Iranian Association of Chemical Engineers, Unit 11, No. 13 (Block 3), Maad Building, Shahid Akbari Boulevard, Azadi Ave., Tehran - Iran.

Tel: +98 21 6604 2719 **Fax:** +98 21 6602 2196

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A Review on the Hazardous Materials Removal Using the Activated Carbon Derived from the Walnut (*Juglans regia* L.) Shells

***A. Jahanban-Esfahlan*[1], *R. Jahanban-Esfahlan*[2,3], *M. Tabibiazar*[4,5], *L. Roufegarinejad*[6], *R. Amarowicz*[7*]**

[1] *Nutrition Research Center, Tabriz University of Medical Sciences, Tabriz, Iran*
[2] *Biotechnology Research Center, Tabriz University of Medical Sciences, Tabriz, Iran*
[3] *Department of Medical Biotechnology, School of Advanced Medical Sciences, Tabriz University of Medical Sciences, Tabriz, Iran*
[4] *Drug Applied Research Center, Tabriz University of Medical Sciences, Tabriz, Iran*
[5] *Department of Food Science and Technology, Faculty of Nutrition and Food Science, Tabriz University of Medical Sciences, Tabriz, Iran*
[6] *Department of Food Sciences, Tabriz Branch, Islamic Azad University, Tabriz, Iran*
[7] *Division of Food Sciences, Institute of Animal Reproduction and Food Research of the Polish Academy of Sciences, Olsztyn, Poland*

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ABSTRACT

The shell of the walnut fruit is an agricultural byproduct generated in considerable amounts upon the processing of the fruit to obtain its valuable kernel. Walnut is recognized as an appreciated tree nut belonging to the Juglandaceae family. The fruit is mainly composed of a kernel, seed coat, shell, and husk. In recent years, the shell portion of the walnut fruit has been widely used in the development of different high-value materials. In this regard, high carbon and low ash contents of the walnut shell (WS) make it a suitable material, as an inexpensive agricultural waste product, for the preparation of the activated carbon (AC). In this review, recent developments in the preparation of AC from the shell of the walnut fruit and the characterization methods are highlighted. Additionally, the applications of AC mainly in the removal of different hazardous materials such as heavy metals (HMs) ions, dyes as well as pharmaceuticals and other dangerous materials are comprehensively discussed.

1. Introduction

Recently, the utilization of the activated carbon (AC) has noticeably increased because of its applications in pharmaceutical, chemical, and food industries [1]. There are many precursors considered for the preparation of AC. Choosing an appropriate raw material for the generation of AC depends on its price, purity, stability of supply, and possible extent of activation. Today, wood/coconut (45 %) and coal/lignite (42 %) are the primary sources considered for the generation of the commercial AC [2].

Many investigations are now recorded in the scientific literature describing the AC generation from biomass. In the recent decades, various types of crop waste materials and forestry residues, or the conventional biomass, have been utilized as starting materials in the production of the low-priced AC. For example, it has been shown that AC can be produced from different plant-based

[*]Corresponding author: amaro@pan.olsztyn.pl

waste crops including stone fruits (apricot, cherry, and peach), nutshells (walnut, almond, and pecan), acorns, bagasse, rice hulls, corncobs, grape seeds, wheat straw pellets, wheat straws, rice straws, olive stones, beachwood, hard coals, pistachios shells, etc. [3].

Agricultural byproducts can be proposed as low-priced and renewable resources for obtaining AC because they are available in the form of lignocellulosic waste materials in large volumes [4]. Their easy availability in high volumes is a critical point because different crops, being harvested and processed worldwide every year, produce considerable amounts of agricultural byproducts. Also, choosing appropriate raw materials and making effective use of such waste products can reduce the pollution caused by the release of substantial amounts of agricultural crop wastes into the environment while reducing the cost of the raw material in the production of AC. Clearly, the production of AC from the discarded agricultural byproducts, as waste and low-priced materials, can reduce the environmental pollution and increase the economic efficiency [5]. Such agricultural residues are commonly cheap and without any useful applications proposed for them yet. In addition, the AC derived from plant-based materials shows a high specific active surface area. Hence, the generation of AC using agricultural byproducts has stimulated a lot of interest [6].

The results of some studies have revealed that the walnut shell (WS) is a suitable source, and it could be employed in the preparation of AC [7]. The volatility and carbon content of WS are high, in contrast, the amount of its ash is low. Moreover, it shows reasonably excellent hardness. In this review, firstly, the chemical composition of WS and the obtained AC are discussed. Then, recent developments in the preparation, the characterization of the AC from the WS, are highlighted. Besides, the practical uses of the prepared AC for the removal of hazardous materials such as heavy metals (HMs) and dyes, as well as other dangerous materials are comprehensively discussed.

