as Al ions from wastewater using STL, Turkish coffee, spent coffee, and nut and walnut shells as adsorbents in a batch mode experiment. Their results showed good adsorption potential for Al ions with removal efficiencies of 98%, 99%, 96%, and 96%, respectively.

A similar adsorbent was the aim of another research study achieved by Hadi (2012) [109] when he investigated the possibility of using STL in comparison with commercial AC for removing toxic hexavalent chromium ions Cr(VI) from synthetic wastewater using a batch mode experiment. The equilibrium experiments were carried out for 180 min. with the STL adsorbent dose range between 0.05 and 0.9 g, and 100 ml of Cr(VI) solution of initial concentrations ranged between 25 and 300 mg/l. In conclusion, the maximum adsorption capacities of Cr(VI) were 42.46 mg/g and 42.42 mg/g using STL and AC, respectively. Another extensive study carried out by Rafie (2012) [17] focused

on the use of a black STL for the removal of some HMs (Co, Cd, and Zn) from wastewater. The batch adsorption experiment was observed for the three HMs at 180 min. The results of the experiment showed that the rate of adsorption was affected by the process conditions such as initial metal concentration, adsorbent dose, solution pH, and contact time. The quantities adsorbed per half gram of STL at equilibrium (q_e) were 15.39 mg/g, 13.77 mg/g, and 12.24 mg/g for Co, Cd, and Zn, respectively.

A kinetic investigation was carried out by Hossain et al. (2005) [110] to evaluate the applicability of black STL as an adsorbent for the removal of Cr(VI) from aqueous solution in a batch mode experiment. They found that the adsorption of Cr(VI) occurred rapidly in the first 24 hr; then was followed by a slow process that required more than 10 days to reach its equilibrium. According to the experimental data, they also found that the initial Cr(VI) concentrations, pH, and temperature were very effective parameters on the rate of adsorption. An alkali-treated STL (AT-STL) was used as a novel adsorbent to remove Pb ions from aqueous solution. The investigation was reported by Yang and Cui (2013) [60], whose comparative study of Pb ion removal from aqueous solution onto AT-STL, green tea leaves (GTL), and green spent tea leaves (GSTL) was conducted. The study was carried out at room temperature by adding 0.1 g of the aforementioned three adsorbents into a number of 250 ml glass-stoppered conical flasks containing 100 ml of 50 mg/l Pb solution. The comparative study showed that AT-STL displayed a significantly higher removal rate of Pb ions than GTL and GSTL. According to the data obtained from the Langmuir model, the optimum adsorption capacity (q_0) for Pb was obtained with a value of 64.10 mg/g.

Tan (1985) [107] investigated the adsorption of Cu(II) by waste tea leaves and coffee powder using batch adsorption experiments. The results of the experiment showed that the tea leaves and coffee wastes are able to remove metal ions such as Cu(II) from solution. The extent of removal is a function of pH, ionic strength, metal ion concentration, the nature of waste substrate used, and the presence of other competing ions or molecules.

Zuorro and Lavecchia (2010) [111] have investigated the removal of Pb (II) from aqueous solution using green and black STLs in a batch mode technique. Batch adsorption experiments were made at 25 and 40°C at initial lead-ion concentrations between 0.01 and 2 g/l at 25°C and 40°C. The percent lead removal efficiency by black and green STLs was found to be 98.4% and 98% at 25°C, and 99.3% and 98% at 40°C, respectively. The experimental data fit the Langmuir isotherm model well, with maximum adsorption of 101 mg/g and 83.3 mg/g at 40°C for black and green tea leaves, respectively. The results of this study indicate that STL was more effective in removing Pb(II) than conventional adsorbents such as activated carbon.

In concern with the treatment of organic pollutants, SD is one large group that can pose an environmental problem when industrial effluents are not treated efficiently before being discharged to streams. Hameed (2009) [65] has

focused on the use of STL as a new non-conventional adsorbent for the adsorption of methylene blue (MB) dye solutions in a batch mode process at 30°C. As a result, the Langmuir isotherm monolayer adsorption capacity was found to be 300.052 mg/g. The adsorption removal of basic violet-10 dye (BV-10) from aqueous solution using black STL was the center of a research study conducted by Mohamed and Rahman (2013) [92]. Their equilibrium adsorption experiments were carried out at different temperatures at pH 6. According to the data obtained from the Langmuir model, the maximum amount of BV-10 adsorbed by the black STL was 71.4 mg/g at 30°C.

Similarly, adsorbent from agricultural by-product was the aim of research by Ramesh et al. (2014) [112], when they investigated the possibility of using the spent tea dust (STD) and raw coir pith (RCP) for the removal of methylene blue (MB) from aqueous solution using batch adsorption experiments. Batch experiments were carried out by placing 0.35 g of STD and 0.1 g of RCP separately in 100 ml of aqueous solution containing 25 mg/l of MB and then agitating the mixtures at 130 rpm with varying contact times from 2 to 240 min, pH range from 2 to 10. Separation of adsorbent and adsorbate was done by centrifuge at 4,500 rpm for 10 min. The effects of the contact time, adsorbent dosage, and solution pH were studied at 27°C. Based on the experimental results of this study, the following conclusion was drawn: the equilibrium adsorption was achieved in about 180 min with STD and 60 min with RCP, the optimal pH for favorable adsorption of MB is 7 by both adsorbents, and the adsorption capacities of STD and RCP were found to be 86.21 mg/g and 142.86 mg/g, respectively. They also concluded that spent tea dust and raw coir pith could be employed as low-cost alternatives to commercial activated carbon for the removal of dyes.

A kinetic evaluation on the adsorptive removal of malachite green (MG) was carried out by Abul Hossain and Hossain (2014) [113] to evaluate the adsorptive removal of (MG) by used black tea leaves (UBTL) as a low-cost adsorbent in a batch mode system. Their results showed good adsorption capacity of UBTL to MG at 227.3 mg /g at pH 6.0 and 30°C.

In contrast to the batch mode process, Joodi and Abbas (2014) [114] have investigated the applicability of STL as an adsorbent for the removal of phosphorus pollutant ions from water using different design parameters by a fixed-bed column adsorption process. The experimental adsorption unit was conducted in order to test phosphorus ion removal from simulated synthetic aqueous solutions (SSAS). According to the data obtained, the removal of phosphorus pollutant ions was very much possible by STL adsorbents. Besides, it was reported that the highest percentage removal of phosphorus ions from (SSAS) was 97.68%.

Another research study was conducted by Malko and Nuhoglu (2006) [115], when they used tea factory waste for the adsorption of Cr(VI) ions from aqueous solutions using a fixed-bed column. Experiments were carried out as a function of liquid flow rate, initial feed of Cr(VI)

concentration, particle size, feed solution pH, and bed depth. According to the data obtained, the maximum bed capacities for the tested flow rates were found to be 55.65, 40.41, and 33.71 mg/g at 5, 10, and 20 ml/min, respectively. When the initial Cr(VI) concentration is increased from 50 to 200 mg/l, the corresponding adsorption bed capacity appears to increase from 27.67 to 43.67 mg/g. Breakthrough volume varies with bed depth and the treated volume considerably increases from about 4,200 to 11,800 ml as bed depth increases from 5 to 30 cm.

A continuous flow mode study using a fixed-bed column of a 130 mm height and a 12 mm internal diameter (ID) was carried out to evaluate the efficiency of STL as a low-cost adsorbent for the removal of CV from its aqueous solution. According to the data obtained, the removal of CV was possible by STL and very efficient up to the breakpoint time of about 7 min., where the removal percentage accounted for 68, when CV concentrations, bed height, and flow rate were optimized at 30 mg/l, 20 cm, and 5 ml/min, respectively [18].

Different Adsorbents Derived from Agricultural By-products/Wastes

Biosorption of arsenic(V) by *Moringa oleifera* seed powder using a batch and continuous mode techniques was studied by Rajeswari and Pushpa (2014) [116]. Batch adsorption experiments were performed as a function of solution pH, biosorbent dose, contact time, and initial metal concentration. In addition, the effect of bed height (4 and 8 cm) and flow rate of 2 ml min⁻¹ and 5 ml min⁻¹ on the bio-sorption process by fixed-bed column was also investigated. The obtained results in this study showed that biosorbent dosage, pH, volume of solution, metal ion concentration, and contact time highly affected the biosorption of As (V), and the maximum break-through time of 320 min was achieved at the operating condition of 2 ml/min influent flow rate and bed height of 8 cm.

Today, rice husk (RH) is one of the low-value agricultural by-products that have been used as source raw material for the synthesis and development of new phases and compounds, as well as natural sorbents for many metals and basic dyes. The rice husk is in the either untreated, treated, or in modified form using different agents [5, 50].

Kulkarni and Kaware (2015) [117] have investigated the removal of metal ions in a packed bed adsorption column using rice husk as cadmium sorbent. It was observed that increasing the initial cadmium concentration from 10 mg/l to 50 mg/l decreased exhaustion time from 830 min to 570 min and break point time decreased from 330 min to 120 min. Also, with an increase in flow rate, exhaust time and break-through time decreased significantly. The optimum operating conditions (bed height, initial metal ion concentration, flow rate, and pH values) were found to be 50 cm, 30 mg/l, 60 ml/min, and 6, respectively. The adsorption efficiency was obtained as 69% for optimum conditions.

On the other hand, there were a number of studies that focused on fixed bed column study for the removal of heavy metals such as Pb(II), Cu(II), and Zn(II) from wastewater by sodium carbonate-treated rice husk (NCRH). The experimental results of these studies allowed for the following conclusions: the NCRH was found to be an efficient media for the removal of heavy metals from wastewater. The column having a diameter of 2 cm, with bed depth 10 cm, metal ions concentration 10 mg/l, and flow rate 10 ml/min could treat 2.28 l, 2.22 l, and 2.15 l of Zn(II), Pb(II), and Cu(II), respectively, at breakthrough. The results also reported that about 3.74 g and 3.90 g of NCRH were required per liter of Pb(II) and Cu(II) treatment, respectively [118-120].

George Z. Kyzas (2012) [121] studied the use of two types of coffee residues (treated and untreated) in removal of Cu(II) and Cr(VI) from aqueous solution. The effect of some parameter such as pH, initial metal concentration, contact time, and agitation rate on the rate of adsorption were investigated. Equilibrium data were fitted to the Langmuir, Freundlich, and Langmuir-Freundlich (L-F) models. According to the experimental data of this study, the conclusions are summarized as follows: 1) the best correlation factor (R_2) was found to be 0.998 for the (L-F) model, 2) the maximum agitation rate was found to be 140 rpm, 3) the pH selected as optimum adsorption experiments was PH 5.0, and 4) the optimum pH found after desorption experiments was pH 2 both for Cu(II) and Cr(VI).

Evaluation of coffee waste adsorbent for malachite green (MG) removal from aqueous solution was the purpose of another study conducted by Franca et al. (2010) [122]. The adsorbent was obtained by microwave activation system. The results of the experiment showed that the rate of adsorption was affected by the process conditions such as: adsorbent dose, solution pH, and contact time. This study indicated that spent coffee grounds present great potential as an inexpensive and easily available alternative adsorbent for the removal of cationic dyes in wastewater treatment.

