

Agricultural by-Products/Waste as Dye and Metal Ions Adsorbents: A Review

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Abstract: A major treat to the comfort of human life has been imposed by the unintentional and great increased industrialization and urbanization. Their generations and land disposals of huge amounts of toxic materials and pollutants have contributed in contaminating our environment frighteningly. Synthetic dyes (SD) and heavy metals (HM) are becoming increasingly prevalent in soil and surface water environments, as the most dangerous pollutants. They are present a great concern worldwide, due to their toxicity to many life forms. Environment-friendly utilization of agricultural by-products/waste materials either as raw materials or in production of the 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 the inexpensiveness, the local availability and their efficiencies in removal of heavy metals and dyes from contaminated water. A number of different agricultural by-product/wastes as renewable and potential sources for green adsorbent production has been listed in this review. Additionally, the paper has provided the reader with an overview of a number of case studies which were conducted by scientists and researchers. These case studies have pointed out to the efficient removal of SD/HM ions from aqueous solutions by the agricultural by-products/wastes in the form of a raw material, spent tea leaves (STL), spent coffee ground(SCG), and rice husk (RH) wastes were selected as a good examples. Besides, the efficient removal of such ions by AC produced from the same raw materials has been also reviewed. Both kinds are widely used adsorbents in the treatment of wastewaters. High adsorption capacity, cost effectiveness, and environmentally friendly, and their abundance in nature are the important factors which explain why the adsorbent materials derived from an agricultural by-product/wastes is economical for the removal of dye and metal ions from contaminated water. Comparison of different technologies of wastewater treatment especially heavy metals and dyes were also listed in this review.

Keywords: Adsorption, Activated carbon, Coffee grounds, Dyes, Heavy metal, Rice husk, Spent tea leaves

I. Introduction

Global developments concerned with the increase in comfort of human life have unintentionally and greatly increased industrialization and urbanization. However this kind of concern has contributed in contaminating our ecosystem frighteningly, because of the generations of huge amounts of toxic materials and pollutants to the atmosphere, soil and surface water. Heavy metals (HM) and dyes are considered as the most dangerous pollutants and of a great concern worldwide, due to their toxicity to many life forms. According to the United World Water Development Report, 2,000,000 tons of wastes are discharged to the receptor water bodies every day including industrial wastes, dyes and chemicals, and etc[1]. More than 600 organic and inorganic pollutants have been reported in receptor water[1], around 40,000 dyes and pigments are listed, which consist of more than 7000 different chemical structures[2] and over 700,000 tons are produced annually worldwide[3]. On the other hand, heavy metal contamination exists in aqueous waste streams from many industries such as metal plating, mining, tanneries, car radiator manufacturing, as well as agricultural sources where fertilizer and fungicidal spray are intensively used. Cu, Cd, Zn, Pd, Cr, and etc., are harmful wastes produced by industry that pose a disk of contaminating groundwater and other water resources[4]. Water pollution is a major global problem which requires ongoing evaluation and revision of water resources policy at all levels. Water pollution accounts for the deaths of more than 14,000 people daily[1]. According to EPA U.S., 2007, the top toxics release inventory emitters to surface water by industry 2005 are shown in Figure (1)[5]. On the other hand, the environmental benefits of reducing U.S. Office Paper Use by 540,000 tons are shown in Table (1)[6].

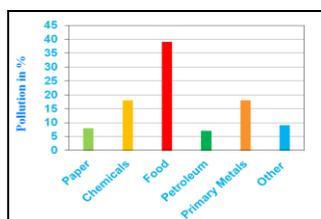


Figure 1: Top toxics release inventory emitters to surface water by industry,2005[5].

Table. 1: Environmental benefits of reducing U.S. office paper use by 540,000 Tons [6]

Environmental benefits		Annual equivalent
Total energy	21 Trillion (BTUS)	Enough to provide power to 228,000 homes
Green house gas emissions	1.6 Million tons	CO2 emissions from 279,000 cars
Solid waste	600,000 tons	44,000 fully loaded garbage trucks
Wastewater	11 Billion gallons	Enough to fill 16,000 Olympic-Sized swimming pools
Wood use	1.9 Million tons	13 Million typical trees

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [4]. Due to low biodegradation of dyes, a conventional biological treatment process is not very effective in treating dye wastewater [7]. Research work done by Pearce and his coworkers (2003), had reviewed a method using bacteria cell for dye removal from textile industries [8]. Since biological method is not very efficient in dye removal, the physical or chemical processes are the better option.

Currently, several techniques (physical or chemical) processes have been employed for the removal of dyes from wastewater. However, these processes are either costly and cannot efficiently be used to treat wide range of dye wastewater [7]. The following represent some conventional techniques of metal ions and dyes removal from wastewater [4, 7, 9]; 1) **Ion exchange:** in this technique, metal ions from diluted solution are exchanged with ions held by electrostatic forces on the exchange resin. The advantages include metal selective, effective for wide range of dyes, no loss of sorbent on generation, high generation of materials. While, the disadvantages are: high expensive not effective for disperse dyes, 2) **Chemical precipitation:** this process is simply operation, non-metal selective and low-cost. But the large production of sludge with high cost of disposal sludge is the main disadvantage, 3) **Membrane separation:** the low production of solid waste, and low chemical consumption, high quality of treated effluent are the main advantages. While, disadvantages include: low flow rate, concentrated sludge produced during the process, incapable of treating high volume, and high cost and high pressure requirements, 4) **Electrochemical treatment:** this method is rapid process and effective certain metal ions, as well as metal selective. But, the high initial capital cost and high energy costs and formation of by-products are disadvantages, 5) **Oxidation:** the disadvantage include: high energy cost and formation of by-products, chemical required and short half life. While. Advantage of this technique is rapid and efficient process for dye removal, 6) **Coagulation/flocculation:** this process is simple operation and economical. But, the disadvantage are formation of large particles, handling and disposal and sludge production problems, 7) **Irradiation method:** a greener cleaner process, but required a lot of dissolved O₂, 8) **Photochemical:** free sludge production. But formation of by-products is the main disadvantage, 9) **Fentons reagents:** the main disadvantage of this process is sludge generation. But the advantages include: effective decolourisation of both soluble and insoluble dyes, 9) **Biological treatment method:** this method is feasible in removing limited dyes and metals. But technology yet to be established and commercialized.

The cost of water purification by these technologies, ranges from 10 to 450 \$/m³ of treated water. While the cost of water treatment by using adsorption technique ranges 5 to 200 \$/m³ [1]. Adsorption process has gained interest as a more promising method for the long term as it is seen to be more effective and economic approach for pollutants removal (i.e. heavy metals and dyes) from polluted water sources. Adsorption is a fundamental process today due to its low space requirements for batch and continuous operation unit, simplicity and flexibility of design and ease of operation, non-pollutant to water, no odor emissions and low cost of adsorbent, another main advantage of the adsorption technique in removing or minimizing the pollutants such as heavy metals and dyes event at low concentration enhance the application of adsorption as one practical treatment [1, 9]. Figure (2) shows the adsorption process system (fixed-bed column and batch mode system used in laboratory scale.

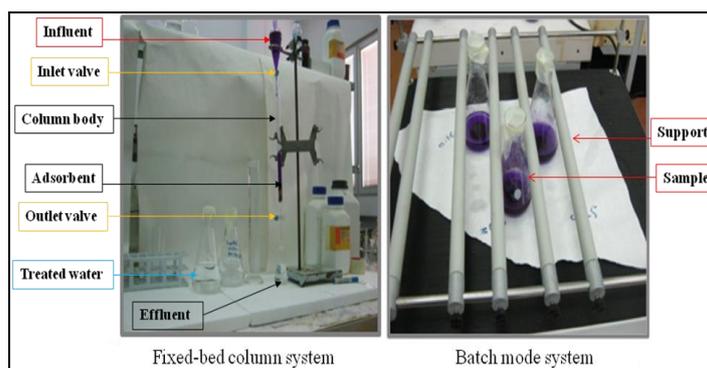


Figure.2: The adsorption processes using at the Laboratory scale [done by author].

A number of factors such as initial concentration of pollutant, pH, flow rate, and etc., play an important role in the adsorption process should be considered during the adsorption process between adsorbent and pollutants. pH is playing the most important factor than others [9]. See Figure (3).