2. Activated carbon

AC has been extensively considered as a useful sorbent in the separation and refinery systems containing gaseous or aqueous solutions. In the catalytic reactions, AC is used as a catalyst or catalyst protector. Therefore, it has a central function in different fields, including food, pharmaceutical, and chemical industries. Some characteristics of AC, such as the presence of functional groups on the hydrophilic surface, high porosity, and hydrophobic graphene layer make it a suitable material for the sorption and catalytic applications [8].

Generally speaking, the type of feedstock and the operational conditions for the execution of activation processes such as the impregnation rate of the chemical reagent, activation time, and final activation temperature are considered as the key factors that determine the quality of the obtained AC. AC may be produced using either a physical [9, 10] or a chemical process [11, 12]. In the physical activation (PA), a carbonaceous precursor is carbonized following the gasification of the obtained char. Generally, steam, carbon dioxide (CO_2), and a combination of both agents are used as chemical activators for the direct activation of the original material [13]. The gasification or activation process selectively removes the most reactive carbon atoms in the AC, causing the porosity in the structure of the

obtained AC. Typically, the chemical activation (CA) is useful because it is done at a shorter time and a lower temperature, which is the condition required in the PA. Also, the AC is achieved with an acceptable porous structure during the execution of the CA. In comparison to the PA process, the yield of the produced carbon in the CA procedure is high. Due to dehydrogenation properties of chemical agents used as activators, the development of tar and generation of some volatile constituents decrease during the CA production [14, 15].

3. Walnut byproducts and characteristics

Walnut is recognized as a valuable tree nut belonging to the Juglandaceae family [16-18]. In recent years, the global production of walnut has been rapidly increased predominantly in Asian countries due to the valuable kernel. Walnut is a high-density nutrient nut which is rich in essential fatty acids and protein. It has been well-evidenced in many documents that the high nutritional value and antioxidant properties of walnut are associated with its edible kernel [19-25]. It has also been mentioned that walnut contains the highest amount of antioxidants among different studied nuts [26-28] and thus, it could be named the "King of Nuts". There are many reports in the scientific texts demonstrating the benefits of the walnut consumption for the human health [29-32]. Besides, it has been well-documented that the regular consumption of walnut is associated with the reduction of the risk of coronary artery diseases, various cancers, and also Alzheimer [33-43]. Recently, the anticancer activity of a naphthoquinone, namely juglone, has aroused highly-increasing interests [44-47]. Other portions of the walnut tree have been comprehensively studied and various chemicals, with excellent biological activities, have been identified and isolated from its husk [48-53], shell [54-62], leaf [63-70], branch [71], shoot [72], and bark [73, 74]. The husk, shell, leaf, and branch of walnut, which are considered as waste materials, are widely used in the folk medicines of different countries for the treatment of various diseases.

The fruit is the most crucial portion of the walnut tree, which contains the valuable meat. It comprises four distinct portions (for further details, see Figure 1). The edible part of the fruit is the kernel or meat which is consumed as food in human nutrition. A thin leathery light brown layer surrounds the kernel of walnut. This part of the fruit is known as the seed coat or skin. Like in other nut trees, the high content of phytochemicals with excellent antioxidant and antiradical properties are concentrated in this part of the fruit [4, 48]. The high concentration of antioxidants in the seed coat protects kernel constituents against different deleterious effects resulting from UV irradiation or viral, bacterial, and fungal contaminations. The shell is a hard material with limited uses and considered to be the middle part of the fruit and must be mechanically cracked to separate the edible kernel. The outer layer of the walnut fruit is named husk, hull, or green husk. After the full ripening of the walnut fruit on the tree, it cracks and thus, could be easily separated. The remaining part of the fruit after removing the husk is known as the nut [24].

Undoubtedly and from the nutritional point of view, the importance of walnut is due to its appreciated seed. All over the world, the trees of walnut are widely cultivated in order to obtain its valuable meat. In walnut production centers, upon the processing of the fruit, the husk and shell portions are available in

considerable volumes as agricultural byproducts (Figure 1). Approximately, more than 60 % of the walnut fruit is its husk and shell discarded without any practical use defined for them [62, 24].

Generally, the shell of the walnut fruit is described as a solid lignocellulosic abrasive material that is non-toxic, biodegradable, and chemically inert. Upon grounding and sizing, it will show different uses. WS is applied as a media in the abrasive blasting for polishing and cleaning plastics, wood, stone, and soft metals. Before painting different tools and parts, their surface can be prepared by using the WS. It is also considered a helpful product used for castings, moldings, electrical purposes, etc. Additionally, it can be employed as a polisher and cleaner in different applications, including barrel tumbling. As the scrubber in the soap and cosmetic industries, loss circulation material in the oil industry, extender in the adhesives, filler in the castings and filter device in the hydromation systems are other utilizations reported for WS [57, 75, 76].