Most of the adsorption research studies concerning the remediation of dyes have been conducted in batch modes, which are generally very easy to apply in the laboratory and limited to the treatment of small quantities of wastewater [123]. The data obtained under batch conditions are generally not applicable to most treatment systems, i.e., column operations, where contact time in batch mode is too short to attain an equilibrium state in column systems [124]. In fact, it is very necessary to run a continuous flow process when needed to obtain basic engineering data [36, 125]. Besides, the continuous flow process is a low reagent handling and accordingly very low in operating cost and has the ability to adapt to versatile processes [126-127].

Tea and coffee wastes can be also used as radioactive heavy metal adsorbents. However, a few studies have addressed the potential use of tea and coffee wastes for the extraction of uranium from aqueous solutions. Uranium extraction from aqueous solution using dried and pyrolyzed tea and coffee wastes was the aim of [128].



The maximum adsorption capacity of uranium by dried tea and coffee wastes was found to be 59.5 and 34.8 mg/g, respectively, at 291K.

Production of Activated Carbon

Background

Historically, porous carbons, especially activated porous carbons, constitute one of the most important types of industrial carbons and have been in use for thousands of years. Their use in water purification can be dated back to 2000 BC, when ancient Egyptians used charcoal to purify water for medicinal purposes. It was during World War I that a major development in the use of porous carbon began and there was no going back [129]. Newer and more technologies have since then developed both for the manufacturing and application of this versatile material [130].

In the 1940s, activated carbon was introduced for the first time as the main water industry's standard adsorbent for the reclamation of municipal and industrial wastewater to a potable water quality [2], while powder-activated carbon (PAC) was first produced commercially in Europe in the early 19th century [131].

Today, AC can be available commercially, and different grades are found at the markets [132], and the major sources for the production of commercial activated carbon are still from coal, asphalt, and petroleum coke. It has been reported that about 60% of the production of activated carbon globally is obtained from coal [5]. These commercial AC substances actually require complexing agents to improve their removal performance for contaminant matters. However, their high cost is the most limiting factor of their use as adsorbents [133]. Therefore, in the last few years the growing need of researchers to search for alternatives and develop low-cost AC adsorbent materials from cheaper and locally available agriculture-by products had to occur.

One main advantage of utilizing the agricultural (forestry) by-products/wastes is the ability to synthesize and produce cheap and eco-friendly AC as an alternative substitution for commercial AC, in addition to the ability of utilizing these precursors in the form of non-carbonized raw material in sorption processes. These agricultural by-products/waste materials usually have no economic value. They, as alternatives, may present a disposal problem leading to environmental pollution. In the case of forestry by-products/waste, a huge quantity of leaves fall down on the ground as a result of a natural withering at the autumn seasons and thus create piles in public gardens and national forests. Therefore, considerable economic value would be attained from the conversion of these waste materials into AC [18].

Carbon-containing materials such as agricultural by-products/waste are converted to AC through a process called activation, which is essentially composed of a two-phase process. Phase one requires a pyrolysis of

agricultural by-products/wastes such as wood, coal, peat, fruit stones, and shells. It is a burn off of amorphous decomposition products (tars) that work on freeing the pore openings and increasing the number of pores. While in phase two, the enlargement of pores in the carbonized material is achieved [134]. They are considered one of the feasible alternatives both in terms of environmental and economical points of view.

Carbonization Technologies

Historically, hydrothermal carbonization (HTC) was discovered by Bergius in 1913, and has been re-discovered and further developed under the direction of Professor Antonietti, director of the Department of Colloid Chemistry at the Max-Planck Institute of Colloids and Interfaces in Golm/Potsdam (MPI). HTC is now being mentioned as a promising technology to convert biomass into multiple bioproducts: a solid fuel compared to brown coal; liquid fuel or bio-oil; as a soil amendment to increase soil fertility and crop yields; carbon material that could be either activated to work as an adsorbent for water purification or CO₂ sorption and as a low-cost adsorbent or permeable reactive barrier for uranium(VI)-, copper-, and cadmium-contaminated waters; nanostructure carbon material, carbon catalyst, which could be used in the production of fine chemicals; and a carbon material that could increase fuel cell efficiency [135]. When compared to fermentation and anaerobic digestion, HTC is referred to as the most exothermic and efficient process for carbon fixation [136]. Therefore, HTC is now seen as a promising technology (also for CO₂ sequestration). In addition, some feed stocks are toxic and cannot be converted biochemically. Microwave technology is gaining importance as a promising technology for research and industrial applications [137]. Microwave heating offers a potential means of cost reduction as it is capable of reducing the heating period, energy consumption, and gas consumption. Additionally, microwave irradiation may promote rapid and precise temperature control and compact equipment size. However, there are very few studies that report the use of microwave heating for preparation of activated carbon [138].

Selection of Raw Materials for AC Synthesis

The nature of the precursor (in addition to the method of activation) has a strong influence on the porous structure and the adsorption properties of the resulting AC [139]. Therefore, the preparation of AC usually requires the selection of the appropriate raw material, which in turn implies the consideration of inexpensiveness, an increase in carbon content, and a decrease in inorganic content (i.e., low ash). The high density of the precursor represents a considerable importance that it contributes to enhance structural strength of the carbon. Sufficient volatile content is also important, since porous chars which are essential for making AC are produced as a result of the evolution



Table 3. Proximate and ultimate analysis of some low-cost adsorbents as reported in literature.

Adsorbent type	Characteristics								Ref.
	Proximate analysis (%)				Ultimate analysis (%)				
	FC	VM	Ash	MC	C	H	N	O	
Raw Bagasse	10.5	83.3	6.2	na	41.55	5.55	0.03	52.86	[140]
Bagasse AC	84.5	13.6	1.9	na	64.12	1.25	0.34	34.29	[140]
Raw Rice Husk	15.8	67.5	16.7	na	36.52	4.82	0.86	41.10	[140]
Rice Husk AC	62.8	11.8	25.4	na	54.75	1.31	0.50	18.04	[140]
Coir pith AC	34	53	11	12	no	No	no	no	[42]
Raw (<i>Jatropha curcas</i> L.)	37.2	55.4	6.30	0.68	45.50	7.20	4.00	43.30	[141]
Date palm leaf	9.7	68.0	15.2	7.1	40.8	6.0	0.63	35.2	[40]
Date palm rachis	8.3	73.6	6.0	12.1	39.8	5.7	0.19	43.0	[40]
Date stones	17.5	74.1	1.2	6.4	51.2	6.4	0.73	40.9	[40]
Raw tomato waste	12.8	82.67	1.58	2.95	59.84	8.79	4.08	27.03	[46]
Tomato waste AC	68.32	22.73	1.47	7.48	72.93	3.49	3.42	19.83	[46]
Waste tea	na	na	4.29	5.88	52.72	6.34	2.61	38.15	[142]
Coconut shell	na	na	na	1.43	88.18	1.32	0.40	9.87	[143]
Globe artichoke leaves	na	na	3.41	na	55.22	2.86	2.6	31.28	[144]
Oak cups pulp AC	na	71.0	6.7	11.5	48.91	6.85	1.31	42.81	[145]
Corn cob	na	78.7	0.9	4.3	46.8	6.0	0.9	46.3	[146]
Almond shell	na	80.3	0.6	10.0	50.5	6.6	0.2	42.69	[147]
Olive stones	42.90	na	2.36	27.21	na	Na	na	na	[58]

of volatiles during the carbonization step. One good example can be represented by softwood; an agricultural by-product/waste characterized by 40-45%, 55-60%, 0.3-1.1%, and 0.4-0.5 kg/l in respect to the contents of carbon, volatile matters, ash, and density. Raw materials used for the preparation of AC vary with their application. Conventional raw materials in order of their importance as porous carbon production capacity, characteristics, and market are: wood, coal, lignite, coco-nut shell, peat, and others [129]. Some characteristics such as proximate and ultimate analysis as well as surface area and pore volume for different low-cost adsorbents examined by several studies are presented in Tables 3 and 4.

Features of AC

Activated carbons are black solid substances, disordered, and microporous forms of carbon, with very high porosities and surface areas. They are one type of substance that comprise a large and important class of porous solids. Besides, they have found a wide range of technological applications – particularly in water treatment where such substances work on the removal of inorganic and organic pollutants. This AC unique versatility comes from its high surface area, porous structure, high adsorption capacity, and surface chemical nature, which

can be appropriately modified by physical and chemical treatments to enhance the extent of a given adsorption process [139]. This carbon can be partially oxidized when its pores need to enlarge. They resemble a granular or powdered charcoal and carbonaceous material [154] that has a porous surface structure, which provides it with a high surface area, harmlessness to the environment, and ease in operation [155]. They are characterized with an internal surface area of more than 400 m²/g and relatively high mechanical strength [154]. Activated carbon substances can be available in the form of either granular activated carbon (GAC) or powdered activated carbon (PAC). The GAC particle is almost greater than 0.1 mm in size (about the size of coarse sand) [14], while the PAC is composed of even smaller particles. Exact specifications vary, but GAC is generally said to have a larger internal surface area and smaller internal pores than PAC [154]. The PAC characteristic of fastness in adsorption rate made PAC more applicable in the past, but its difficulties in disposing and handling have made GAC a more popular alternative for most applications [154]. Experimentally, a comparative research study was carried out by Yadav et al. (2004) [156] using GAC and PAC as adsorbents for the retention of arsenic ions (As) from aqueous solution. The results of their analysis proved a much more adsorption capacity obtained by the GAC. Figure 5 shows the different

Table 4. Surface area and pore volume results of AC produced from low-cost materials reported in literature.

Source of AC	Properties				Ref.
	BET surface area (m ² /g)	Micropore volume, V _μ (cm ³ /g)	Mesopore volume, V _m (cm ³ /g)	Total pore volume, V _p cm ³ /g	
Sugarcane bagasse	1620	0.515	0.464	0.979	[148]
Banana frond	847	0.169	0.557	0.726	[149]
Tomato waste	722	0.201	0.275	0.476	[46]
Pumpkin seed hull	737.9	0.301	na	0.370	[138]
Globe artichoke L.	2038	0.608	1.80	2.466	[144]
(<i>Delonix regia</i>)	2854	1.44	0.16	1.60	[150]
Tea seed shells	1530	0.5989	0.1837	0.7826	[151]
Coffee ground	1021	0.350	0.950	1.300	[152]
Cotton stalk	594	0.280	0.030	0.381	[153]
Flamboyant pods AC	2854	1.44	0.16	1.6	[150]
Posidonio oceanic(L.)	1483	0.494	0.456	1.022	[55]
Olive stones	368.3	0.12	na	0.20	[57]

pore sizes and their estimated values in nanometer found within the AC granular; macro pores were more than 50 nm, meso pores 2-50 nm, and finally micro pore with less than 2 nm in value [157].