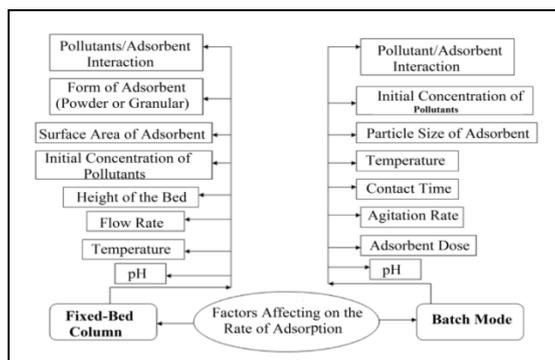


Figure. 3: Main parameters affecting on the rate of adsorption [drawn by author]

II. Sources, Quantities and Environmental Impacts of Different Agricultural by-Products/Wastes.

Expanding fruit production has naturally resulted in increased amounts of waste every year [10]. It was reported that in the world several million tons of agricultural wastes are being disposed every year. In India alone more than 400 million tones of agricultural residue is generated annually [11], it is estimated that production of Coir pith in India is 0.5 million tons, and coir pith is disposed as a waste and its accumulation around coir-processing centers is creating a menace [12], and about 3.5 million tons of tea are consumed worldwide [13].

The global production of dates was recorded 7,429,811 tons in 2009[10, 14], while 198,000 tons of date leaves are generated each year in Tunisia [15, 10], the main components of the date palm leaves are cellulose 38.10% , hemicellulose 22.74%, lignin 11.95%, ash 7.71% [16]. Libya is considered one of the major countries engaged in taking care and cultivating date trees that the number of these trees cultivated and distributed in many regions of the country at many regions particularly at the oases were estimated to be around 5.0 million trees[17], Therefore, a great advantage can be taken from the huge number and abundance of this type of trees for use in mass applications. Modern technological developments have made it possible to look at the palm as a raw material source for industrial purposes. Practically all parts of the date palm, except perhaps the roots, are used for a purpose best suited to them[18].

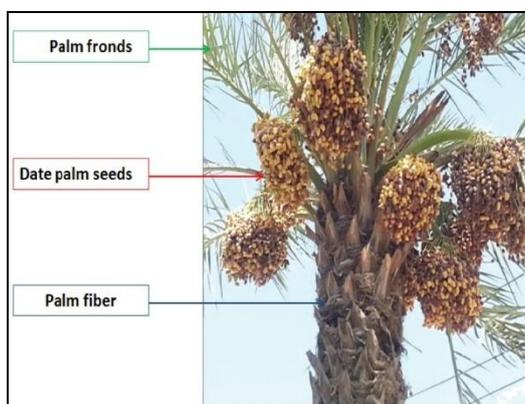


Figure.4: Diagrammatic representation of date palm structure[19].

According to the records of 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 [20], a new nonporous carbon from tomato waste as low-cost adsorbent was prepared by Fuat et al., (2014) [20].

While 68 million tons of global orange production according to (FAO), and the generation of these solid wastes is estimated to be in the range of 15 to 25 million tons, a big volume of this wastes is 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 [21].

In the United States about 30 million tons of oak leaves are collected and burned annually. A new activated carbon from Oak L. dead leaves as low-cost adsorbent for dye removal was prepared by Sulyman et al., (2014)[22].

In India, the national walnut production oscillates between 40,000 to 45,000 tons per year, and the process involved to obtain unshelled walnut, generates more than 25000 tons of shell. Also, generating approximately 11000 tons of almond shell waste every year [23].

Olive oil is nearly totally produced in the Mediterranean region. As the demand of olive oil is rapidly increasing worldwide, environmental pollution posed by olive mill wastes (OMW) such as olive cake (husk) is a growing problem especially in the Mediterranean region. According to the International Olive Council (IOC, 2012), the provisional figures of worldwide olive oil production for (2010/2011) is 3,018,500 tons of olive oil, giving a rise of 45,000 tons or 1.5% from the 2009/2010 season [24].

The olive mill generate a big quantities of waste accumulate around the olive mill, it was reported that the 1000 kg of olive fruit can be produced 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 cake produced is granted to farmers, who use it for heating after drying, as well as for animal feeding. The remaining quantities are then dumped in open lands [24] the exhausted olive cake has a high lignin, cellulose, and hemicelluloses, as well as, a low ash; were found to be 14.18%, 24.14%, 11.0%, and 2.36% respectively [25]. Due to its high cellulose, hemicelluloses, and lignin content a proper method of disposal and recycling of olive cake has get to be developed.

In this review, rice husk, coffee grounds, and spent tea leaves has been selected as renewable and potential sources for green adsorbents production for use in heavy metals and dyes removal from contaminated water, more details and scientific application were presented as followings:

a. Rice husk

Rice, the staple food for huge number of people worldwide. According to IRRI “International Rice Research Institute” the total rough rice production in the world was more than 600million tones in 2004[26, 27], and Bangladesh, the 4th largest rice producing country, about 6% of the total world rice production in 2004. Another research study reported that that about 500 million tons of rice are processed in the world which give a 100 million tons of rice husk[28]. More than 180 million tons of rice are produced in Malaysia annually which give an over 36 million tons rice husk [29]. While, Vietnam become the world’s top rice exported and exported 5.949million tons of rice in 2012[30].

Rice husk(RH) is the major by-product of the rice milling industry, accounting for 20% of the total weight of rice plant [29, 31] and contains74.5% organic matter which consists of about (32% cellulose, 21% hemicelluloses, 21% lignin, and 3% crude protein)[28], and about 20% silica [4, 28]. As rice plant is the main cereal crop in many countries especially Asian. So far in many Asian countries, where the bulk of rice is produced and consumed, a major proportion of the husk in carried to open areas for disposal by burning, and this which releases carbon dioxide (CO₂) into the atmosphere [32, 33].

Research study was done in Bangladesh, and reported that, the total CO₂ emission of rice processing in Bangladesh was estimated to be 6.1 million tones in 2000. Out of the total emissions, the biogenic carbon dioxide emissions estimated to as 5.7 million tons in 2000 . The biogenic CO₂ emission occurred due to the burning of RH and this mass of CO₂ is renewed every year by the rice plant [27]. Huge amount of CO₂ emissions could easily be reduced by increasing the efficiency of rice parboiling boiler. Improve of rice parboiling boiler could enable availability of RH. On the other hand, the environmental issue is a great concern for country like Bangladesh, especially for the adverse effects of sea level rise due to global warming [27].

RH possessed a granular structure, is resistance to water, has chemical stability and high mechanical strength and high ash content. Typical composition, physicochemical characteristics, and chemical content of rice husk are presented in Table (2)[4, 34] . Due to its high ash content, a proper method of disposal and utilization of RH has yet to be developed [4]. However, studies have shown that RH is suitable for the production of Activated Carbon(AC). Another study showed that RH also has a good value as a biomass fuel, and can be used as fuel for parboiling and drying of paddy before milling[27]. It was also reported that, rice husk mostly used as fuel in boiler furnaces of various industries to produce steam[35]. Therefore, this project can be developed for use in mass applications. Figure (5), representation the block diagram of rice husk as renewable sources for different applications.

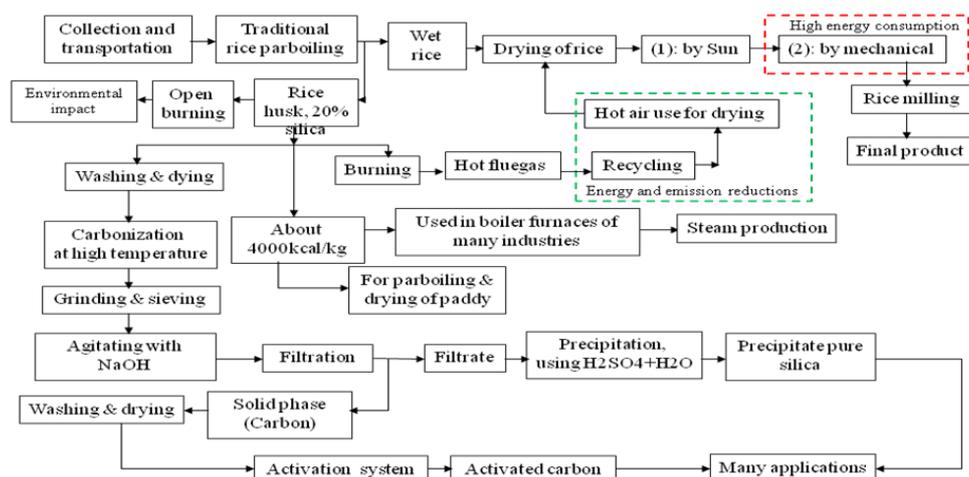


Figure. 5: Block diagram of rice husk as renewable sources for different applications (drawn by author).