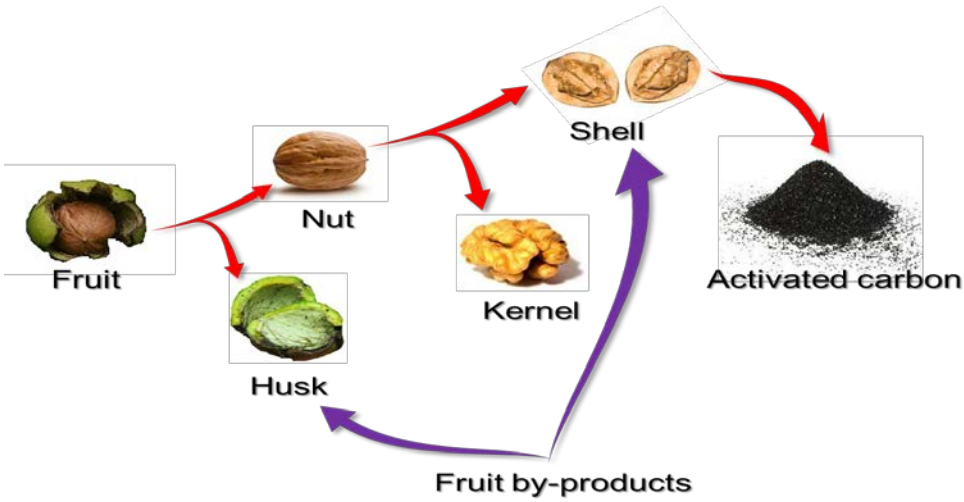

Figure 1. Representation of different parts of the walnut fruit in a cartoon image. The walnut fruit includes four main parts namely the husk, shell, pellicle, and kernel. The pellicle is not shown here in the separated form of other portions. The husk and shell are considered as the main waste materials of the walnut fruit.

As an agricultural waste material, WS shows some advantages such as excellent durability and elasticity, being environmentally friendly, and being cost-effective. It also cleans well without leaving pits or scratches. Its color is light brown, and its specific gravity is between 1.2 and 1.4. The shell of walnut is an organic material, which is mainly composed of 40-60 % cellulose and 23-30 % lignin. The nitrogenous matter and ash contents have been reported to be in low amounts. The primary carbonaceous material existing in the cell wall is lignocellulose, and its composition may vary among different plant species [8]. Commonly, the walnut kernel is considered as a vital nutrient crop, while its shell has no economic value and is discarded. Hence, for the conversion of the waste WS to a useful product, the production of AC can be a suitable option [77].

Table 1 presents the corresponding elemental or ultimate analyses reported in different scientific literatures. The raw material of WS is mainly composed of carbon (C) [78, 79, 8, 80-86, 3, 87, 54, 88-91], oxygen (O) [78, 8, 83, 84, 86, 3, 54, 88, 89, 91], and the trace amounts of nitrogen [78,

80, 81, 83-86, 3, 75, 76, 54, 88, 89, 91]. As an agricultural crop waste, WS contains approximately a little aluminum (Al) [8, 86], sulfur (S) [78, 8, 83-85, 3, 88, 89], calcium (Ca) [8, 80, 86], magnesium (Mg) [8 80, 86], chlorine (Cl) [3, 75, 76], phosphorous (P) [8, 80], potassium (K) [8, 80], sodium (Na) [80], silicon (Si) [8], and additionally, has a low amount of hydrogen (H) [86, 78, 79, 81, 83-85, 3, 87, 54, 88-91]. The high contents of carbon and oxygen are associated with the presence of polysaccharides such as lignin, cellulose, and hemicellulose in the WS. As seen, due to its high contents of carbon, WS is a suitable material for the production of AC [87].

Table 1
The ultimate analysis of the WS.