The characteristics of AC depend on the physical and chemical properties of the precursor (i.e., agricultural by-product/waste) as well as on the activation method applied (chemical or physical). The structural properties of the resulting AC can be affected by a number of factors, such as time of activation, temperature of activation, and the oxidizing agent used in addition to the starting precursor [158]. The adsorption capacity of the activated carbon for a specific adsorbate varies strongly with the type of raw material and the processing techniques used [159].

Methods of Preparation and Activation of Activated Carbon

The production of the AC initially involves dehydrating the natural carbon-containing precursors (i.e., agricultural by-products/wastes) followed by carbonization at slowly

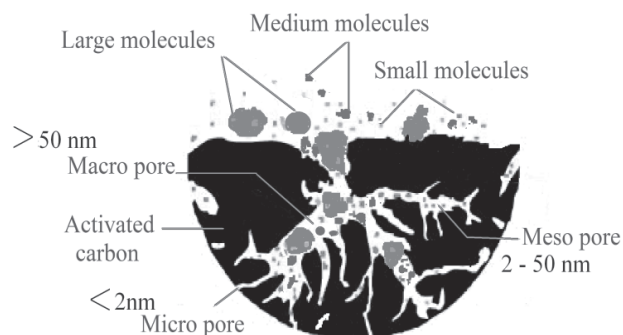


Fig. 5. Different pore structures of AC [157].

heating in the absence of air; it is also called pyrolysis. Next, the carbonized product is activated by either physical or chemical means; it is an important step to eliminate these in-pore deposited decomposed products and tars [134]. While the effectiveness of AC to act as adsorbents for a wide range of contaminants is well noted [160, 161], more and more research on AC modification is gaining prominence due to the need to enable ACs to develop an affinity for certain contaminants to outfit their removal from varying types of wastewater in the industries. It is therefore essential to understand the various factors that influence the adsorption capacity of AC prior to their modification so that it can be adapted to their specific physical and chemical attributes to enhance their affinities toward metal and inorganic and/or organic species present in aqueous solutions. These factors include the following: (i) specific surface area, (ii) pore-size distribution, (iii) pore volume, and (iv) the presence of surface functional groups. Accordingly, in terms of AC attainment, there are two famous basic methods for the preparation of ACs: physical and chemical activation [162].

Physical Activation: the source material is developed into activated carbon using hot gases. This generally is carried out by using one or a combination of carbonization in the presence of an inert gas to convert this organic precursor to primary carbon, which is a mixture of ash, tars, amorphous carbon, and crystalline carbon, and activation/oxidation where high temperature in the presence of carbon dioxide, steam is required [163]. Undesirably, in the step of carbonization, some decomposition products or tars are deposited in the pores.

Chemical Activation: Prior to carbonization, the agricultural by-product/waste is impregnated with certain chemicals, which is typically an acid such as H₃PO₄, a strong base such as KOH, and NaOH or a salt such as

ZnCl₂. This step is done to restrict the formation of tar; in this way a carbonized product with a well-developed porosity may be obtained in a single operation [139]. Then the agricultural by-product/waste is carbonized at lower temperatures (450-900°C). It is believed that the carbonization/activation step proceeds simultaneously with the chemical activation. It is also believed that the chemical incorporated to the interior of the precursor particles reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of the particle; in this way the conversion of the precursor to carbon is high, and once the chemical is eliminated after heat treatment, a large amount of porosity is formed [164]. Chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating the material. The chemical activation method presents many advantages over the physical activation method and therefore it has been employed enormously in many studies when the preparation of AC from agricultural by-products/wastes is concerned. It was reported that the major advantages of the chemical activation compared to the physical activation are lower treatment temperatures and shorter treatment times [141]. In addition, activated carbon obtained by chemical activation exhibits a larger surface area and better developed mesoporosity than physical activation. Figure 6 shows the process of activated carbon manufacturing [131].

Many scientific papers concern the different methods of AC preparation and can be available and documented in scientific journals. This paper is intended to represent some of them and make them recognizable to the readers. Date stone as an agricultural by-product/waste was selected by Yahia (2002) [15] for testing a physical activation technique. These precursors were first dried in the oven, ground, and sieved. Then ZnCl₂ is added to the sieved fraction. Trace of water is removed by heating in an oven and the impregnated stones are packed into long Pyrex tubes and placed in a furnace. After cooling, the final product is ground into a fine powder followed by washing thoroughly using water. Diluted HCl is added to the sample and let stand for 24 hr. Then the sample is filtered and washed with water again until the complete

disappearance of Cl ions in the filtrate. Yahia clarified that as very satisfying and anticipated results were attained using this method. In contrast to chemical activation, the most common method for the preparation of AC requires only one simple step, which is the heating treatment sometimes at a lower temperature than used in physical activation in the presence of some chemical agents.

A study was conducted by Zoulikha and Fatima (2008) to analyze the differences between a prepared AC from date stones by carbonization without the addition of an impregnating chemical and the same AC prepared by chemical activation with ZnCl₂ or KOH. According to the nature of the impregnating chemical, AC presented different porosities. Chemical activation with KOH and ZnCl₂ resulted in an AC product having mesoporosity. However, activation with ZnCl₂ developed microporosity more than activation with KOH. Chemical activation of the date stones with both chemicals (KOH and ZnCl₂) produced AC with a high specific surface area of 880 and 1,030 m²/g for samples impregnated with 3.52 mmol of ZnCl₂ and pyrolysed at 873 K and samples impregnated with 9 mmol of KOH and then pyrolysed at 1,073 K [139].

Carbon adsorbents prepared from Hulls of *S. alterniflora* were a targeted study carried out by Kunquan and Xiaohua (2009). They have reported a chemical activation of their stalks, which were initially crushed and sieved to 2 mm. The sample was impregnated with H₃PO₄ for 1 hr at room temperature. After drying, the sample was placed in a crucible and into a horizontal tubular furnace for carbonization at 250°C for 1.5 hr. The process was carried out under pure N₂ gas flow of 80 cm³/min. Temperature was subsequently raised at a rate of 10°C/min until it reached 700°C, where it was maintained for 2 hr. Based on data results, the process was very satisfying in obtaining efficient AC [165].

Hassan et al. (2011) [12] have found that in order to optimize the surface area of AC derived from Saudi Arabian date tree frond waste, the highest value of 1,139 m²/g surface area was obtained by the use of 60% concentration of H₃PO₄ as the most favorable concentration among 0.0%, 20.0%, 40.0%, and 80.0%. In contrast, the surface area of raw date fronds at 0.0% concentration of (H₃PO₄) was 4.6 m²/g. The results of thermo-gravimetric analysis (TGA) have revealed that the best temperature for activation was 400°C. Authors have concluded that any temperature above this might affect the production of AC with a high surface area.

However, Hourieh et al. (1997) have studied the effect of ZnCl₂ concentrations on the characteristics of AC derived from pistachio-nut shell. In this study, pistachio shells were chemically activated using ZnCl₂ as an oxidizing agent and then physically activated by CO₂ passed through water. As a result, ACs produced from pistachio shells treated with 40% ZnCl₂ and 40% HCl at room temperature and then activated at 900°C for 90 min had higher surface areas of: (i) 3,256 m²/g of Brunauer-Emmett-Teller (BET) surface area, (ii) 3,822 m²/g of Dubinin-Radushkevich (DR) surface area, and 1.36 cm³/g of DR micropore volume. In contrast, it was found

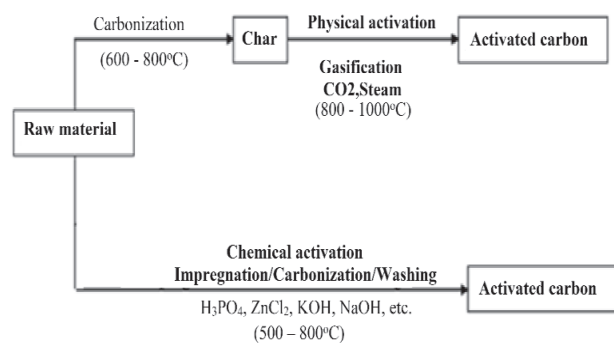


Fig. 6. Scheme of the process of activated carbon manufacturing [131].

that the AC produced from pistachio shells treated with 40% NaCl and activated at 900°C for 90 min had 3,895 m²/g of BET surface area and 5,235 m²/g DR surface area and 1.86 cm³/g of DR micropore volume [166]. It was concluded that AC prepared from pistachio shells may be used for both gaseous and liquid adsorption applications, depending on the different activation conditions [167].

Foo and Lee (2010) have prepared AC with relatively high surface areas of 190 m²/g and pore volume of 0.0950 cm³/g from *Parkia speciosa* pods and concluded that these two attained surface area and pore volume of the produced AC were greatly dependent on the carbonization temperature; 600°C was the most appropriate among temperatures ranging from 450 to 650°C. They also added that AC preparation was also dependent on mass ratio of acid to precursor; mass ratio of 1:1 was more favorable than 1:2. However, the yield of the final product decreased as the carbonization temperature increased [168].

Application of Activated Carbon

Different physical forms of activated carbon are produced depending on their application among these forms, the two most common forms are granular (GAC) forms to be used in adsorption columns and powder (PAC) forms for use in batch adsorption followed by filtration [131]. The main adsorbent used in industry is the activated carbon, which is involved in many fields such as separation of minerals, water, air, and gas purification (i.e., cigarette filters, motor vehicle exhaust controls), pollution treatment, de-colorization of tanning industrial wastewater, de-odorization of vegetable oils and fats, and food and pharmaceutical industries [16, 162, 169]. Activated carbon has been also used for gold and silver recovery and application as a catalyst and catalyst support.

In general, the primary application of activated carbon can be categorized into two groups of gas and liquid phase adsorption. Removal of colour, taste, and undesirable organic impurities from water has been one of the common liquid phase applications of activated carbons [170-172]. The reasons for making AC adsorbents widely used in the treatment of wastewaters is that these substances are characterized with exceptionally high surface areas that range from 500 to 1,500 m²/g, well-developed internal microporosity structure as well as the presence of a wide spectrum of surface functional groups [173]. As an inert porous carrier substance, it is capable of distributing chemicals on its large hydrophobic internal surface, thus making them accessible to reactants [132]. They can be found in radioactive protection in nuclear plants [174]. In recent years, several scientific papers, technical works, reports, and literature reviews have focused on the utilization of AC derived from agricultural by-product/wastes for the adsorptive removal of HMs and SD from contaminated water. It was reported that more than 5,000 and about 6,500 works have been published for the removal of dyes and HMs, respectively [5, 175].