Table. 2: Typical composition, physicochemical characteristics, and chemical content of rice husk [4, 28, 34]

Composition	Value, %	Technical characteristics	Value
Cellulose	32.24	Moisture content, %	8.84
Hemicelluloses	21.34	Volatile matter, %	57.95
lignin	21.44	Ash content, %	15.24
Chemical content	Value, %	Fixed carbon, %	18.64
C	31.65	High heating value, Kcal/kg	3800
H	6.12	Physicochemical characteristics	Value
O	36.08	Bulk density, (g/ml)	0.73
N	1.87	Surface area, (m ² /g)	272.5

A study was done by International Development Research Center, Canada, and reported that theoretically the net energy demand for hot soaking, steaming and drying were 360MJ, 105.5MJ and 574MJ respectively, to process one tone of paddy [27, 36].

In recent year, many countries have been focused on the utilizing of biomass for the production of non-conventional energy. However, producing electricity and bio-fuel using non-conventional renewable sources like rice husk is the main challenge to the conventional electricity sector and oil company. In Sri Lanka, a research study was done by Asanka and his co-workers [37], found that 30% of excess RH can be exploited for power generation with an annual energy potential of 180GWh. Rice husk can be also used as raw material for the production of activated carbon, zeolite, silica, and concrete[30]. Elemental silica is used as a constituent of building material. In amorphous form it is used as desiccant, adsorbent catalyst compound. It is also used as a basic material for glass, ceramic and refractory industries. It also finds uses in reinforcing filter, in natural and synthetic rubber and is used in adhesives to enhance bond strength. It can be also used as a catalyst support for fine chemical synthesis[38].

b. Coffee grounds waste

Coffee fruits processing is one of the most pollutant activities in agriculture due to a large amount of waste generated in the process. According to the “International Coffee Organization” the production of coffee amounted to about 680,000,000 tons in 2008[39]. Nevertheless, the ten largest coffee producing countries are responsible for approximately 80% of the world production. Of this percentage, South America participates about 43%, Asia with 24%, Central America 18%, and Africa with 16%. The largest world producers are Brazil, Vietnam, Colombia, and Indonesia respectively [40]. Coffee is the second biggest traded commodity in the world, after petroleum, and after the processing of coffee (coffee industry, coffee shops) the generation of large quantity of residues is amount of no use and disposal off. Up to now, only a small portion of it is used as a fertilizer, but most of the coffee grounds waste are dumped or burned[41].

It was reported that, 77million bags of green coffee were simply burned and released to the sea and in landfills [40, 42]. However, coffee grounds are carbonaceous and have the potential to be converted into an adsorbent. This conversion could solve the disposal and pollution problem of coffee 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 [41]. It was reported that the amount of carbon dioxide produced by the combustion of 1000g of coffee grounds is estimated to 538g [43]. In Libya in particular, coffee and tea as a beverage are second most consumed by all citizens after water. In the last few years, the consumption of coffee has been rapidly increased specially by young people. According to the survey done by the author in December-2015, which included 25 cafe in Tripoli. The preliminary study reported that the coffee grounds wastes ” generated

only by 25 cafe ” is estimated to be in the range of (36-45) tons annually, a big amount of this wastes is still kept in a big plastic bags and then transported to the open area for disposal by burning or dumping. It is also estimated that in one of these cafes, more than 100 cups of coffee are drunk within an hour. However, recycling such waste as a feedstock for the other process could be the better option to minimizing the disposal landfill and pollution problems of coffee waste, and economically at the same time. In some cases, spent coffee grounds is utilized as fuel in industrial boilers of the same industry due to its high calorific value of approximately 5000kcal/kg[40, 44].

The possibility of coffee grounds use as potential source to produce biodiesel and fuel pellets, among other value-added products, such as H₂ and ethanol has been also studied Figure(6)[40, 45]. As a consequence of this big market, the coffee industry is responsible for the generation of huge quantities of coffee wastes. Finding alternatives for use of these wastes of great importance due to their toxic character, which can be harmful if discharged into the environment. Up to now, there are limited reports about the use of coffee wastes as feedstock for other process[40]. Besides to add value to these unused materials, finding alternative forms to use them would be useful to reduction their impact to the environment. However, the typical composition, physicochemical characteristics, and chemical content of coffee grounds are given in table (3).

Table.3: composition, physicochemical characteristics, and chemical content of coffee grounds

Elemental Compositions [46]	Value, %	Chemical components [47]	Value
C	57.16	Cellulose (Glucose)	12.40±0.79
H	7.17	Hemicelluloses	39.10±1.94
N	1.18	Lignin	23.90±1.70
H/C	1.51	Proximate analysis[48]	Value
O/C	0.45	Moisture	4.29 ± 0.04
C/N	56.51	Volatile matter	82.81 ± 0.02
O+N/C	0.47	Ash	3.92 ± 0.02

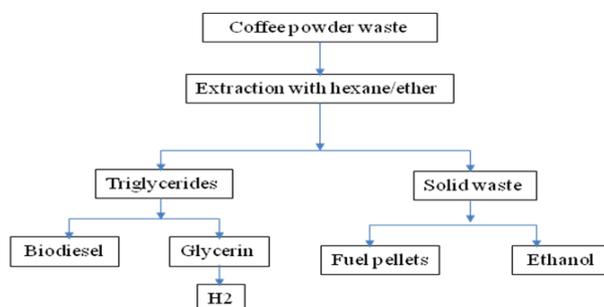


Figure. 6: Schematic presentation of biodiesel and fuel pellets production process from spent coffee grounds[40, 45].

c. Spent tea leaves

Tea is the dried and processed leaves of (*Camellia sinensis*) and is consumed by a huge number of people worldwide[49, 50]. Black tea, made from the mild oxidation of tea leaves, amounts to around 78% of the whole production, followed by green tea (22%). Both of them, however, are obtained from the basic tea leaves (*Camellia sinensis L.*) [51]. Only water is rated higher in the world consumption than tea. It is estimated that somewhere between 18 and 20 billion cups of tea are drunk daily[50]. After hot water extraction of tea leaves, the residual mass is of no use and hence is disposed off [22]. The insoluble part of STL consists of mainly cellulose (37%), hemicellulose and lignin (14%), and polyphenols (25%). According to chemical analyses reported by Harler (1963)[52], these components constitute almost 80% of the insoluble portion of STLs. It is proposed that the presence of hydroxyl and phenolic groups as polar groups could work as active sorption sites for the uptake of HM ions and SD. Some other chemical and physical properties of STL are shown in table (4).

Several studies were showed that, Spent tea leaves (STL) as a novel sorbent for effective Pb(II) removal [53], Cu(II) removal [50], STL represent a good example of a low cost adsorbent and an agricultural waste, is found in abundance, and usually require little or no processing materials[50, 54]. STL, a solid waste that is available in large amounts worldwide, as attested by the over 3,000,000 tons of tea leaves produced each year[49].

Table. 4: Some Chemical and Physical Properties of STL[55].

Elemental analysis	%	Physical properties (unit)	Value
C	44.424	Moisture content (%)	12.30
H	6.372	Pore volume (ml/g)	2.900
N	3.421	Percent porosity (%)	75
O	27.202	Specific surface area (m ² /g)	1.141

III. Recycling of Agricultural by-Products/Wastes

Figure (7) shows the possibility of recycling of agriculture by-products/wastes as main precursor to synthesize either AC through carbonization (track 1 in Figure 7) or can be used as raw materials that need little or infrequently no processing (track 2 in Figure 7). They afterwards can be used as adsorbents for different applications.