No.	Ultimate analysis	Content	Ref.
1	C	49.50[d]	Xie et al. [88]
		48.59[b]	Wei et al. [54]
		17.29[e]	Kuśmierek, Świątkowski [86]
		65[e]	Jafari-Mansoorian et al. [82]
		48.34[e]	Ac¸ıkalın [78]
		66.3[d]	Ghasemi et al. [81]
		42.6[d]	Zabihi et al. [90]
		88.7[e]	Alighardashi, Shahali [79]
		516[g]	Feizi, Jalali [80]
		46.64 ± 0.01[d]	Kim et al. [85]
		48.7[d]	Yang, Qiu [89]
		49.00[d]	Soleimani, Kaghazchi [137]
		50.7[d]	Schröder et al. [3]
		47.97[d]	Kar [83]
		44.7[f]	Zhu et al. [91]
		57.54[h]	Azat et al. [8]
		53.77[d]	Karatas, Akgun [84]
2	H	6.80 [d]	Xie et al. [88]
		6.81[b]	Wei et al. [54]
		6.16[e]	Ac¸ıkalın [78]
		4.74[d]	Ghasemi et al. [81]
		4.74[d]	Zabihi et al. [90]
		0	Alighardashi, Shahali [79]
		6.05 ± 0.02 [d]	Kim et al. [85]
		7.11[d]	Yang, Qiu [89]
		5.75[d]	Soleimani, Kaghazchi [137]
		6[d]	Schröder et al. [3]
		6.35[d]	Kar [83]
		6.3[f]	Zhu et al. [91]
		5.39[d]	Karatas, Akgun [84]
3	N	1.59 [d]	Xie et al. [88]
		0.63[b]	Wei et al. [54]
		6.10[e]	Kuśmierek, Świątkowski [86]
		0.69[e]	Ac¸ıkalın [78]
		0.435[d]	Ghasemi et al. [81]
		0.10	Srinivasan, Viraraghavan [76, 75]
		4.9[g]	Feizi, Jalali [80]
		0.73 ± 0.03 [d]	Kim et al. [85]
		0.76	Yang, Qiu [89]
		-	Schröder et al. [3]

		0.15[d]	Kar [83]
		1.8[f]	Zhu et al. [91]
		0.43[d]	Karatas, Akgun [84]
4	O	42.11[c]	Xie et al. [88]
		41.84[b]	Wei et al. [54]
		72.28[e]	Kuśmierek, Świątkowski [86]
		44.78[c]	Ac¸ıkalın [78]
		42.84[d]	Yang, Qiu [89]
		-	Schröder et al. [3]
		45.50[d]	Kar [83]
		47.2[f]	Zhu et al. [91]
		39.5[h]	Azat et al. [8]
		38.34[d]	Karatas, Akgun [84]
5	Al	4.33[e]	Kuśmierek, Świątkowski [86]
		-	Azat et al. [8]
6	S	-	Xie et al. [88]
		0.03	Ac¸ıkalın [78]
		0.03 ± 0.01[d]	Kim et al. [85]
		1.22[d]	Yang, Qiu [89]
		-	Schröder et al. [3]
		0.03[d]	Kar [83]
		0.98[h]	Azat et al. [8]
		0.12[d]	Karatas, Akgun [84]
7	Ca	-	Kuśmierek, Świątkowski [86]
		6.2[g]	Feizi, Jalali [80]
		1.62[h]	Azat et al. [8]
8	Mg	-	Kuśmierek, Świątkowski [86]
		2.9[g]	Feizi, Jalali [80]
		0.16[h]	Azat et al. [8]
9	Cl	0.1[f]	Srinivasan, Viraraghavan [76, 75]
		-	Schröder et al. [3]
10	P	1.2[g]	Feizi, Jalali [80]
		-	Azat et al. [8]
11	K	20.6[g]	Feizi, Jalali [80]
		0.80[h]	Azat et al. [8]
12	Na	4.9[g]	Feizi, Jalali [80]
13	Si	0.60[h]	Azat et al. [8]

[a] On the moisture-free basis.
[b] On the as-received basis.
[c] Calculated by the difference.
[d] Dry basis, wt (%).
[e] Mass (%).
[f] By weight (%).
[g] mg/g.
[h] %.

The analysis results for the constituents of WS indicate that it contains low amounts of extractives [92, 83, 87, 88], cutin [75, 76], protein [93], and benzene-alcohol extractives [89]. But the contents of hemicellulose [92, 83, 54, 88, 89, 93], lignin and cellulose [83, 87, 75, 76, 54, 88, 89, 93] are considerable in the WS (Table 2). According to the proximate analysis, the moisture [78, 79, 81, 83, 84, 3, 75, 76, 54, 88, 89] and ash [78, 79, 81-84, 3, 87, 75, 76, 54, 88, 89, 93] contents of WS are not significant while it contains high amounts

of fixed carbon and volatiles [78, 92, 83, 84, 71, 89] (Table 3). A high iodine number and specific surface area have been reported for the AC obtained from the shell of the walnut fruit. These properties are associated with the low ash and high lignin contents of the shells. Hard shells such as WS have relatively low ash contents [84]. For the above reason, these agricultural waste products have a high potential to be employed as a low-cost starting material in the production of a low-priced AC. The high ash content in the employed material as a precursor is not desirable because it affects the mechanical properties of the generated AC and decreases its adsorption capacity. For example, it has been revealed that raw waste materials such as the straw of rice contain high amounts of ash, which is mainly composed of silica leading to a decrease in the quality of the generated AC and subsequently, the active surface area per mass unit is not considerable [3]. The ash content of different raw materials can be related to the composition of their inorganic constituents. It seems that the active surface area of the produced AC mainly depends on the ash content. Thus, it could be said that a higher ash content decreases the active specific surface area of the developed AC.