Adsorption

Adsorption is one of the separation methods for contaminant removal. The process is described as the adhesion of atoms, molecules or ions of gas, liquid, or solid on a surface material [176]. There are many advantages of adsorption, among which are the low space requirements for batch and continuous fixed bed units, simplicity of design and ease of operation, non-pollutant to water, no odor emissions, and the low cost of the adsorbent [57]. The adsorption process is generally classified as physical adsorption or chemical adsorption. Physical adsorption is achieved by Van der Waals forces, dipole interactions, and hydrogen binding. There is no electron exchange between adsorbent and adsorbate. Because there is no activation energy required for physical adsorption, the time needed to reach equilibrium is very short. Physical adsorption is a non-specific and a reversible process. While chemical adsorption results from the chemical link between adsorbent and adsorbate molecule, therefore it is specific as well as irreversible and chemical as well as electronic properties of adsorbent are changed. The binding between the adsorbent and adsorbate by covalent bond is called weak chemical adsorption, and that by ionic bonds is called strong chemical adsorption [131].

Adsorption Mechanisms

The adsorption process of the adsorbate molecules from the bulk liquid phase into the solid (adsorbent) phase is described by the following four steps:

- 1) The mass transfer of the adsorbate molecules across the external boundary layer toward the solid particle.
- 2) Adsorbate molecules are transported from the particle surface into the active sites by diffusion within the pore-filled liquid and migrate along the solid surface of the pore.
- 3) Solute molecule adsorption on the active sites on the interior surfaces of the pores.
- 4) The molecule gets approached inside the pores of the adsorbent as presented by Fig. 7.

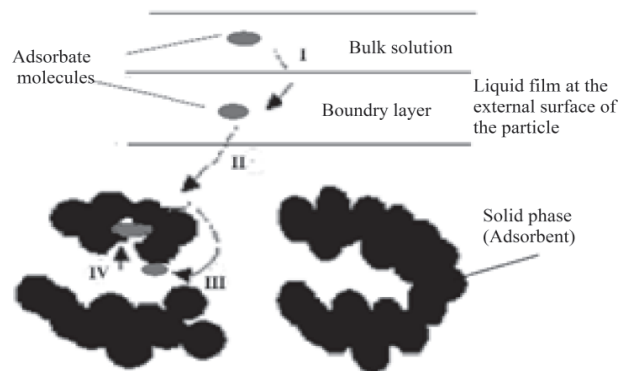


Fig. 7. Scheme of the mechanism of molecule adsorption using microporous adsorbent [177].

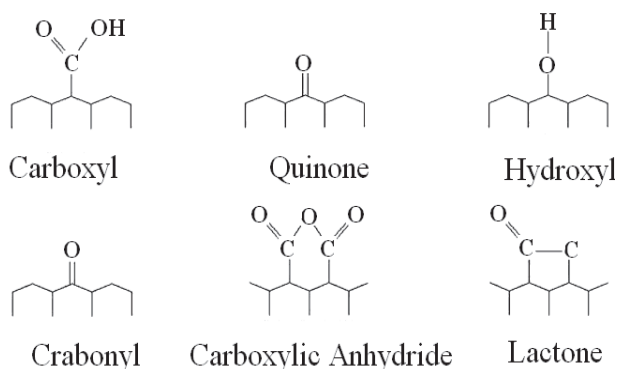
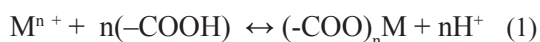


Fig. 8. Simplified schematic of some acidic surface groups bonded to aromatic rings on AC.

In contrast, an adsorption process occurs by a chemical link between the substance being absorbed (i.e., HM ion, Pb (II)) and the adsorbent (i.e., AC), which usually in this case is pre-exposed to some chemical modifications to create some surface functional groups (i.e., acidic functional groups); the ones shown in Fig. 8 are the predominant types of surface functional groups [161, 178]. And thus in adsorption, these functional groups hold the absorbed substance much more strongly, requiring much more energy to release the absorbed substance.

A cation exchange reaction is shown for a chemically modified AC, a cation exchange reaction occurs due to certain mechanisms where the metal cation exchange site with hydrogen ions previously was attracted as a whole carboxylic group. The carbon substance is with specific functional groups that are essential for the adsorption of heavy metal ions (i.e., Pb(II), Cu(II), Mn(II), etc.) due to the chelating attribute of these groups where alkaline-earth metal cations can be integrated with the groups to form complexes as indicated in the following equation [132, 178-180].



Some published reports pointed out that the sorption of HM/basic SD ions from solution sometimes is a mixed process involving more than a single species, and usually more than one species is being adsorbed into more than one type of surface site [181]. And the type of reaction often involved as a mechanism for the sorption of these HM/SD ions is chemical, which is actually a reaction between the functional groups on the sorbent and the HM/SD ions, or cation-exchange reaction (Fig. 9) due to the high cation-exchange capacity (CEC) of the sorbent [182]. Besides, some other mechanisms which may also be involved in the sorption of HM/SD ions are such as transport in the bulk of liquid phase, diffusion across the liquid film surrounding the solid particles, and diffusion into macro-pores or micro-pores has been shown in Figure 7. The chemical reaction for the adsorption of HMs onto a solid substance is described by the following simple equation [183]:

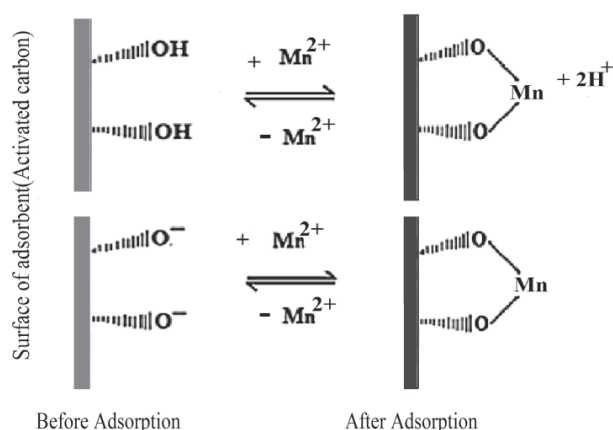


Fig. 9. The surface functional groups and the reaction of sorption [184].



...where M is the metal-named sorbate, S is the solid sorbent, and MS is the metal-solid sorbent complex.

A new nonporous carbon from tomato paste waste (TWNC) for the removal of crystal violet (CV) from aqueous solution was prepared by Fuat et al. (2014) [46], which shows a possible mechanism for adsorption of CV onto TWNC as shown in Fig. 10.

On the surface of the AC sorbent primarily the sorption follows two mechanisms: chemisorption and physical adsorption. The amount of sorbate (M) that AC sorbent can accumulate is a key parameter for process engineering design. This capacity is determined by engineering an equilibrium sorption isotherm [181, 185] and has found

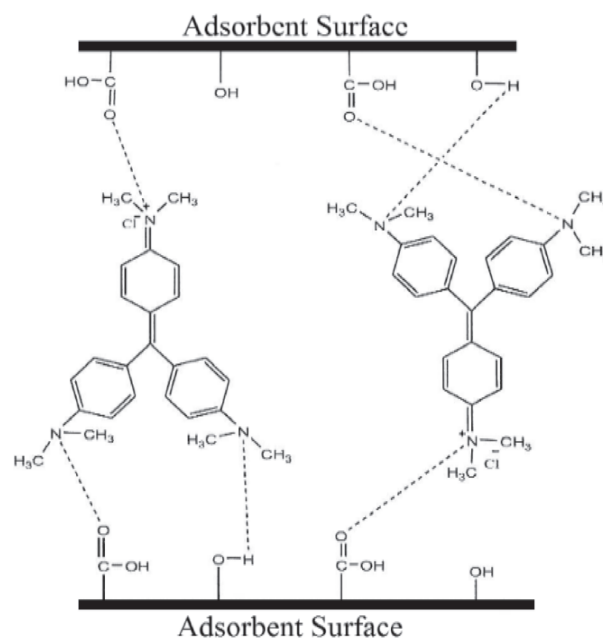


Fig. 10. Binding mechanism for the adsorption of CV molecules onto TWNC [46].

out that surface complexation, ion-exchange, diffusion, and precipitation of metal carbonate can be considered as other possible mechanisms. The significant differences between the amounts of metals desorbed from phosphoric clay suggest differences in their sorption mechanisms. Bio-sorption of HMs by non-living biomass of microbial or plant origin is a novel technique for the removal of these pollutants from aqueous solution. Due to unique chemical composition biomass sequesters the HM ion by forming complexes from solution [182].

The types of mechanisms occurring in AC and their mystery have been uncovered by the availability and utilization of very high tech instrumentations. Fourier transform infrared spectroscopy (FTIR) studies of adsorption demonstrated the main adsorption groups to be considered for the AC are carboxylic acid, phenols, pyrones, and the aromatic structure of the graphene layer. On the other hand, due to the cationic properties (i.e., MB), its charge is delocalized throughout the chromophoric system, although it is probably more localized on the nitrogen atoms [186].

Fig. 11 shows the mechanisms that may happen in the process of MB removal by an AC. The mechanisms were divided into electrostatic interactions (mechanism I), hydrogen bonding formation (mechanism II), electron donor-acceptor (mechanism III), and π - π dispersion interaction (mechanism IV) [150]. While there has been a different study regarding biologically modified AC, the study has involved the utilization of x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy (FTIR). They both uncovered the mysterious type of mechanisms involved in the adsorption of HMs on biomass of *Padina Sp.* and *Sargassum Sp.* before and after adsorption. They have indicated the functional groups in the cell wall of the biomass involved in bivalent metal bio-

sorption, including carboxyl, ether, alcoholic, and amino groups. Sulfonate groups did not play a major role in the binding bivalent ions [183]. Once again, through the utilization of FTIR techniques, Alexandro et al., (2011) in their research study aimed to investigate the adsorption of MB onto AC produced from flamboyant pods (*Delonix regia*). They concluded that the functional groups present in the FT-IR spectra of AC, MB, and MB adsorbed onto AC allowed assessing the adsorption of MB, such as the SEM images. The mechanisms of electrostatic interactions, hydrogen bonding formation, electron donor-acceptor, and π - π dispersion interactions confirm that different interactions may occur in the MB-AC system.

Batch Mode and Fixed-bed Column Techniques

The adsorption process of some undesirable polluted materials such as HM and SD on the ACs can be carried out in a laboratory using either batch mode or fixed-bed column adsorption techniques. Batch laboratory adsorption studies provide useful information on the application of adsorption to the removal of specific pollutant constituents. In contrast, continuous column studies provide the most practical application of the adsorption process in wastewater treatments [154]. As stated in some scientific studies [187], the continuous adsorption process is more applicable and suitable in real water treatment industries due to its low operating cost and the ability of columns to adapt to versatile processes.