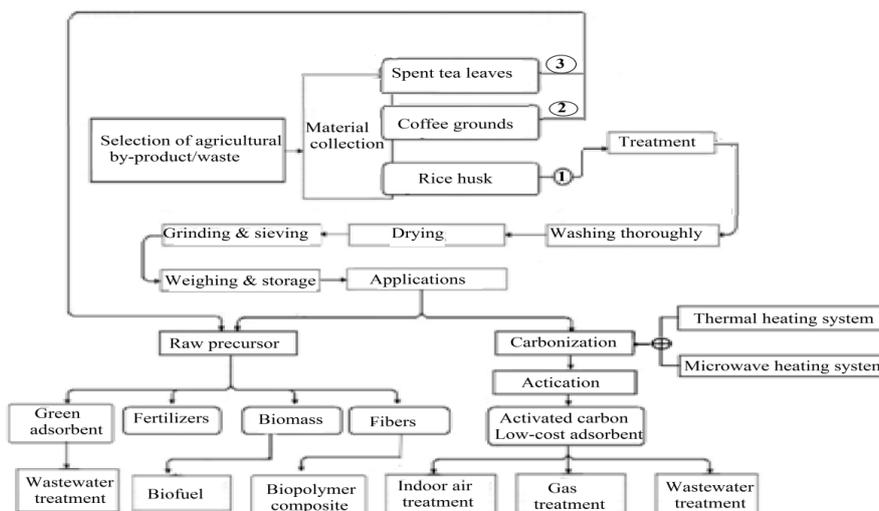


Figure .7: Scheme of agricultural by-products/wastes recycling (Source: drawn by author).

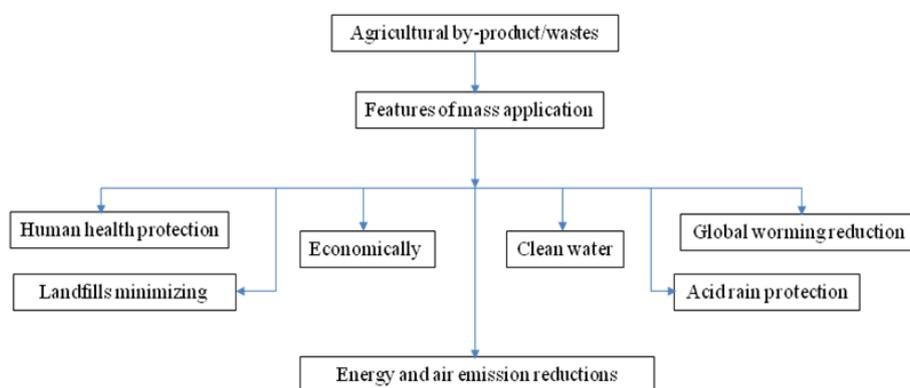


Figure. 8: Scheme representation of features of mass application derived from agricultural by-products/wastes.

d. Raw coffee and tea wastes as natural sorbents: Case studies

Coffee and Tea are consumed by a huge number of people worldwide. Only water is rated higher in the world consumption than them. It is estimated that somewhere between 18 and 20 billion cups of tea are drunk daily[54]. Coffee has been also consumed for over 1000 years and today it is most consumed drink in the world (more than 400 billion cups yearly) [40, 56]. After hot water extraction of tea leaves, and the processing of coffee the residual mass is of no use and hence is disposed off.[55]. In the last decade, the use of such waste material has been subject of many studies, but this concern did not exist in past decades(1930 to 1943) when 77 million bags of green coffee were collected and simply burned and released to the sea and open land “landfills”, which are toxic and represent serious environmental problems[40, 42]. However, this is an important topic explored nowadays.

Sorption of toxic metals and organics by using spent coffee grounds(SCG) and spent tea leaves (STL) have been studied extensively in recent years due to their aforementioned advantageous properties and economic value. In the following section represented some examples on (SCG) and (STL) wastes to remove basic dyes or heavy metal ions from contaminated water respectively.

Decolorization of real textile wastewaters and synthetic dye mixtures in a batch mode and in fixed-bed columns methods using “Greek coffee” wastes (COF) as low-cost adsorbent was studied by Kyzas and his coworkers(2012), results of this study showed that the maximum adsorption capacities (q_m) for total dye removal at 25 °C was found to be 241 mg/g and 179 mg/g at pH=2 and pH=10 respectively. Equilibrium data were fitted to the Langmuir, Freundlich and Langmuir-Freundlich (L-F) model. The best correlation factor was

for L-F model ($R^2 \sim 0.999$) [57]. In a related study, spent coffee powdered residue from the soluble coffee industry was evaluated as an adsorbent for the removal of MB from aqueous solution with 18.7 mg/g adsorption capacity at 25°C [58]

Seven dyes (crystal violet, malachite green, amido black 10B, Congo red, Bismarck brown Y, acridine orange and safranin O) were used to study the adsorption process using new type of magnetically responsive biocomposite materials [59]. The magnetic modification of coffee grounds (MMCG) procedure was done as follows: 5g of coffee grounds were suspended in 40 mL of methanol and then 5 mL of ferrofluid was added. The suspension was mixed on a rotary mixer for 60min. The (MMCG) were then repeatedly washed with methanol and air dried. Maximum adsorption capacities reached the value 73.4 mg of dye per g of dried (MMCG) for acridine orange.

Evaluation of coffee waste adsorbent for malachite green (MG) removal from aqueous solution using was the purpose of another study conducted by Franca et al., (2010)[60]. 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 indicate that spent coffee grounds presents great potential as an inexpensive and easily available alternative adsorbent for the removal of cationic dyes in wastewater treatments.

For metal ions, the order of adsorption capacity was Cd(II); Zn(II); Pb(II); Cu(II) and the effectiveness of metal removal was found to be higher between pH values of 4 and 10 [61, 62]. Another application exploiting the ability of Spent coffee grounds (SCG) to bind metal ions is the use of Fe-treated SCG to increase Fe availability to plants in neutral to alkaline soils [62, 63]. According to the authors, the Fe-containing material can be prepared easily by adding appropriate amounts of a soluble ferric compound to SCG and composting the resulting material. In a reported example, dried SCG and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were mixed in a ratio of 4:1 by weight and composted in plastic bags at 60 °C for 60 days.

George Z. Kyzas, (2012) [64], studied that 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 conclusion are summarized as follows: 1) the best correlation factor (R^2) was found to be 0.998 for (L-F) model, 2) the maximum agitation rate was found to be 140rpm, 3) the pH selected as optimum adsorption experiments was PH 5.0, 4) the optimum pH found after desorption experiments was pH 2 both for Cu(II) and Cr(VI).

In similar, Chung-Hsin et al., (2015), in this work, untreated coffee residues (UCRs) were used to remove Pd(II), Zn(II) ions from aqueous solutions. The effect of heavy metals ions concentrations, solution pH, adsorbent concentration were investigated using batch experiments. According to the results data obtained in this study, the adsorption percentage of Pd(II), and Zn(II) was 96% and 44% respectively; moreover, the adsorption density of Pd(II) and Zn(II) onto UCRs was 9.7mg/g and 4.4mg/g respectively after reaction for 180min at operation conditions (adsorbate = 20mg/l), (UCRs = 2g/l), and pH 5 after reaction for 180min [65].

Azouaou and his coworkers, (2014), have investigated the adsorption of Pd(II) onto untreated coffee grounds (UCG) using fixed-bed column adsorption study. The experiments were conducted to study the effect of important deign parameter such as flow rate (5, 7 and 10) ml/min. data obtained from this study confirmed that the uptake of lead ion through a fixed-bed column was dependent on flow rate, and the adsorption capacity was found to be 78.95 mg/g at a bed height of 7.5cm and flow rate of 10ml/min. Surface area (BET) was found to be 298.60m²/g[66].

Removal of copper (Cu^{+2}) and lead (Pb^{+2}) from contaminated aqueous solutions has been investigated using coffee grounds as a natural adsorbent by Jurgita et al., (2014). Their equilibrium adsorption experiments were carried out at different fractions ($>200\mu\text{m}$ and $<200\mu\text{m}$ particle size) of adsorbent, different concentrations of both metals(0.5, 1.0, 1.5, and 3mg/l). Based upon the experimental results of this study, following conclusions is drawn: 1) smaller fraction coffee grounds treatment efficiency increased by 6-11%, 2) the copper adsorption efficiency was increased with the decrease particle size of adsorbent and was found to be 86% with high particle size ($>200\mu\text{m}$). While, 97% with low particle size ($<200\mu\text{m}$) when Cu^{+2} concentration is 0.5mg/l. 3) the lead adsorption efficiency was increased with the decrease particle size of adsorbent and was found to be 87% with high particle size ($>200\mu\text{m}$). While, 97% with low particle size ($<200\mu\text{m}$) when Pb^{+2} concentration is 0.5mg/l. 4) experiment and result analysis of this study indicateted that coffee grounds can be excellent natural adsorbent for heavy metal adsorption from aqueous solutions, like wastewater of landfill leachate [67].