For the most considered plant-based waste crops, the carbon content increases, but the content of hydrogen in the prepared AC decreases compared to their precursors. The release of volatile constituents can explain these changes during the pyrolysis process that leads to the elimination of non-carbon species and the enrichment of the carbon content [79]. Accordingly, the WS as a waste product shows a good potential for obtaining AC because it contains relatively high carbon and low ash contents [89].

Table 2
The component analysis of the WS.

No.	Component analysis	Content	Ref.
1	Extractives	6.73 [b]	Xie et al. [88]
		2.8[c]	Demirbas [92]
		2.6[b]	Kar [83]
2	Hemicellulose	28.30[b]	Xie et al. [88]
		21.32[a]	Wei et al. [54]
		30.2[b]	Yang et al. [93]
		29.28[b]	Yang, Qiu [89]
		22.1[c]	Demirbas [92]
		22.45[b]	Kar [83]
3	Lignin	32.50 [b]	Xie et al. [88]
		53.52[a]	Wei et al. [54]
		20.30[c]	Srinivasan, Viraraghavan [76, 75]
		39.1[b]	Yang et al. [93]
		37.14[b]	Yang, Qiu [89]
		33.30[c]	Soleimani, Kaghazchi [87]
		52.3[c]	Demirbas [92]
		47.68[b]	Kar [83]
4	Cellulose	32.47 [b]	Xie et al. [88]
		25.16[a]	Wei et al. [54]
		40.60[c]	Srinivasan, Viraraghavan [76, 75]
		27.9[b]	Yang et al. [93]
		23.55[b]	Yang, Qiu [89]
		34.50[c]	Soleimani, Kaghazchi [137]

		25.6[c]	Demirbas [92]
		26.87[b]	Kar [83]
5	Cutin	1.0[c]	Srinivasan, Viraraghavan [76, 75]
6	Protein	5.1[b]	Yang et al. [93]
7	Benzene-alcohol extractives	5.21[b]	Yang, Qiu [89]

[a] On the as-received basis.
[b] Dry basis, wt (%).
[c] By weight (%).

Table 3
The proximate analysis of the WS.

No.	Proximate analysis	Content	Ref.
1	Moisture	1.23[b]	Xie et al. [88]
		6.65[a]	Wei et al. [54]
		2.57[b]	Ac¸ıkalın [78]
		2.2[c]	Ghasemi et al. [81]
		1.97[d]	Srinivasan, Viraraghavan [76, 75]
		9[e]	Alighardashi, Shahali [79]
		3.42[f]	Yang, Qiu [89]
		10.7[b]	Schröder et al. [3]
		7.71[e]	Kar [83]
		0.00[b]	Karatas, Akgun [84]
2	Ash	1.92[b]	Xie et al. [88]
		2.13[a]	Wei et al. [54]
		10.4[b]	Jafari-Mansoorian et al. [82]
		0.64[b]	Ac¸ıkalın [78]
		2.6[c]	Ghasemi et al. [81]
		1.5[e]	Srinivasan, Viraraghavan [76, 75]
		2.6[d]	Alighardashi, Shahali [79]
		1.3[b]	Yang et al. [93]
		0.53[f]	Yang, Qiu [89]
		1.70[e]	Soleimani, Kaghazchi [137]
		0.9[b]	Schröder et al. [3]
		0.94[e]	Kar [83]
		1.95[b]	Karatas, Akgun [84]
3	Fixed carbon	21.57[a]	Wei et al. [54]
		18.75[b]	Ac¸ıkalın [78]
		17.61[f]	Yang, Qiu [89]
		37.9[e]	Demirbas [92]
		13.48[e]	Kar [83]
		23.82[b]	Karatas, Akgun [84]
4	Volatiles	69.65[a]	Wei et al. [54]
		78.04[b]	Ac¸ıkalın [78]
		78.44[b]	Yang, Qiu [89]
		59.3[e]	Demirbas [92]
		77.87[e]	Kar [83]
		74.23[b]	Karatas, Akgun [84]

[a] On the moisture-free basis.
[b] Dry basis, wt (%).
[c] Mass (%).
[d] (%).
[e] By weight (%).
[f] As received, wt (%).