While batch reactors are easy for researchers to use in laboratory studies, they definitely are less convenient for pilot-scale work (i.e., industrial applications) [188]. Most of the reported studies on the adsorption of dyes (as well as HM) by AC were conducted in batch mode techniques [123, 187]. The sorption capacity of the sorbent, obtained from the batch equilibrium experiment, is useful for providing fundamental information about the effectiveness of the sorbate-sorbent system. Nevertheless, the data obtained from such a technique cannot in general be applicable to most treatment processes (i.e., the column process), as the contact time in batch process is not enough to attain equilibrium in continuous flow process [124, 126]. A schematic diagram of batch sorption is shown in Fig. 12 [95], where the effluent contains $V(L)$ of water and initial pollutant concentrations of C_0 , which is to be reduced to C_1 in the adsorption process. In the treatment stage, $W(g)$ adsorbent (pollutant-free) is added to the solution and the pollutant concentration on the solid changes from $q_0 = 0$ (initially) to q_1 . The mass balance for the pollutant in the single-stage is given by the following:

$$V(C_0 - C_1) = W(q_0 - q_1) \quad (3)$$

Under equilibrium conditions: $C_1 \rightarrow C_e$ and $q_1 \rightarrow q_e$
Then:

$$(VC_0 + Wq_0) = (VC_e + Wq_e) \quad (4)$$

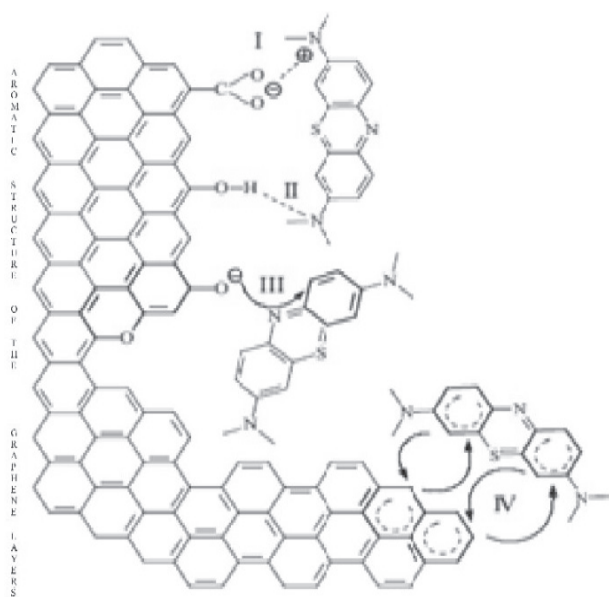


Fig. 11. Interaction mechanisms between MB and AC systems [150].

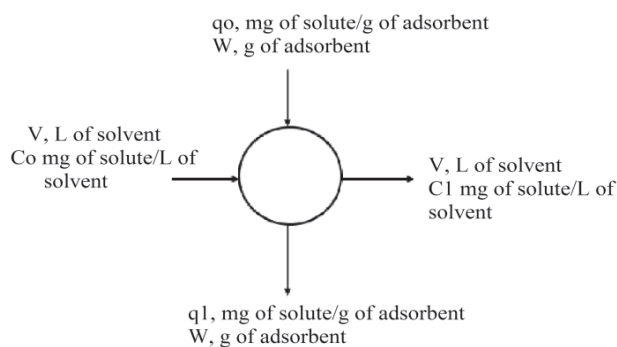


Fig. 12. A single-stage batch adsorbent [95].

And finally:

$$W/V = (C_0 - C_1) / q_e = (C_0 - C_e) / [(Q_0 b C_e) / (1 + b C_e)] \quad (5)$$

In contrast, the fixed-bed columns (Fig. 13) are widely used in various chemical industries because of their simple operation. Besides, with the high volume of wastewater to be treated, as compared to batch mode treatment, the continuous treatment is a lot more time efficient [187]. The fixed-bed column technique is used to determine the experimental breakthrough curve. A number of scientific articles have demonstrated that fixed-bed column adsorptions using AC have been applied to remove organic contaminants for many years with very satisfying results [33, 36, 187, 189]. The reason for this is that the accomplishment of high adsorption capacities in equilibrium occurs with the influent concentration rather than the effluent concentration. In batch mode adsorption studies (static mode), the same solution remains in contact with a given quantity of the AC adsorbent. However, the adsorption process continues to proceed until reaching equilibrium between the solute concentration in solution and the solute adsorbed (i.e., SD) per unit weight of the AC adsorbents. In this case, equilibrium is static in nature, as it does not change further with time. Nevertheless, in dynamic column adsorption, the solution continues to enter and simultaneously leave the column, and equilibrium

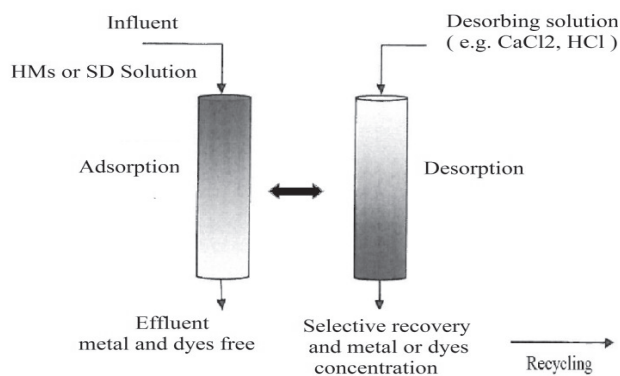


Fig. 13. Fixed-bed column sorption system principle (adsorption and desorption) [191].

will never be reached at any stage or time. Equilibrium has to be continuously established, as each time it meets the fresh concentration and hence equilibrium in column mode is termed as dynamic equilibrium [190].

Affecting Factors on the Rate of Adsorption

The number of physical and chemical factors that play an important role in the adsorption processes and influence the adsorption capacity of potential adsorbents during the adsorption process cannot all be conveniently shown here in this review paper. However, some studies chosen from literature were projected to demonstrate how strongly the efficiencies of these adsorbents are influenced by the physical and chemical characteristics of the solutions. The following paragraphs will represent the most common and effective factors.

Effect of Solution pH

The pH value of the aqueous solution is an important controlling parameter in the adsorption process of HM/SD using either batch mode process or fixed bed column. These pH values affect the adsorbent surface charge, the degree of ionization, and speciation of adsorbate during adsorption [192]. In general, the adsorption of most metals on AC adsorbents increased with the increase of pH [193-194]. This was attributed to the fact that, at low pH (< 4), the protonation of the active sites at carbon surface was enhanced and this refused the formation of links between cationic metals and protonated active sites. Some authors have reported that at higher pH, metal complex forms and results in precipitation and therefore the separation may not be due to adsorption [195-196].

Effect of Agitation Speed and Contact Time

Equilibrium time is a very important element to study when considering an economical wastewater treatment application [197]. Simply put, there are three stages (phases) for the sorption process as follows: in the initial state the sorption process is very rapid and the rate of removal is higher because of the large amount of adsorbate attached to the sorbent within the first period time of adsorption. For the higher sorption rate at the beginning, this can be attributed to the presence of a larger surface area represented by the adsorbent and the availability of free active sites at the beginning time for the adsorption of adsorbate. After this period, as the contact time increases the sorption rate gradually becomes relatively slower and at some point in time, reached a constant value where no more adsorbate was removed from the solution (transition phase). Finally, the process attains plateau state (saturation phase). The lack of free active sites on the adsorbents at this time was the reason behind this behavior.

A number of research studies have also obtained similar results. Some of them have concluded that the

results of the effect of exposure time for CV adsorption under shaking onto *Chaetophora alga* showed a rapid rate of adsorption in the first 3.0 min, and the equilibrium state was attained almost after 15.0 to 20.0 min [198]. Other comparable results were obtained by the adsorption of some basic dye onto *Citrullus Lanatus Rind* [199], and the adsorption of CV from aqueous solutions using different natural materials [83]. In addition, Cengiz and Cavasl (2010) [200] and Awala and Jamal (2010) [201] have also obtained almost similar results by the adsorption of methyl violet (MV) onto dead leaves of *Poisdonia Oceanica* and by the adsorption of methylene blue (MB) onto feldspar respectively. The equilibrium has occurred by agitation at 130 rpm during contact time of 20 min, leading to a sorption percentage of 87.8%. In terms of time creating the equilibrium, the data obtained can be obviously seen as shorter in contact time than in the batch process conducted at 90 rpm [13]. In the process of dye colour adsorption, initially the dye molecule has to first encounter the boundary layer effect and then it has to diffuse from the boundary layer film onto adsorbent surface and then finally it has to diffuse into the porous structure of the adsorbents. This phenomenon will take relatively long contact time [202]. Therefore, a higher agitation speed will be required to improve the diffusion of the adsorbate toward the surface of the adsorbent.

Effect of Flow Rate

When dealing with optimizing the operating conditions of the continuous treatment of wastewater on an industrial scale, the flow rate of such influent wastewater is a very essential parameter to evaluate [36]. In general, the effect of flow rate on sorption of adsorbate material (i.e., dye molecules) onto adsorbents by varying the flow rates, while all other parameters keep constant at optimum values. The breakpoint time, as well as sorption efficiency of adsorbate, were lower at higher flow rates [18, 36, 187, 203]. It is clear that rapid uptake is noticed in the initial stages of flow rate and the rate of uptake starts to decrease thereafter and finally reaches saturation. As increasing the flow rate of the pollutant influent solution, the breakpoint curves become steeper and reach the breakpoint time faster to lower. This is attributed to the fact that as the flow rate becomes higher, the contact time between the adsorbate solutes and the adsorbent is minimized in time, and hence the adsorbate molecules do not have enough time to uptake the binding sites on the adsorbent surface or diffuse into the pores of the adsorbents, causing the adsorbate solutes to leave the column before equilibrium to occur and breakpoint time to be reached earlier. These results were corroborated with a number of reported findings [203-205].

Effect of Initial Adsorbate Concentrations

The effluents of different industries may have different dye concentrations. The initial dye concentration is one

of the important factors that affect adsorption kinetics [199]. In a batch mode experiment planned for the study of kinetics of CV adsorption from aqueous solution using different agricultural by-products, Satish et al., (2011) [83] have proved that percentage sorption of CV from aqueous solution decreased but the amount of CV adsorbed per unit mass of adsorbent (mg/g) increased with the increase in CV concentration. They declared that a driving force created by the initial CV concentrations was the important factor to overcome all mass transfer resistance of the CV between the aqueous and solid phases. Therefore, a higher initial dye concentration of CV dye will definitely encourage the sorption process. In a similar mode technique, the effect of the initial MB concentration on the adsorption rate by coconut bunch waste (CBW) at adsorbent dosage of 0.20 g and mixing speed of 100 rpm has been investigated by Hameed et al. (2008) [95]. During their study, the adsorption at different concentrations was rapid in the initial stages and gradually decreases with the progress of adsorption until the equilibrium was reached. The amount of MB adsorbed at equilibrium (q_e) increased from 30.42 to 65.55 mg/g as the concentration was increased from (50 to 500 mg/L). But the MB percentage removal decreased from 57 to 13%. They declared the same conclusion of Satish et al. (2011) about the role of the driving force created by the initial concentration.