Orhan and Buekguengoer, (1992), have investigated the removal of some metal ions such as (Al) ions from wastewater using Spent tea leaves(STL), Turkish coffee, spent coffee, nut and walnut shells as adsorbents in a batch mode experiment. Their results showed good adsorption potential for (Al) ions with removal efficiency (98%, 99%, 96% and 96%) respectively[68]. A similar adsorbent was the aim of another research study achieved by Hadi, (2012), when he investigated the possibility of using STL, in comparison with

commercial AC, for removing toxic hexavalent chromium ions Cr (VI) from a synthetic wastewater using a batch mode experiment. The equilibrium experiments were carried out for 180 min. with STL adsorbent dose range between (0.05 - 0.9) g, and 100 ml of Cr (VI) solution of an initial concentrations ranged between (25 – 300) mg/l. In conclusion, the maximum adsorption capacities of Cr (VI) were 42.46 mg/g and 42.42 mg/g by using STL and AC respectively[54]. Another extensive research study carried out by Rafie, (2012) who has focused on the use of a Black STL for the removal of some HMs: Co, Cd and Zn from wastewater. 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 a half gram of STL at equilibrium (qe) were 15.39 mg/g, 13.77 mg/g and 12.24 mg/g for Co, Cd, and Zn respectively[13].

A kinetic investigation was carried out by Hossain *et al.*, (2005), 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 out that adsorption of Cr (VI) onto STL 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 out that the initial Cr (VI) concentrations, pH, temperature were very effective parameters on the rate of adsorption[69].

A modified STL, an alkali treated STL (AT-STL) was used as a novel adsorbent to remove Pb(II) ions from aqueous solution. The investigation was reported by Xiaoping Yang and Xiaoning Cui, (2013) [53]. Their comparative study of Pb ions 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(II) ions than GTL and GSTL. According to the data obtained from Langmuir model, the optimum adsorption capacity (q_0) for Pb(II) was obtained with a value of 64.10 mg/g [53].

Tan (1985), have 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, nature of waste substrate used and presence of other competing ions or molecules[70].

Zuorro and Lavecchia(2010)[71], have investigated the removal of Pb (II) from aqueous solution using green and black spent tea leaves 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⁻¹ at 25°C and 40°C. The percent lead removal efficiency by black and green spent tea leaves was found to be 98.4% and 98% at 25°C, and 99.3% and 98% at 40°C respectively. The experimental data fitted well to Langmuir isotherm model, with maximum adsorption 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 spent tea leaves 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 discharging to the streams. Researcher Hameed, (2009)[72] 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 a center of a research study conducted by Mohamed and Rahman, (2013)[73], Their equilibrium adsorption experiments were carried out at different temperatures at pH 6. According to the data obtained from 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 another research work achieved by Ramesh *et al.*, (2014)[74], 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 agitation 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 were done by centrifugation at 4500 rpm for 10 minutes. The effects of the contact time, adsorbent dosage and solution pH were studied at 27°C. Based upon the experimental results of this study, the following conclusion were 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 the 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), 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 was obtained 227.3 mg /g at 30°C and pH 6.0 [75].

In contrast to the batch mode process, Joodi and Abbas (2014)[76] 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 ions 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 %.

Malko and Nuhoglu (2006)[77], have used tea factory waste for the adsorption of Cr (VI) ions from aqueous solutions using 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 4200 to 11 800 ml as the bed depth increases from 5 to 30 cm.

Another research study on fixed-bed column, which consisted of a 130mm height column with 12mm internal diameter (ID) was investigated to evaluate the efficiency of STL as low-cost adsorbent for the removal of Crystal Violet (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 7min where the percentage accounted for 68%, when the concentrations of the dye, bed height, and flow rate were optimized at 30mg/l, 20cm and 5ml/min respectively[78].

IV. Activated Carbon (AC)

e. Background

Activated carbon (powder or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. 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 and. Furthermore, regeneration using solution produces small additional effluent while regeneration by refractory technique results in a 10-15% loss of adsorbents and its uptake capacity [7, 79]. Also these sources are non-renewable and contribute to the high cost in the preparation of activated carbon[7]. It was reported that about 60% of the production of activated carbon globally are obtained from coal nowadays[80]. Producing inexpensive AC is one of the main challenge in commercial manufacturing[81]. One main advantage of utilizing agricultural by-products/wastes and forestry residual is the ability to synthesize and produce cheap and eco-friendly AC as an alternative substitution for commercial AC [22]. It was reported that, “Humphery and Keller (1997) were estimated of worldwide sales of AC 1 billion \$”[28].

A prime concern, always, 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 \$2.00 (20 times less than the cost of zeolite)[82]. 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 cheap and local available agricultural by-product/wastes, it is considered an excellent alternative, especially when used for the treatment of wastewater for the removal of Heavy metal (HM) ions and Synthetic dyes (SD) pollutants. Therefore, this project can be developed for use in mass recycling.

In recent years, several scientific papers, technical works, reports and literature review have been focused on the utilization of AC for the adsorption of HMs and SD from contaminated water. It was reported that more than 5000 published works for removal of dyes, and about 6000 for HMs removal have been studied [83]. AC's are also involved in many fields that they can be used as a green adsorbents for separation, purification, decolorization and deodorization of vegetable oils and fats, water purification, air and gas purification (cigarette filters, motor vehicles exhaust control) and food and pharmaceutical industries. Also at some scientific laboratories such as biological, medical, pharmaceutical and chemical laboratories at universities when dyes were involved in research [22]. They can be found in radioactive protection in nuclear plants [80].

Conventional heating one of the most applicable preparation method for producing AC. In this method, heat is transferred to the raw samples by three different transfer mechanisms which are, conduction, convection, and radiation. This thermal gradient leads as inhomogeneous microstructure for high heating rates [81]. As an alternative heating method, microwave technology is gaining importance as a promising technology for research and industrial applications[84]. Microwave heating offers a potential means of cost reduction as it is capable of

reducing the heating period, energy consumption, gases consumption. Additionally, microwave irradiation may promotes rapid and precise temperature control, and compact equipment size. However, there are very few studies which reported the use of microwave heating for preparation of activated carbon [85]. Figures(9) and (10) represented the main steps used to produce activated carbon from agricultural by-product/wastes using thermal heating system.



Figure 9. The production process of AC from date stones[86]

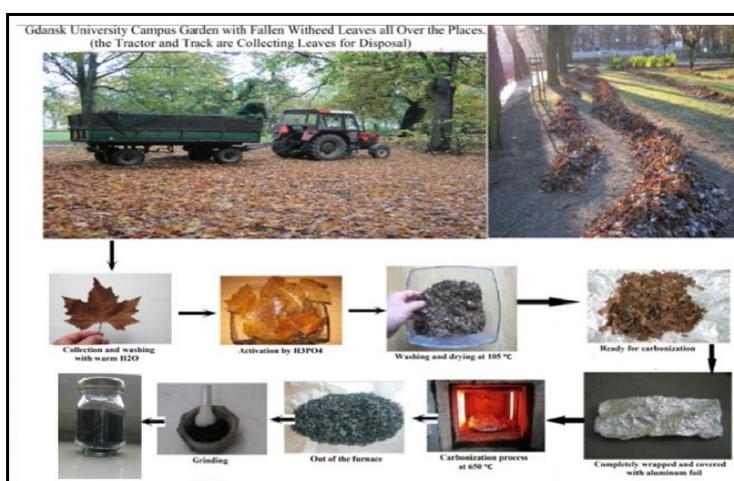


Figure.10: Step by step illustration of AC preparation from withered Oak tree leaves [22].

f. AC prepared from coffee and tea waste: Case studies

There are a number of studies which focused on the preparation and characterization of AC from coffee and tea wastes using different activating agent for the adsorption of dyes from aqueous solution. 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)[87]. 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. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models were tested and the adsorption of AB25 dye onto WTAC was fitted to Langmuir model and maximum adsorption capacity was found to be 203.34 mg/g.

Gao *et al.*, (2013)[88] have carried out an 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 followings: a high yield of 44.1% of AC was obtained with chemical activation method using $ZnCl_2$; the surface area (Brunauer-Emmett-Teller (BET)), of the obtained AC was found to be $1530.67m^2/g$; the equilibrium adsorption results were complied with Langmuir isotherm model and its maximum monolayer adsorption capacity was 324.7 mg/g for MB.