4. Activated carbon from the walnut shell

Dehydration, carbonization, and activation are three main stages regarded in the generation of AC. In the dehydration step, the raw material is dried in order to remove its moisture. During the execution of the carbonization step, the content of the organic matter in the initial material is converted to a primary carbon, which contains a mixture of crystallized and amorphous carbon, ash, and tar. The primary step in the preparation of AC is the activation process. It is commonly performed using two procedures, the activation by gas and chemical activation. The first one is a physical process because the used material is carbonized at low temperatures. Generally, air, the water steam, and CO_2 are the most considered activators. Long treatment conditions and the employment of the water steam as the gas activator at high temperatures (800-1000 °C) are the most used methods in the gas activation process. The lack of homogeneity and a low yield of the produced carbonized material are the significant disadvantages proposed for the gas activation process [94, 95]. In contrast, the yield of the produced AC is high because of chemical agents, such as sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH), zinc chloride ($ZnCl_2$), and calcium chloride ($CaCl_2$) with dehydration and oxidation properties utilized in the CA process which induce the pyrolytic decomposition and subsequently, inhibiting the formation of tar. Usually, in the CA process, the carbonization and activation steps are carried out at the same time [96, 2].

For a long time, the use of different chemical agents has been considered in the CA process, and generally, $ZnCl_2$ and H_3PO_4 have been the most used chemicals as activation reagents. It is also known that the CA procedure could be considered as an efficient process in the production of AC, which is used in the removal of hazardous materials from wastewater. According to the results of several studies, the kind of used chemical agents and the operating conditions during the activation process could affect the adsorbent capacity and specific surface area of the prepared AC [97, 85].

In order to characterize the developed AC, its iodine value, the specific active surface area, the amounts of ash and some other chemical/physical properties must be determined. The iodine number (mg I_2/g of carbon) indicates the degree of the micropores distribution in the structure of the generated carbonized material and is obtainable by titration experiments at 30 °C. The adsorption capacity of the prepared AC can be determined using this method. The iodine (I) number is defined as the content of the adsorbed iodine in the unit weight of the AC. It is calculated using the presented equation [85]:

$$I = \frac{[(10\times f\prime - K\times f)\times 12.69\times\times 5]}{S} \quad (1)$$

In this equation, I is the amount of the adsorbed iodine (mg/g), K is the titration volume of the 0.1 M sodium thiosulfate solution (ml), f' and f are the concentration factors of iodine and the 0.1 M sodium thiosulfate solution respectively. 12.69 is the content of iodine in 1 ml of the 0.1 M sodium thiosulfate solution (mg), and S is the weight of the dried AC (g).

The specific active surface area for the obtained AC is measured by the BET (Brunaeur-Emmet-Teller) method. The adsorption-desorption isotherm of nitrogen (N_2) at 77 K is used for obtaining the BET value. The thermal desorption of argon can

also be used for the determination of the specific active surface area [8]. If the carbonaceous content of the raw material is entirely burned off, the remained residue is known as the ash amount of the prepared AC. The content of ash for the produced AC can be calculated by some other standard methods [87]. The liquid volumes of N_2 at a relatively high pressure are used for the determination of total pore volumes. The absence or presence of functional groups on the surface of the generated AC and its structure are considered by the Fourier transform infrared spectroscopy (FT-IR). Thus, the similarities and differences in the functional groups between the used raw material and the prepared AC can be quickly investigated. Also, the thermogravimetric (TG) analysis is useful in order to study the thermal stability of the prepared AC. The point of zero charge (PZC) is performed to obtain information about the superficial charge of the developed carbonized mass. This method is carried out using different weights of the AC in a solution prepared by NaCl. The PZC of AC is the value when the pH is constant [98]. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are useful for the observation of the microporous surface structure and the morphology of the produced AC [89].

The preparation of AC from WS using the CA process has been described in some research studies (Table 4). H_3PO_4, KOH, $ZnCl_2$, and NaOH are the most used activating agents in such studies. The temperature of the CA process was in the range of 400-900 °C. In most of performed studies, the time for preparing the AC from the WS was almost 1 h. The generated AC showed the iodine number in the range of 676-1300 mg I_2/g; the surface BET (S_{BET}) of 424-1800 m ^{2}/g and the total pore volume of 0.304-1.221 cm^3/g. Most of the prepared AC from WS has been produced using the CA process (Table 4), and the PA procedure has only been used in a few studies (Table 5). In these cases, the CO_2 and steam atmosphere were used as the activating agents, and the time of the PA process was 1h. Only the S_{BET} values of the generated AC from WS have been reported in these investigations. The comparison of S_{BET} values for the AC prepared from WS by using CA and PA processes demonstrated that S_{BET} values of the obtained AC from the WS using the CA process were higher than those generated using the PA procedure. Thus, it could be said that the CA process is an effective way for obtaining AC from WS with a high S_{BET} value.

Table 4
The preparation conditions and textural properties reported for the AC obtained from WS using the CA process.