In a continuous adsorption mode process, the effect of initial concentrations of the adsorbate on the continuous adsorption process by varying the concentrations, while all other operating conditions kept constant, can attract attention that the breakpoint and exhaustion times would decrease. This result was obtained in literature dealing with the removal of basic red 46 by granular activated carbon [187], the removal of crystal violet (CV) by *Citrullus lanatus rind* [199], and the removal of (CV) by STL [18]. The findings were attributed to the increase in the driving force made by the increase of the influent adsorbate concentration, leading to quick saturation of the adsorbent active sites, which in turn lead to fast breakpoint and exhausted times, as corroborated with the clarification made by Goel et al. (2005) [206], Kandaswamy and Sirkrishna (2013) [36], and Abbas et al. (2012) [207]. The percentage of adsorbate removal is the highest at lowest initial adsorbate concentration. This is due to the slower transport caused by decreased diffusion coefficient or decreased mass transfer coefficient and the effect of a low concentration gradient [187, 208]. The slower transport gives the adsorbate molecules more time to bind to the adsorption sites, thus increasing the removal efficiency and leading to slow breakpoint and exhausted times.

Effect of Bed Height

The effect of bed height on sorption of adsorbate material onto adsorbents has been well studied by a number of investigators [36, 209-210]. It was observed that the breakpoint time, as well as sorption efficiency of adsorbates, were both lower at lower bed height. Experimental studies indicate that the breakpoint and

exhaustion times increased with the increase of bed height of the adsorbent [18, 36, 187]. As the bed height increased, the adsorbate molecules would have more time to contact with the adsorbents, which in turn would result in a higher adsorbate molecule removal efficiency in the column. Besides, the increase in the bed height leads to a decrease in adsorbate solution concentration in the effluent at the same time. On the other hand, the slope of the breakpoint curve was decreased with increasing bed height, which resulted in a broadened mass transfer zone.

The mass transfer zone (MTZ) is a band within the fixed bed length along which the adsorption takes place. MTZ extends from the influent end toward the effluent end of the adsorbent bed. The activated carbon behind the MTZ is completely saturated with adsorbate at $C_e = C_i$ [57, 211-212]. The length of the mass transfer zone is defined as L_{MTZ} . When $L_{MTZ} = \text{bed depth}$, it becomes L_{CRIT} , or the theoretical minimum bed depth necessary to obtain the desired removal (ACE, 2001). In general, it is desired to have short MTZ in fixed bed adsorption. Smaller particle size of the adsorbent, higher diffusion coefficients, and high strength of adsorbate adsorbent bonding (large capacity) reduce the length of MTZ. For ideal adsorption, MTZ is considered negligible and the system has plug flow behavior [211]. Figure 14 demonstrates the movement of (MTZ) in fixed bed and development of the breakpoint curve.

Hamdaoui (2006) [209] and Vijayaraghavan et al. (2004) [213] have both stated that with the increase in bed height, the mass of the adsorbents increase and thus the surface area would also increase, which in turn provides an increase in the active binding site numbers, leading to a larger sorption capacity. Foo and Hameed (2012) have both stated that at lower adsorbent bed height an axial dispersion phenomenon predominates and reduces the diffusion of adsorbate molecules [210]. Similar findings were obtained in research studies: one dealing with the removal of CV by *Citrullus lanatus* rind and *Cyperus rotundus* [36], and the other dealing with the removal of acid blue 92 and basic red 29 dyes by *Euphorbia antiqorum* L AC using a packed bed column [203].

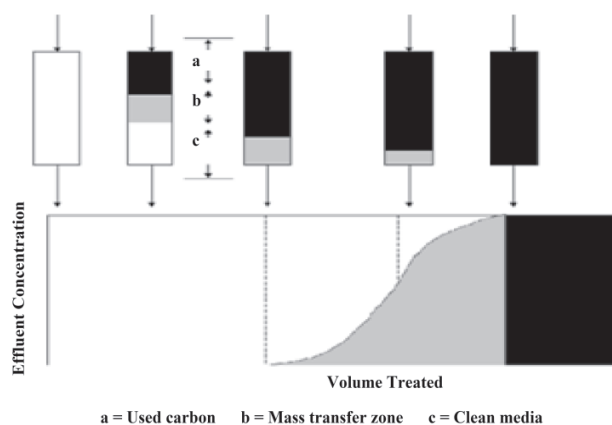


Fig. 14. Mass transfer zone and breakpoint curve in fixed bed adsorption [212].

Effect of Adsorbent Dose

On the other hand, when dealing with the batch mode technique, the amount of adsorbents (concentrations) is always and theoretically considered as a correspondent to the bed height factor. The percentage of adsorption increased with increases in adsorbent dosage, but the amount of molecules adsorbed per unit mass of adsorbent decreased [13]. As the amount of adsorbent increases, this definitely enhances the increase in the number of adsorption sites and thus increases the adsorbent surface area. A similar conclusion was stated in literature dealing with the removal of CV by *Chaetophora elegans* alga [198], adsorption of CV using different natural materials [83], and the removal of Pb(II) from aqueous solution on AC and modified AC prepared from dried water hyacinth plant [214]. In addition, Ashly and Thirumalisamy (2012) [35] and Bharathi and Ramesh (2012) [199] have also both obtained almost similar results from adsorption of CV and Rhodamine B (RHB) onto *Acacia nilotica* leaves, and a basic dye onto *Citrullus lanatus* rind, respectively.

Effect of Particle Size

The particle sizes of adsorbent materials is an important parameter in the adsorption process. For example, powder activated carbon (PAC) was better than granular activated carbon (GAC) in terms of metal adsorption capacity due to its larger pores and faster adsorption rate [215]. The larger pores of PAC allow by entrance the additional removal of these metals from their aqueous phase to take place, as Nadeem et al. (2009) [216] reported by applying three adsorbent particle sizes of 0.25, 0.149, and 0.074 mm. Sorption is directly related to available surface area; hence the adsorbent with highest surface area (i.e., the lower particle size of 0.074 mm depicted as maximum removal percentage). The authors also attributed the result to PAC larger pores, permitting HMs to be more quickly adsorbed inside internal sites and thus fully occupying these active sites. Satish Patil et al., (2011) also reported that the adsorption capacity of CV dye decreased with particle size increases, and hence the percentage removal of dye also decreases when they using different natural materials as adsorbent for adsorption of CV dye [83].

Case Studies on AC Derived from Agricultural By-product/Wastes

AC has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media. It is a widely used adsorbent in the treatment of wastewater due to its exceptionally high surface areas, well-developed internal microporosity structure, and the presence of a wide spectrum of surface functional groups [173]. Today, the major sources for the production of commercial ACs are still from coal, asphalt, and petroleum coke. But commercially available activated carbon is very expensive. Furthermore, regeneration using solution produces small

additional effluent while regeneration by the refractory technique results in a 10-15% loss of adsorbents and its uptake capacity [217-218]. Also, these sources are non-renewable and contribute to the high cost in the preparation of activated carbon [217]. It was reported that about 60% of the production of activated carbon globally today is obtained from coal [174]. Humphery and Keller (1997) estimated worldwide sales of AC at \$1 billion [161, 219]. Producing inexpensive AC is one of the main challenges in commercial manufacturing [220].

Always of prime concern is the cost of AC, which is considered the cheapest adsorbents, and the cost per pound of AC prepared from agricultural by-product/waste is about \$2 (20 times less than the cost of zeolite) [221]. Then, the conservation of the environment clean and free from pollutants can also be of great concern. A moral step is put into consideration when scientists produce cheap AC to avoid the landfill disposal by agricultural wastes. When AC adsorbent material is obtained from low-cost and locally available agricultural by-product/wastes, it is considered an excellent alternative, especially when used for the treatment of wastewater for the removal of HM ions and SD molecules. These ACs have been successfully employed as an adsorbent for the removal of dyes by various researchers. For instance, a remarkable research study was conducted by Sulyman et al. (2014) [13], when they took advantage of carbonizing the waste leaves of *Quercus robur l.* oak trees; their withered leaves created piles of waste at public gardens and in national woods. The carbonized leaves were used for the removal of CV dye from an aqueous solution. The data obtained showed high removal efficiency, and the equilibrium state could be achieved in 20 minutes for different initial CV concentration. Finally, the adsorption process followed Freundlich isotherm with a linear regression value (R^2) of 0.9937.

It is, therefore, essential to provide readers with understanding the various factors that influence the adsorption capacity of AC prior to their preparations so that it can be synthesized to their specific physical and chemical attributes to enhance their affinities toward SD/HM species present in aqueous solutions. These factors include specific surface area, pore-size distribution, pore volume, and the presence of surface functional groups. In general, it has been reported that the adsorption capacity increases with specific surface area due to the availability of adsorption sites while pore size and micropore distribution are closely related to the composition of the AC, the type of raw material used, the degree of activation during the production stage, and the frequency of regeneration [222].

Activated carbons derived from agricultural-by products/wastes present comparable adsorption capacities and in some cases even better than those of commercially made AC. It was evident that adsorbents, soybean hulls modified by citric acid, maize bran, orange peel, and chitosan coated on acid-treated palm shell charcoal, coir pith, coir pith AC, and oil palm shell AC have all demonstrated outstanding removal capacities as follows: [Cr(VI), 154.90 mg/g], [Pb(II), 142.90 mg/g], [Ni(II),

158.00 mg/g], [Cr(VI), 154.00 mg/g], [Ni(II), 91.60 mg/g], [Cd(II), 93.40 mg/g], and [Pb(II), 95.20 mg/g], respectively [223]. These adsorbents were found to have superior metal adsorbing capabilities when compared with commercial activated carbon (CAC), which had adsorption capacity as follows: Cd(II), 146.00 mg/g; Cr(VI), 145.00 mg/g; Cu(II), 15.47 mg/g; Pb(II), 41.00 mg/g; and Zn(II), 20.00 mg/g [224]. Therefore, the low-cost adsorbents from agricultural by-products/wastes are good for substituting the very expensive commercial ones, and it is a great chance for those developing countries in particular which face numerous challenges that sometime restrict investments geared toward preserving the environment. Anirudhan and Radhakirshnan (2008) have demonstrated the adsorption of Cu(II) from aqueous solution using Tamarinda fruit shell TFS in the presence of (N, N'-methyl bis-acrylamide) as a cross-linking agent. Results showed that the obtained adsorption data (R^2) at different temperatures has fit better with the Langmuir model than the Freundlich model. Copper (Cu(II)) ions adsorbed on TFS as a monolayer adsorption, and the increase of the adsorption capacity was followed by an increase in temperature [225].

Early in 1994, Srivastava et al. carried out an experimental work showing the adsorption of Pb(II) and Zn(II) ions onto lignin – a bio-material found as a waste product in paper factories. Their data analysis showed that the adsorption capacity of lignin for both ions was 1,865 mg/g and 94.83 mg/g at 40°C, respectively. Data also proved that those high adsorption capacities were a result of functional groups' presence on the surface of lignin. Besides, it was also concluded that since the adsorption capacity was increasing with temperature increase (from -26.17 KJ/mol at 30°C to -28.47 KJ/mol at 40°C for Pb(II) and from -32.49 KJ/mol at 30°C to -36.79 KJ/mol at 40°C for Zn), it demonstrated that the process was endothermic [226].

An adsorption study of mercury Hg(II) from aqueous solution was studied by Namasivay and Kadirvelu (1999) using AC prepared from an agricultural by-product of coir-pith. The adsorption capacity of coir-pith carbon was 154 mg/g at pH 5.0 [44].