Another paper aims to investigate the adsorption properties of activated carbon prepared from brewed tea waste (TWAC), was studied by Gamzenur *et al.*, (2013). The activated carbon from a household waste is carried out by microwave activation using potassium carbonate (K_2CO_3) as 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. The adsorption data of TWAC were fitted with the Freundlich isotherm model with a high regression coefficient was 0.9831. All the results of this study was also showed that brewed tea waste can be a suitable candidate to use as activated carbon precursor and microwave activation with K₂CO₃ yields carbon with good adsorptive properties [89].

Another study has focused on the use of carbonized spent green tea as an adsorbent for the Remazol Brilliant Yellow (RBY) dye adsorption in a batch process. The results revealed that the spent tea have the potential to be used as a low-cost adsorbent for the removal of RBY. Based upon the experimental results of this study, following conclusions is drawn: the equilibrium time period for removal of RBY onto CGT adsorbent is 7 hours, the maximum removal of the dye occurs at pH= 9.5, and the experimental data were better fit in Langmuir model [90].

In a comparison study, Khenniche and Benissad-Aissani (2010), in their study, five carbons prepared from coffee residue (CR) by varying the activating agent ratio using chemical activation with zinc chloride (ZnCl₂) was investigated. Comparative study of prepared activated carbon and a commercial activated carbon (CAC) was undertaken to determine their capacities for phenol adsorption. The determined surface area and total porous volume of the prepared carbon from (CR) were 520 m²/g and 0.28 cm³/g respectively. It is essentially microporous compared to a commercial carbon since the prepared activated carbon microporosity is about 96 % while the commercial activated carbon is about 56 % [91].

Similarly, Six types of activated carbons were prepared from coffee residues by varying activating agents of zinc chloride, nitrogen, carbon dioxide and steam was carried out by Boonamnuayvitaya and his coworkers (2004). Prepared activated carbon in this study was used as formaldehyde adsorbent. They concluded that, the highest total surface area and total pore volume were found to be 914 ± 21m²g⁻¹ and 1.010 ± 0.003 cc/g respectively [48].

Activated carbon materials were produced from used coffee grounds (CGCs) by chemical and physical activation using KOH and CO₂. Maximum specific surface area (SBET) value was found to be 1971 m²/g [92].

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 H₂SO₄, 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 an pH of 10, and the removal efficiency was increased with decreasing the dye concentration and increasing dose of adsorbent [93].

Another work was also used coffee waste for production of AC by chemical activation using phosphoric acid and then carbonized respectively at 600°C and 700°C for 60min. Based upon the experimental results of this study, following conclusions are drawn: i) the activated carbon obtained at 600 C° and 700°C over one hour (5°C.min⁻¹) in the presence of adjuvant percentage of about 5.678 and 12.78 % gave respectively specific surfaces of 176 and 186 m²/g, ii) the resulting adsorption capacities were respectively 52.63 and 55.56 mg/g, iii) the adsorption is compatible with Langmuir and Freundlich models with a correction factor R² > 0.92, and finally, iv) the adsorption equilibrium was reached after 40 min [94].

Activated carbon (AC) synthesis from coffee waste by chemical activation using (ZnCl₂) and (KOH) was studied by Giraldo and Moreno-Piragan, (2012). Obtained activated carbon was used in the adsorption of ions of Hg(II) and Zn(II) from aqueous solution, there are four types of AC namely ACK3 and ACZ3 for adsorption of Hg(II); ACK2 and ACZ2 for adsorption of Zn(II). Equilibrium adsorption capacities ranging was found to be (0.002 to 0.380) mmol/g for ACK3 and (0.002 to 0.330) mmol/g for ACZ3, and from (0.002 to 0.300) mmol/g for ACK2 and from (0.001 to 0.274) mmol/g for ACZ2 respectively [95].

In related study, the adsorption ability of charcoal from coffee grounds (ACGs) for (acid orange 7) removal was investigated by the batch system. the activated carbon was prepared at three different temperatures of (800, 1000, 1200) °C. The specific surface area and pore volume of (ACGs) were increased by increase of carbonization temperature from 800°C to 1200°C, however, that by charcoal carbonized at 1200°C was almost adequate, and was found to be 61.71 m²/g [96].

Castro et al., (2011), have prepared activated carbon (ACs) from spent coffee grounds using two different activating agents, water vapor (ACW) and (ACK). In this study, the carbons as well as commercial activated carbon (CAC) used as reference, were evaluated as phenol adsorbent showing high adsorption capacity (150mg/g). According to the data obtained, both carbons (ACW) and (ACK) presented the high surface area range (620-950 m²/g) [97].

In a related study, activated carbon produced from coffee pulp (CP) as dye adsorbent by controlled temperature using chemical activation with disodium hydrogen phosphate (Na₂HPO₄). Different (pulp/Na₂HPO₄ ratios (4:1, 2:1, 5:4, and 1:1) was investigated. According to the data obtained and results of this study, the specific surface area were found to be 140m²/g, 150m²/g, 450m²/g, and 440m²/g for AC4:1, AC

2:1, AC 5:4, and AC 1:1, respectively. AC5:4 showed the highest removal capacity of the organic contaminants methylene blue(MB), direct red(DR), and phenol. The maximum capacities for these activated carbon were found to be 150mg/g, 120mg/g, and 120mg/g for MB, DR, and phenol respectively[98].

Tea and coffee wastes can be also used as radioactive heavy metals adsorbents. However, there are a few studies have addressed the potential use of tea and coffee wastes for the extraction of uranium from aqueous solutions[99].Uranium extraction from aqueous solution using dried and pyrolyzed tea and coffee wastes is the aim of research work studied by Zaynab Aly and Victor Luca, (2013)[99]. The maximum adsorption capacity of uranium by tried tea and coffee wastes was found to be 59.5 and 34.8mg/g respectively at 291K.

Low-cost activated carbon prepared from spent ground coffee was conducted by Pasakorn Jutakradsada et al., (2016), the effects of preparation conditions such as pyrolysis rate, concentration of ZnCl₂, impregnation time, and carbonization temperature on properties of the activated carbon obtained in this study were investigate. These conditions were applied as follows: the pyrolysis rate was fixed at 10°C/min for 4hr with three concentrations of ZnCl₂ (5 wt%, 10 wt%, and 15 wt%), three duration impregnation time (8hr, 12hr, and 24hr), and three carbonization temperatures(400, 450, 500) °C. According to the data obtained, the activated carbon with the best properties was obtained at the preparation conditions given by 15 wt% of ZnCl₂, impregnation time of 24hr, and carbonization temperature of 500°C. The specific surface area and a total pore volume were found to be 831m²/g and 0.44cm³/g respectively [100].

g. Raw and AC derived from rice husk as effective sorbent: Case studies

Presently, several attempts were carried out for the conversion of agricultural waste materials into a cheap raw material for natural adsorbents. Rice husk(RH) is one of the low-value agricultural by-products which have been used as source raw material for synthesis and development of new phases and compounds, as well as natural sorbents for many metals and basic dyes [101]. The rice husk is in the either untreated, treated or modified form using different agents [102].

Adsorption studies using untreated or carbonized rice husk at high temperature were carried out by many authors[103-106]. Maximum adsorption capacities of untreated rice with husk (URH), rice husk(RH), rice husk ash(RHA) heated at 300°C(RHA-300) and 600°C(RHA-600), were 0.12, 0.50, 19.09 and 6.49mg Cr/g adsorbent respectively and 0.47, 294, 18.34, and 4.90 mg Bi/g adsorbent respectively. showing RHA-300 as the most effective adsorbent.[107]. While, few works have been reported on removal reactive dyes by using rice husk [4]. However, Verma and Mishra (2010) [108] in their study, have reported that the sorption capacity increase with the increase of pH value when rice husk is used as dyes adsorbent. The authors found that the removal of crystal violet are 80% and 85% at pH 2 and at pH 10 respectively. For direct orange, the removal was increased from 62% to 85% at pH 2 and pH 10. The equilibrium reached in the acidic medium at pH 6 for both of the dyes. In a related study, Ong *et al.* (2007) conducted a study on the removal of Basic blue 3 (BB3) and Reactive orange 16 (RO16) dyes using Ethylenediamine (EDA) modified rice hull. Maximum adsorption capacity was found to be 14.68 mg/g and 60.24 mg/g for Basic blue 3 dye and Reactive orange 16 dye respectively[109].