No.	Activating reagent	Impregnation ratio	Activating reagent purity	Temp. (°C)	Time (h)	Iodine number (mg I_2/g C)	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Ref.
1	H_3PO_4	–	–	400	1	676.0	424.0	–	Soleimani, Kaghazchi [87]
		2	80 %	500	1	–	1000	–	Azat et al. [8]
		0.5	40 %	500	1	–	1097.723	1.221	Xie et al. [88]
		2	40 %	500-700	1.12	–	789	0.304	Moreno-Barbosa et al. [98]
		1.5	85 %	550	1	982	1544	1.046	Mataji, Khoshandam [129]
2	KOH	1	75 %	900	1	–	–	–	Martinez et al. [5]
		4	–	800	0.5	–	2305	1.15	Nowicki et al. [100]
		10-30 mg/l	0.1 N	400	2	–	–	–	Jafari-Mansoorian et al. [82]

		3	–	700	–	–	1636	0.641	Yu et al. [131]
3	$ZnCl_2$	2	–	450	1	–	1800	1.176	Yang, Qiu [89]
		–	–	500	0.5	–	1.480	0.805	Ghanbari Pakdehi, Rezaei [128]
		5	–	375	1	1300	–	–	Kim et al. [85]
		136.28 g/mol	98 %	–	–	737	780	0.45	Zabihi et al. [115]
		136.28 g/mol	98 %	–	–	760	780-803	0.387-0.426	Zabihi et al. [90]
		2.5	98 %	650	1	–	1223	0.85	Ghasemi et al. [81]
		0.66	–	750	–	–	–	–	Taghizadeh, Vahdati [134]
		1.5	98 %	650	1	1190	1233.2	0.704	Mataji, Khoshandam [129]
		–	–	500	0.5	–	450.4	0.3225	Teimouri et al. [101]
4	NaOH	–	–	700	1.5	–	–	–	Nethaji, Sivasamy [77]
5	Ready AC	–	–	–	–	700-1100	590-1500	0.7-1	Yi et al. [112]

–Not reported.

Table 5
The preparation conditions and textural properties reported for the AC obtained from WS in the PA process.

No.	Activating reagent	Flow rate	Temp. (°C)	Time (h)	Iodine number (mg I_2/g C)	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Ref.
1	CO_2	–	500	1	680.9	401.2	0.210	Guo et al. [130]
		50 cm^3/min	700	–	–	337.50	–	Azat et al. [8]
		900 ml/min	800	1	–	–	–	Hall et al. [119]
		170 ml/min	800	1	–	697	0.37	Nowicki et al. [100]
2	Atmospheric steam	–	600	1	–	1100	–	Schröder et al. [3]
3	–	–	800	1/4	–	947	–	Kazemipour et al. [104]

–Not reported.

WS has been used in some studies for the development of AC, and different parameters have been considered to prepare a high-quality AC. In a comprehensive study by Schröder et al. [3], they generated AC from the discarded plant-based materials obtained from different sources including the straws of wheat, straw pellets of wheat, straw of rice, olive stone, shell of pistachios and walnut, hard coal, and beech wood. The results of this study showed that the shells of the studied nuts had high active surface areas (1000-1300 m^2/g) while the active specific surface areas of the considered straw materials did not exceed 800 m^2/g and it could be related to the high carbon content of the nutshells and the high ash amounts of the used straws.

In another investigation, the preparation and characterization of two different types of AC produced from the agro crop matters in Argentina have been reported by Martinez et al. [5]. AC was produced from the shell part of the walnut fruit and the pit of olive using 50 and 75 % KOH (w/w) as chemical activators. The obtained AC was assessed by the adsorption of iodine. It was shown that the yields of the prepared AC from the olive pit were higher than the yield of the AC derived from WS and the maximum carbon yields were achieved using KOH with the concentration of 75 % in both samples. The authors also found that AC derived from WS

had a macroporous structure with a proper pore size distribution, which was more homogeneous than the same from the olive pit.

It has also been attempted to obtain AC by employing WS as the starting material via the CA approach [85]. In that study, the authors found that with the increase in the temperature of activation, the iodine number increased. However, the thermal degradation was observed at temperatures higher than 400 °C. Besides, the application of the activation time more than 1h at 375 °C caused a damage to the microporous structure of the produced AC. In Addition, with increasing the content of the $ZnCl_2$ solution, the iodine value increased. However, the presence of the additional $ZnCl_2$ in the solution caused a decrease in the iodine number. Finally, they compared the amount of the used $ZnCl_2$ for activation and the consumed $CaCl_2$ and suggested that the enhanced iodine value in the CA process was achievable using $ZnCl_2$ as a chemical activator.