Njoku et al. (2013) have investigated the feasibility of using pumpkin seed hull as a potential raw precursor for preparation of mesoporous AC (PSHAC) by micro-wave-assisted KOH activation and a carbonization temperature of 750°C for the adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) using a batch technique. The Brunauer-Emmett-Teller (BET) surface area was estimated to be 737.90 m²/g. The adsorption isotherm in this study was analyzed by the non-linear Langmuir, Freundlich, and Temkin isotherm models. The data analysis showed that the adsorption of 2,4-D onto PSHAC was best represented by the Temkin isotherm model, with a maximum monolayer adsorption capacity of 260.79 mg/g. The experimental result has also led to the conclusion that the solution pH played a key role by regulating the surface properties of PSHAC and the degree of ionization of 2,4-D, with the highest adsorptive uptake in the acidic medium [138].



Nasehir et al. 2011 have investigated the feasibility of using rice husk as a potential raw precursor for preparation of activated carbon (RHAC) $ZnCl_2$ activation and a carbonization temperature of $700^\circ C$ for the removal of Cu(II) from aqueous solution using a fixed-bed technique. The adsorption data in this study were fitted to three well-established fixed-bed adsorption models, namely the Adam-Bohart, Thomas, and Yoon-Nelson models. The results fit well to the Thomas and Yoon-Nelson models with correlation coefficient of $R^2 \geq 0.96$, with a highest bed capacity of 34.56 mg/g [49].

Another paper investigating the adsorption properties of activated carbon prepared from pecan shells (PS276a) was studied by Reyad et al. (2002). This paper discusses the use of pecan shells as a raw material for the production of an activated carbon using a novel activating technique. This study also showed that the activation using phosphoric acid (H_3PO_4) followed by sodium hydroxide (NaOH) treatment produces a carbon (PS276a) with a large adsorption capacity toward solutes in aqueous solution. This adsorption capacity has been compared with that commercial adsorbent resin. A maximum adsorption of Cu(II) and Sr(II) onto PS276a was found to be 95 mg/g and 180 mg/g at pH 3.6 and 8.5, respectively [159].

An AC derived from agricultural by-products/wastes was also studied by Madhava et al. in India (2009), where they have focused on synthesizing AC from hulls of the very widespread tree in India: *ceiba pentandra* (ACCPH) and *phaseolus aureus* (ACPAH). These AC from ACCPH and ACPAH were used for removing mercury (Hg(II)) from aqueous solutions. Their experiment demonstrated that the adsorption process had removal capacities of 25.88 mg/l and 23.66 mg/l , respectively, at an initial concentration of Hg of 40 mg/l at pH of 6.0 and contact time of 60 min. They concluded that adsorption behavior of both AC types was explained on the basis of its chemical nature with more sulphonic functional groups, and adsorbed doses of 200 mg/50ml for the first. In contrast, the adsorption using AC from the ACPAH tree was effective at pH 7 and contact time of 100 min, and the adsorbed dose required by the second was 250 mg/l [227]. Similarly, Cheap AC from agricultural by-product/waste was also the aim of another research study achieved by Kadirvelu et al. (2001), who investigated the feasibility of using AC from coir-pith being discarded as waste from coir processing industry, for the treatment of radiator manufacturing plating industrial effluents. The AC was expected to remove a number of HMs (Cu, Hg, Pb, Cd, and Ni) from wastewater. The results showed that the adsorption of the studied HMs increased with the increase in pH from 2 to 6, and thereafter remained constant up to pH 10 [228].

The olive stone, a predominant product of the Mediterranean countries, has been utilized by Gharaibeh et al. (1998) in treatment of polluted water, instead of being a landfill disposal. The stones, when carbonized, have shown successful adsorption for a number of pollutants in aqueous solutions. They showed a better adsorption capacity of 128.20 mg/g toward Cd(II) ions than any

reported results [229].

Another research study was conducted by Abudaia et al. (2013) when they used raw date stone materials for the synthesis of AC for the adsorption of Cu(II) and Pb(II) ions from aqueous solutions. Powder activated carbon (PAC) showed higher adsorption capacity and rate compared to GAC. Adsorption process data revealed that the initial uptake of both HMs was efficient at pH 6.5, and rapid and equilibrium was achieved within 30 min time for both forms of AC. The optimum parameters for this study were 50.0 mg/100ml of Cu(II) and Pb(II) concentrations, and around 1.0 g/100 ml of AC dose. The removal efficiency of Cu(II) and Pb(II) by PAC was 83% and 91%, showing preference over GAC, which had a removal efficiency of 76% and 82%, respectively [14].

Activated carbon adsorbent from agro-forestry waste was the aim of a research study achieved by Hesham et al. (2012). Their study focused on the preparation of AC in the form of PAC and GAC from such different local agroforestry wastes as marula fruit stones, jackalberry seeds, eembe seeds, efukwa shells, and eembu seeds. The AC was expected to remove HM ions such as Pb(II) and Zn(II) and dyes such as methylene blue (MB) and methyl orange (MO) from wastewater. Phosphoric acid of 50% concentration was used for chemical activation of carbons obtained. Another aim of this study was the comparison of all carbons produced to commercially PAC and GAC forms. Table 5 shows the obtained results [158].

The pore size of AC can also be essential for researchers to consider when needing to pick an AC for use. Activated carbon must have pores larger than the largest molecule (i.e., HM/SD) to be adsorbed. However, AC is characterized with a broad range of pore size, which makes it more applicable than any other adsorbents (i.e., zeolite). The affinity of the AC adsorbent for some types of substances can be much greater than the affinity for others.

Table 5. Comparison of all carbons produced from different agro-forestry wastes for commercial PAC and GAC.

Type of AC	Form of AC	Percentage Removal (%)			
		Zn(II)	Pb(II)	*MO	**MB
Commercial AC	Powder	90	100	92	84
	Granular	89	100	87.5	92.2
Marula fruit stones	Powder	0.0	--	84	83
	Granular	--	100	78	--
Jackalberry seeds	Powder	0.0	100	--	84.4
	Granular	--	--	--	83
Eembe seeds	Powder	60	100	--	81.3
	Granular	0.0	--	--	--
Efukwa shells	Powder	60	--	84	--
	Granular	--	--	--	--
Eembu seeds	Powder	60	100	84	--
	Granular	91	100	87	81.25

Note: * = Methyl Orange, ** = Methylene Blue

As a result, when there is a stronger affinity for some of the molecules, the molecules having lesser affinity either get held with a smaller adsorption capacity or get released in favor of the molecules for which the affinity is greater. Activated carbon, which is neither fully hydrophobic nor hydrophilic, retains some adsorption area with affinity for both polar and non-polar molecules. Humidity and the presence of water molecules from the surroundings has a noticeable effect on AC because of this.

In many cases while conducting experiments, it can be noticed that desorbing of substances from AC occurs as steam condenses and the water displaces the substance. The affinity has to be considered as part of selecting the particular adsorbent. Carbon needs to be replaced every six months to five years, or when there is a bed fire, even though the replacement of other adsorbents such as zeolite is very rare. The frequency of replacements depends on the type of carbon, the frequency of regeneration, and the temperature at which it operates. The maximum temperature for desorption is less confining for AC, which may be taken to a much higher temperature (121.11°C to 176.67°C) without melting. Carbon frequently catalyzes oxidation reactions when the temperature gets above this range [221].

On the other hand, there have been a number of studies that focused on the preparation and characterization of AC from waste tea (WTAC) using different activating agents for the adsorption of dyes from aqueous solution [230-233]. For instance, an AC produced from waste tea leaves with a novel activating agent such as potassium acetate for the sorption of acid blue 25 (AB25) dye in a batch mode technique was conducted by Auta and Hameed (2011). Their experimental studies showed that the rate of adsorption was found to be effected by the processing conditions such as initial dye concentration, contact time, temperature, etc. The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models were tested and the adsorption of AB25 dye onto WTAC was fitted to the Langmuir model and maximum adsorption capacity was found to be 203.34 mg/g [230].

Gao et al. (2013) have carried out experimental work demonstrating the utilization of tea (*Camellia sinensis* L.) seed shells for the preparation of AC for the adsorption of (MB) dye in a batch mode technique. Their data analysis showed the following: a high yield of 44.1% of AC was obtained with the chemical activation method using $ZnCl_2$; the surface area (Brunauer-Emmett-Teller (BET)), of the obtained AC was found to be 1,530.67 m²/g; the equilibrium adsorption results were compile using the Langmuir isotherm model and its maximum monolayer adsorption capacity was 324.7 mg/g for MB [151].

In a comparative study, Chandra et al. (2008) investigated the adsorption behavior of Pb(II) from aqueous solution system onto (GAC, derived from Agricultural by-product/wastes) using batch mode and continuous mode in a packed bed column. Their experiment was carried out at constant temperature, dimension of column, and packed bed of GAC with variation of flows through the bed and concentration of Pb(II) solution. Results showed the

effectiveness of such a process with adsorption capacity of 2.0132 mg/l feed concentration of Pb(II) at a hydraulic loading rate of 12 m³/hm² and 0.6 m bed height, indicating that practical adsorption capacity using column bed of GAC is far less than batch mode results [154].

Gamzenur et al. (2013) investigated the adsorption properties of activated carbon prepared from brewed tea waste (TWAC) [234]. The activated carbon from a household waste is carried out by microwave activation using potassium carbonate (K_2CO_3) as a chemical activating agent. The phenol was selected as a model solute in the study in order to evaluate the efficiency of the adsorbent tea waste activated carbon. Phenol adsorption studies were performed by the batch technique to obtain equilibrium. According to the experimental results of this study, the following conclusions were drawn: The surface area of the obtained waste tea activated carbon was 971.27 m²/g, and the adsorption data of TWAC was fitted with the Freundlich isotherm model with a high regression coefficient of 0.9831. All the results of this study also showed that brewed tea waste can be a suitable candidate for use as an activated carbon precursor, and microwave activation with K_2CO_3 yields carbon with good adsorptive properties.

Carbonized green tea (CGT) was effectively utilized by Muhammad et al. (2013) for the synthesis of AC, which was further utilized as an adsorbent for the removal of Remazol Brilliant Yellow (RBY) dye in a batch mode technique. Based upon the experimental results of this study, the following conclusions were drawn: CGT had the potential to be used as low-cost adsorbents for the removal of RBY, the equilibrium time period for removal of RBY onto CGT adsorbents was 7.0 hrs, and the maximum removal of the RBY dye occurred at pH was 9.5 [190].

Activated carbon materials were produced from used coffee grounds (CGCs) by chemical and physical activation using KOH and CO_2 . Maximum specific surface area (SBET) value was found to be 1,971 m²/g (Nobuhito, 2014). A similar adsorbent was the aim of another research study achieved by Jahin (2014) when he investigated the possibility of removing methyl red (MR) from aqueous solutions using chemical activation with concentrated H_2SO_4 , followed by carbonization at three different temperatures (400, 500, and 600°C). Batch experiments were carried out as a function of initial dye concentration, contact time, adsorbent dose, and pH. Results showed that the maximum adsorption of MR dye by coffee residue occurred at pH 10, and the removal efficiency was increased by decreasing the dye concentration and increasing the adsorbent dose [235].