In a similar, Sharma and Janveja (2008)[110] conducted a study on the removal of Congo red dye from the effluent of a textile industry using rice husk carbon (RHAC) activated by steam. The study reported that a small amount (0.08 g/l) of rice husk carbon could remove 10 to 99 % of the dye from an aqueous solution of 25 ppm with the contact time increasing from 20 min to 200 min.

In 2001, activated carbon prepared from rice husk at 300°C with chemical activation using 50% H₂SO₄, was conducted by Singh and Srivastava [111]. In their study, have investigated the adsorption capacity for the decolorization of wastewater containing safranin and methylene blue. Maximum capacity was found to be 294.12mg/g and 333.33mg/g for safranin and methylene blue respectively at temperature of 30°C

Chemical modification was commonly used in the modified of rice husk, including H₂SO₄ [103], NaCO₃ [112], HCl [113], KOH and NaOH [114]. Generally, chemical modification of rice husk possessed a better adsorption capacities than unmodified rice husks [93]. Tarley and his co-workers reported that modified rice husk have a higher adsorption capacity on Pb(II) and Cr(II) compared with the unmodified rice husk [115]. Marshall et al. [116] was also showed that better adsorption capacity on metal ions was achieved with treated rice husk. Lee and his colleagues[117] in their research work have concluded that the amount of uptake of As(V) onto rice husk follows the trend of a greater amount of uptake with decreasing As(V) initial concentration. However, adsorption of As(V) was very rapid, taking 20min to achieve equilibrium irrespective of initial concentration. It also attains equilibrium faster than the adsorption such as fly ash and chrome waste, which attained equilibrium after 72min and 120min respectively [94, 118, 119]. Should be transfer to the raw RH as raw material its not AC.

Kumar. and Acharya, (2011)[120]. Investigated a new adsorbent material for the removal of Pd(II) from aqueous solutions. Adsorption studies was conducted by batch mode system using chemically pretreated rice husk as an adsorbent. Equilibrium time was found to be 60min. The value of ΔH and ΔS for Pd(II) were

found to be 21.31kJ/mol and 101.11J/mol respectively. It was observed that an increase in the temperature from 15 °C to 50°C, the removal percent increased from 96% to 98.5%, at the operation conditions of (adsorbent dose =10g/l, initial Pd(II) concentration= 10mg/l. The Gibbs free energy ΔG° values for the adsorption systems of Pd(II) was found to be -7.55, -9.80, -10.41, and -11.06 kJ/mol at temperatures of 15°C, 30 °C, 40 °C, and 50°C respectively. The activation energy for the sorption of Pd(II), was found as 20.02kJ/mol indicating chemisorptions.

Using the same adsorbent, Cd(II) was removed from aqueous solutions. It was observed that with increase in temperature from 15 °C to 40°C, the removal percent increased from 93% to 97% at the adsorbent mass of 10g/l, initial Pd(II) concentration of 10mg/l. Equilibrium time was found to be 60min. The values of ΔH and ΔS for Cd(II) were obtained as 26.4KJ/mol and 101.11J/mol respectively. The activation energy for the sorption of Cd(II), was found to be 11.37kJ/mol indicating chemisorptions[121].

Morcali et al., (2013), Rich husk, a biomass waste product, and Lewatit TP214, a thiosemi-carbazide sorbent, were investigated as adsorbents for the adsorption of platinum (IV) ions from synthetically prepared dilute chloroplatinic acid solutions. The effect of the important adsorption parameters such as sorbent dose, contact time, pH of the solution, and temperature of the reaction on the rate of adsorption were studied using batch experiment. The maximum adsorption capacity was found to be 42.02mg/g and 33.22mg/g for the rice hulls and Lewatit TP214, respectively at temperature of 25°C. The results indicate that the rice hulls could be effectively used for the removal of platinum from aqueous solution[122].

Another research report, the adsorption of Cu(II) and Zn(II) ions from aqueous solutions at low concentrations range (5-100mg/l) in batch systems using rice husk ash (RHA) was investigated by Feroze and his coworkers, (2010)[123]. Their adsorption experiments were carried out at different parameters such as pH of the solution, equilibrium time, and initial of Cu(II) and Zn(II) ions concentrations. According to the data obtained, Freundlich isotherm model was best fits the experimental results.

Similarly, adsorbent from rice husk ash (RHA), was the aim of another research work achieved by Naeem S. et al., (2009)[124], when they investigated the possibility of using the rice husk for the removal of Cr(VI) from aqueous solution using batch-technique. Percentage adsorption was estimated for RHA-Chromim solution system as a function of initial Cr(VI) concentration, pH, contact time, and temperature of the adsorption. In the isotherm studies the experimental adsorption data fitted with the Langmuir and Freundlich models. The optimum pH was found to be 1. The value of ΔH was found as 16.4708kJ/mol.

On the other hand, there are number of studies which 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). Based upon the experimental results of these studies, the following conclusions were drawn: 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 liters), (2.22 liters) and (2.15 liters) of Zn(II), Pb(II), and Cu(II) respectively at breakthrough. The results was also reported that, about (3.74 g), (3.90 g) of NCRH were required per liter of Pb(II) and Cu(II) treatment respectively [125, 126, 127].

A similar adsorbent was the aim of another research study achieved by Nasehir et al., (2011) [29] the aim of the study was to evaluate the process of Cu (II) sorption onto rice husk based activated carbon (RHAC). Carbonization step was carried out at 700°C for 30 min under nitrogen (99.99%) at flow rate of 150 mL/min, and (ZnCl₂) was used as an activator. Experiments were carried out in a laboratory column for differential flow rate, height of bed and initial concentration of Cu (II).The breakthrough characteristics of the adsorption system were determined. The maximum capacity was found to be 34.56 mg/g at operating conditions of 10 mg/l initial Cu (II) concentration, 80 mm sorption bed height and 10 ml/min flow rate.

Rice husk adsorbent for removal of metal ion, in a packed bed adsorption column were used by Kulkarni and Kaware, (2015). The removal of cadmium in a packed bed was studied by them. It was observed that an increase in the initial cadmium concentration from 10 mg/l to 50 mg/l, the exhaustion time decreased from 830 min to 570 min and break point time decreased from 330 minutes to 120 minutes. Also with increase in flow rate, exhaust time and break through time decreased significantly. The optimum operation 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 [128].

Low-cost activated carbon derive from rice husk was the aim of study conducted by Esra Altintig et al., (2015), the activated carbon (AC) was prepared by chemical activation using (ZnCl₂) at 700°C in nitrogen atmosphere. The BET surface area of the highest yield of AC was found to be 922.319m²/g [129]. The authors was also reported that the source of the activated carbon is an important factor for its properties.

In a related study, kalderis et al.,(2008) [130] have produced activated carbon from rice husk and sugarcane bagasse by chemical activation with H₃PO₄, NaOH, and ZnCl₂ at the carbonation temperatures of 600°C, 700°C, and 800°C, and the optimum carbonization temperature was found to be 700°C as the highest surface area has been obtained at that temperature with ZnCl₂.

In 2016, rice husk (RH) an agricultural by-product was used as mass application for the production of activated carbon(AC) by chemical activation using $ZnCl_2$ - $CuCl_2$ composite activator. The effect of process conditions, such as $ZnCl_2$ and $CuCl_2$ concentrations, activation temperature and activation time were investigate. Results of this study showed that the BET surface area of the produced AC was as high as $1924m^2/g$ and the total pore volume was found to be $1.493cm^3/g$ [131].

Adsorption behavior of different low-cost adsorbents like peanut husk charcoal, fly ash, and natural zeolite, with respect to $Cu(II)$ and $Zn(II)$ ions were studied by Abdel Salam et al., (2011). The batch experiments under different experimental conditions has been studied to evaluate the uptake levels of the metal ions. The optimum ph for copper and zinc removal was 6 in the case of peanut husk charcoal and natural zeolite, and it was 8 in case of fly ash. The equilibrium was done after 2h for the adsorption of $Cu(II)$ and $Zn(II)$ by peanut husk charcoal and fly ash and after 3h for the adsorption of the same ions onto natural zeolite [132].