Another work also used coffee waste for the production of AC by chemical activation using phosphoric acid and then carbonized respectively at 600°C and 700°C for 60 min. Based on the experimental results of this study, the following conclusions are drawn:

- The activated carbon obtained at 600°C and 700°C over one hour (5°C/min) in the presence of adjuvant percentage of about 5.678 and 12.78% gave respectively specific surfaces of 176 and 186 m²/g.

- The resulting adsorption capacities were respectively 52.63 and 55.56 mg/g.
- The adsorption is compatible with Langmuir and Freundlich models with a correction factor $R^2 > 0.92$.
- Adsorption equilibrium was reached after 40 min [236].

Agricultural by-product in Egypt ranged from 30-35 million tons annually, of which only 7 million tons are used as animal feed and 4 million tons as organic manure,

rice husk ash production by open-field burning and by combustion at 1,000°C for 4 hr was conducted by Abdel Rahim and his coworkers (2015). Their results revealed that higher growth rates and larger crystals had been obtained by combustion at 1,000°C and the occurrence polymorphs of silica. Activation of rice husk ash with (3.5 N NaOH), followed by the acid deposition technique, resulted in high silica in the agglomerate form with dimensions of 7 nm and the particle shape distribution was found to be

Table 6. Comparison between results of several studies for enhancing contaminant uptakes by AC.

Activated carbon type	CT, °C	BET, m ² /g	q _m , mg/g	Pollutant type	Ref.
Rosa canina seeds	500	799.2	47.2	Methylene Blue	[239]
Banana frond	700	847.66	11.09	Boron	[149]
Globe artichoke L.	500	2038	780	Methylene Blue	[144]
Posidonia oceanic L.	873	1483	270.3	Methylene Blue	[55]
Tea seed shells	500	1530.67	324.7	Methylene Blue	[151]
Brazilian pine- fruit-shell	850	1436	328	Procion Red MX 3B	[240]
Spent tea leaves	450	134	256.4	Malachite Green	[233]
Tomato paste waste	500	722.17	68.97	Crystal violet	[46]
Waste tea	760	830	200	Cibacron yellow	[233]
Mango seed	500	1667.8	-	Methylene Blue	[241]
Rock Melon	400-650	38.77	14.28	Cu(II)	[242]
Rock Melon	400-650	38.77	5.62	Ni (II)	[242]
Rock Melon	400-650	38.77	3.38	Cd (II)	[242]
Date stones	650	495.71	147.09	Phenol P-Nitro	[243]
Date stones	600	495.71	179.62	Phenol	[243]
Date stones	550	-	148	Methylene Blue	[15]
Date stones	550	950	149.9	Pd(II)	[244]
Date stones	600	950	91.3	Cd(II)	[244]
Olive Stones	600	920	303	Methylen Blue,	[245]
Olive Stones	600	920	217	Rhodamine B Congo,	[245]
Olive Stones	600	920	167	Red liste	[245]
Olive Stones	400-850	953-1383	-	Hg(II)	[246]
Eucalyptus. Bark	500	1239	-	Cu(II), Pb(II)	[247]
Ziziphus spina-christi seeds	700	914.23	172	Mn(II)	[248]
Alkaline impregnated hazelnut shell	838	10.1	39.54	Cu(II)	[249]
Ceiba pentandra hulls	200	521	25.88	Hg (II)	[227]
Ceiba pentandra hulls	200	521	20.8	Cu(II)	250
Ceiba pentandra hulls	200	521	19.5	Cd(II)	[250]
Rice husk	700	-	34.56	Cu(II)	[49]
Sugarcane bagasse	700	1620.29	138.46	Ammonical nitrogen,	[148]
Sugarcane bagasse	700	1620.29	12.81	Orthophosphate	[148]

Note: CT = Carbonization temperature, BET= Surface area, q_m = Maximum capacity

uniform. The value-added activated carbon of rice husk can also be simply produced by chemical activation of rice husk ash at 900°C for carbonization time of 120 min [237].

Activated carbon produced from rice husk and its characteristics is the aim of a research study achieved by Hariprasad et al. (2016). Produced rice husk activated carbon was carried out using physical and chemical activation methods as follows: the material selected is initially physically activated at a temperature ranging from 300°C to 700°C for 60 min, and then the carbonized material thus obtained was soaked into 1N KOH at a 1:1 ratio overnight and was followed by physical activation at 300°C for 120 min. The BET surface area was found to range from 11.9985 m²/g to 279.7752 m²/g. Their studies indicated that the phenol adsorption capacity increased with increased temperatures. Maximum adsorption capacity was obtained at 25.6%, 66.66%, 87.4, 94.6%, and 95.8% at temperatures of 300, 400, 500, 600, and 700°C, respectively [238].

Conclusions

In this review, details were provided to show that the study on low-cost adsorbents for HM and SD removal has attracted the attention of more scientists. A wide spectrum of carbonaceous adsorbent materials derived from either agricultural by-product or their wastes were found to be good alternative low-cost adsorbents to commercial AC for the removal of HM and SD from aqueous solutions. The most physical and chemical features, methods of synthesis in the form of raw materials or AC, were found to be of great interest to the reader to know. Either naturally achieved adsorbents or activated carbons via physical or/and chemical activation by any effective chemical perhaps attributed to its enriched content of carbonaceous substances, the availability of oxidizing agents (mostly as aqueous solutions), and the established nature of the technique that has been used for the past several decades.

A light was shed on the type of techniques that can be managed to eliminate undesirable polluted materials; these techniques were either batch mode or fixed-bed column adsorption techniques. It was made clear that the continuous adsorption technique was more applicable and suitable in real water treatment industries due to its low operating cost and ability of columns to adapt to versatile processes. While batch reactors are easy for researchers to use in laboratory studies, they definitely are less convenient for pilot-scale work. The sorption capacity of the sorbent, obtained from the batch equilibrium experiment, is useful in providing fundamental information about the effectiveness of the sorbate-sorbent system. Nevertheless, the data obtained from such a technique cannot in general be applicable to the column process. The review has covered some studies which were chosen from literature and projected to demonstrate how strongly the removal efficiency of HM/SD by these adsorbents were influenced by the physical and chemical characteristics of the solutions. This review also showed the most affecting

factors on the rate of adsorption, which are pH solution, agitation speed and contact time, flow rate, bed height of adsorbent, initial concentration of adsorbate, mass, and particle size of adsorbent. These factors play an important role in the adsorption process.

Recommendations

In the last few years, it has been observed that the utilization of synthetic dyes (SD) such as methylene blue (MB), crystal violet (CV), basic violet-10 (BV-10), and malachite green (MG), and heavy metals (HMs) such as Cu(II), Pb(II), Zn(II), Cd(II), etc. in the field of scientific research increasingly have become a main axis of research. This practice is common, especially at universities and research centers where students and researchers at organic, analytical, microorganisms, medical, and pharmaceutical laboratories customarily intend to engage a number of them [18]. Conducting laboratory studies and research is considered a very essential part of academic and post-graduate studies where synthetic dyes are usually engaged in studies. However, a huge amount of colored liquids mostly derived from SD; as well as heavy metals solutions, are generated in the form of wastes. All of them usually find their ways disposed of in sinks and then to the main sewage network. So far in many countries, particularly in developing ones, the final reservoir is usually superficial waters represented by seawater and rivers. According to some annoying characteristics of those (SD) and/or HMs, they are considered problem makers to human health and

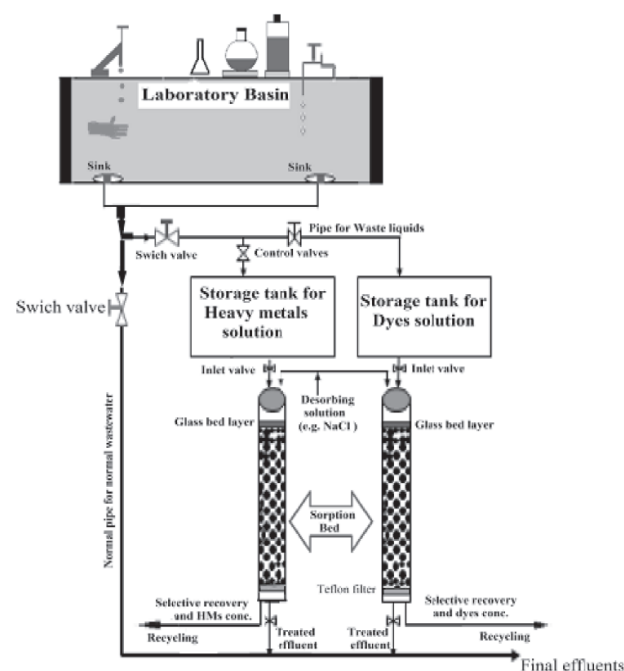


Fig. 15. A new proposed design of fixed-bed column filled with adsorbents for the adsorption of HMs and/or SD from waste liquids at university laboratories; multiple of columns can be used.

aquatic animals. So their removal from effluents before being discharged to the environment and offering it for public use is very essential for the protection of health and the environment. The concept came into sight by the authors as a proposed design to be utilized at these workplaces mentioned above. In short, the concept involves the influents that are usually discharged in the form of batches, for the reason that after termination of any research studies at these sites, the residues become wastes and hence find their way drained through these proposed manageable bed columns filled with local activated carbon or dry plant and tree leaves prepared from agricultural by-products/waste and forestry wastes for the treatment of colored and HM solutions. Fig. 15 shows the proposed manageable-bed column as a new design that can be made available at university laboratories.

Abbreviations

SD	Synthetic dyes
HM	Heavy metals
HTC	Hydrothermal carbonization
MPI	Max-Planck Institute
AC	Activated carbon
STL	Spent tea leaves
FAO	Food and agriculture organization
OMW	Olive mill wastes
IOC	International olive council
AT-STL	Alkali-treated spent tea leaves
GTL	Green tea leaves
MB	Methylene blue
CV	Crystal violet
STD	Spent tea dust
RCP	Raw coir pith
MG	Malachite green
UBTL	Used black tea leaves
SSAS	Simulated synthetic aqueous solutions
PAC	Powder activated carbon
GAC	Granular activated carbon
CEC	Cation-exchange capacity
MTZ	Mass transfer zone
US EPA	United States Environmental Protection Agency
PSHAC	Pumpkin seed hull activated carbon
RHAC	Rice husk activated carbon
ACCPH	Activated carbon <i>ceiba pentandrea</i>
ACPAH	Activated carbon <i>phaseolus aureus</i>
MO	Methyl orange
BET	Brunauer-Emmett-Teller
AB-25	Acid blue 25
TWAC	Brewed tea waste activated carbon
CGT	Carbonized green tea
RBY	Remazol brilliant yellow

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