Daffalla and Mukhtar, (2012)[35] have produced activated carbon from rice husk by chemical activation with ($ZnCl_2$) and (H_3PO_4) under different activation conditions at carbonization temperatures of $500^\circ C$ and $600^\circ C$ for the removal of phenol from artificial wastewater. Results showed that the efficiency of phenol removal by H_3PO_4 activated carbon generally lower than that of $ZnCl_2$. It was reported that, for 0.1 g $ZnCl_2$ activated carbon, an efficiency of 80% to 85% and 69% to 74% could be achieved at $500^\circ C$ and $600^\circ C$ activation temperature respectively. While, the removal efficiency of up to 90% could be achieved with 0.5 g $ZnCl_2$ either prepared at $500^\circ C$ or $600^\circ C$ activation temperature. On the other hand, the efficiency of 0.1g and 0.5 g H_3PO_4 activated carbon was found to be 45% to 48% and 48% to 56% respectively at $500^\circ C$. While, for H_3PO_4 activated carbon prepared at $600^\circ C$, an efficiency of 41% to 45% and 43% to 51% could be achieved with 0.1g and 0.5g respectively.

Gasoline adsorption onto activated carbon rice husk(ACRH), which activated by H_3PO_4 at temperature of $450^\circ C$ was the aim of study conducted by Cheenmatchaya and Kungwankunakorn, (2014). According to the results and gasoline adsorption in this study, the optimum condition were 0.1g activated carbon adsorbent, adsorption temperature of $70^\circ C$ and contact time of 30min. The results reported that the (RHAC) possesses a high apparent surface area ($S_{BET} = 336.35m^2/g$)[133].

Effect of preparation conditions of activated carbon derived from rice husk (RHAC) by chemical activation using $ZnCl_2$ for removal of $Cu(II)$ from aqueous solution was conducted by Nasehir Khan E M Yahaya and his coworkers, (2010), their batch adsorption studies was done as follows: 0.3g of adsorbent were mixed with 100ml aqueous solutions of 50mg/l initial in 13 sets of 250ml Erlenmeyer flasks. The mixture was agitated at temperature and agitation rate of $30^\circ C$ and 400rpm, respectively until equilibrium was reached. The experimental design work was also applied to study the variables for preparing the activated carbon from (RHAC) the variables studies were activation temperature, activation time and impregnation ratio(IR)as follows: activation temperature of (500, 600, and 700) $^\circ C$, activation time of (0.6, 1.3, and 2.0) hr, and IR of (0.6, 1.3, and 2). According to the data obtained, the optimum RHAC was obtained by using activation temperature, activation time, and IR of $500^\circ C$, 1.71hr, and 1.04 respectively, which resulted RHAC yield of 34.21%, and $Cu(II)$ removal of 33.92% [134].

Agricultural by-product in Egypt amount range from 30-35million tons annually of which only 7million tons are used as animal feed and 4million tons as organic manure[135]. Rice husk ash production by Open -field burning and by combustion at $1000^\circ C$ for 4hr was conducted by Abdel Rahim and his coworkers[135] their results revealed that higher growth rates and larger crystals had been obtained by combustion at $1000^\circ C$ and the occurrence polymorphs of silica. Activation of rice husk ash with (3.5N NaOH) followed by acid deposition technique resulted in high silica in the agglomerate form with dimension of 7nm and the particle shape distribution was found to be uniform. The value-added activated carbon of rice husk can be also simply produced by chemical activation of rice husk ash at $900^\circ C$ for carbonization time of 120min.

Mahvi and his assistant, (2005) have carried out $Cd(II)$ ion removal from the wastewater using rice husk (RH) and rice husk ash (RHA)[136]. Their studies indicated that the $Cd(II)$ removal efficiency increased with increase in the pH value until pH of 6.0. The maximum adsorption capacity was found to be 97.2% and 99.2 % for (RH) and (RHA) respectively.

The removal of $Zn(II)$ from aqueous solution by different adsorbent was investigated by Bhattacharya and coworkers[137]. The adsorbed materials were clarified sludge (steel industry waste materials), rice husk ash, neem bark, and a chemical adsorbent activated alumina. Results proved that the adsorption of $Zn(II)$ increased with the increase concentration of the adsorbents and reached max. uptake at 10 g/l and pH between 5 and 7. The equilibrium time using batch mode techniques was achieved after 1 hr for clarified sludge, 3 hr for rice husk and 4 hr for activated alumina and neem bark. Researchers of this work explained the increase in removal efficiency as the mass of the adsorbent, as due to the increase of the active sites on adsorbents. Maximum adsorption of $Zn(II)$ obtained at adsorbent dose of 10 g/l for all adsorbents. Thermodynamics calculation proved that $Zn(II)$ adsorption occurs spontaneous in nature.

Daifullah and his coworkers (2003), utilized (RH) in removal of heavy metals from a complex matrix containing six metal ions (Fe, Mn, Zn, Cu, Cd, and Pd). They found a high metal removal efficiency of sorbent was approximately 100% [138]

Awwad et al., (2010)[139] have produced activated carbon from (RH) by chemical activation with phosphoric acid (H₃PO₄). The effect of adsorption parameters such as initial concentration, temperature, pH, and contact time of carbon on the adsorption capacity of lanthanum La(III) and Erbium Er(III) were investigated. Maximum adsorption capacities were found to be 175.4mg/g and 250mg/g for La(III) and Er(III) respectively. Activation energy of La(III) adsorption by (RHAC) was found to be 5.84kJ/mol, while 14.6 kJ/mol for and Er(III).

Activated carbon produced from rice husk and its characteristics is the aim of research study achieved by Hariprasad et al., (2016)[140]. Produced rice husk activated carbon was carried out using physical and chemical activation methods respectively as follows: The material selected were initially physically activated at temperature ranging from 300°C to 700 °C for 60min, then the carbonized material thus obtained was soaked into 1N KOH, in 1:1 ratio for overnight and was followed physical activation at 300°C for 120min. The BET surface area were found to be ranging from 11.9985m²/g to 279.7752m²/g. Their studies indicated that the phenol adsorption capacity in % increased with increase in the temperature. The maximum adsorption capacity was obtained (25.6%, 66.66%, 87.4, 94.6%, and 95.8%) at temperatures of (300, 400, 500, 600, and 700)°C respectively.

Table. 5: Surface area and total pore volume results of AC produced from rice husk reported in literature

Rice husk activated carbon						
S N.	CT, °C	Activation method	Activator	S _{BET} , (m ² /g)	V _{tot} , (cm ³ /g)	Reference
1	400	Chemical	ZnCl ₂	604.34	0.41	[134]
2	400	Chemical	NaOH	2681.0	1.4016	[30]
3	450	Chemical	H ₃ PO ₄	336.35	-	[133]
4	500 & 600	Chemical	ZnCl ₂ & H ₃ PO ₄	-	-	[35]
5	700	Chemical	ZnCl ₂	922.319	-	[129]
6	500	Chemical	ZnCl ₂ -CuCl ₂	1924.0	1.493	[131]
7	900	Chemical	NaOH	-	-	[135]
8	500	Chemical	ZnCl ₂	927.0	0.56	[141]
9	500	Chemical	H ₃ PO ₄	329.87	-	[28]
10	500	Chemical	ZnCl ₂	280	-	[28]
11	500	Chemical	NaOH	59.05	-	[28]
12	500	Physical	CO ₂	201.15	-	[28]
13	300	Physical and chemical	Heat and KOH	11.99	-	[140]
14	700	Physical and chemical	Heat and KOH	279.77	-	[140]

CT= carbonization temperature, S_{BET} = surface area, (V_{tot})= Total pore volume.

V. Final Remarks

The major remarks based on the information gathered from scientific literatures are as follows:

- 1- Based on researches, experimental works and scientific reports proved that agricultural by-product/wastes and especially recycled coffee grounds, spent tea leaves, and rice husk may be applied for wastewater treatment
- 2- Research studies proved that the preparation and application of both raw and activated carbon from agricultural by-product/wastes are eco-friendly adsorbent and no cost required
- 3- Year by year, a huge amount of agricultural waste materials are rapidly increased worldwide, a major of such waste in carried to open area for disposal by burning, and this which releases carbon dioxide into the air.
- 4- Recycling way maybe the best option for use in mass applications and especially agricultural by-product/wastes
- 5- Case studies have showed that rice husk also has a good value as a biomass fuel, and can be used as fuel for parboiling and drying of paddy before milling.
- 6- Research studies reported that coffee is second largest traded commodity in the world, after petroleum.
- 7- Adsorption process is a fundamental process today due to its low space equipments for operation unit, simplicity and flexibility of design and ease of operation, non pollutant to water, and low-cost adsorbent, removing or minimizing the pollutants from water contaminated.

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