Furthermore, the preparation and activation of some agricultural residues, using H_3PO_4 as a chemical activator agent for the development of AC from microporous plant-based waste products, have been investigated [87]. Different agricultural byproducts such as apricot stones, bagasse, hazelnuts, almonds, pistachios, and the shells of walnuts were used as the precursors. That study showed that choosing the appropriate final activation temperature, time of activation and activation proportion is critical since the quality of the prepared AC is mainly affected by such parameters. The authors tested different precursors and reported that the obtained AC from apricot stones possessed the highest adsorption capability and specific active surface area. It has been suggested that the produced AC could be considered in the separation of valuable metal ions such as silver and gold present in water.

In researches using the shell of walnut as the solid waste, a two-step CA process via the $ZnCl_2$ and the thermal pyrolysis leads to the development of AC with a high-performance function [81]. After characterizing the porous structure of the developed AC, the authors demonstrated that it had excellent textural properties such as a high total pore volume and a high BET specific surface area. Finally, the obtained WS-based AC exhibited a higher adsorption capacity in comparison to the AC obtained from other sources in similar conditions.

They have also been considered the effects of the carbonization temperature, the activation temperature, and the ratio of KOH to char on the pore development of the walnut shell activated carbon (WSAC) prepared by the KOH chemical activation [99]. The results of that research showed that the optimal preparation conditions were a carbonization temperature of 700 °C, an activation temperature of 700 °C, and a mass ratio of 3. The BET surface area, the volume, and the micropore volume percentage of the optimal WSAC were determined to be 1636 m^2/g, 0.641 cm^3/g, and 81.97 % respectively. The developed AC contained micropores and a certain amount of meso- and macro-pores.

The impact of the activation processes, temperature, and heating mode on the surface features of the AC obtained from WS has also been examined in the strategy described by Nowicki et al. [100]. In that research, the final resultant carbon products with microporous active carbons possessed a well-developed surface area (2305 m^2/g) and pore volume (1.15 cm^3/g), revealing the distinct acid-based characteristic on the surface. The results of

this study have explicated that both activation process and temperature were significant factors influencing the content and variety of surface oxides formed on the surface of the AC.

For the catalytic conversion of agricultural nutshells (almond and walnut) to AC, in a recent study, a new, fast, and clean method for obtaining an efficiently adsorbent AC with a microporous structure based on a microwave-assisted impregnation was established [101]. In the proposed approach, a catalyst and $ZnCl_2$ with different amounts were impregnated on the powdered shells, using conventional and microwave-assisted methods. Then, tar-like materials in standard and atmospheric N_2 were carbonized in sealed and open ceramic vessels respectively. Under the optimum conditions obtained, i.e. the irradiation power of 600 W and carbonized at 500 °C with an average size of 2.4, an acceptable decoloration performance of 94 % was achieved. The suggested process was not only fast, 30 min, but also economical in developing the microporous AC from waste nutshells in the standard closed vessel. Compared to the fabricated conventional procedure, it showed a noticeable advantage for the AC obtained by the microwave-assisted catalytic conversion.

5. Applications of the activated carbon derived from the walnut shell

5.1. Heavy metals removal

Today, the environmental pollution caused by HMs has become a challenge and a global problem, due to the rapid growth of urban communities and human's industrial activities. The term "heavy metal" generally refers to a group of metals (and metal-like elements) with a density of more than 5 g/cm^3. Their atomic number is more than 20, and at low concentrations are very toxic [102]. HM ions have a significant impact on all forms of life. The pollution caused by HMs is one of the most critical environmental problems today, which is a threat to the human life and the environment due to its toxicity and bioaccumulation [103]. An overview of the maximum adsorption capacity (q_m) for each type of the AC prepared from WS is provided in Table 6. Additionally, as summarized in Table 6, among different types of HM ions, copper (Cu^{2+}), chromium (Cr^{6+}), arsenic (As^{3+}), cadmium (Cd^{2+}), lead (Pb^{2+}), zinc (Zn^{2+}), and mercury (Hg^{2+}) are the leading HM ions which have been tried to be removed by the AC derived from WS.

Table 6
The adsorption capacity of the AC derived from WS for the removal of different HMs.

No.	HMs	q_m	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Ref.
1	Cu^{2+}	30 mg/l	–	–	Kim et al. [85]
		204.08 mg/g	1097.723	1.221	Xie et al. [88]
		3.86 mmol/g	1442	0.68	Milenković et al. [105]
		638 mg/g	–	–	Zbair et al. [113]
2	Cr^{6+}	43.12 mg/g	1223	0.85	Ghasemi et al. [81]
		51.28 mg/g	1097.723	1.221	Xie et al. [88]
		6.01 mg/g	–	–	Nethaji, Sivasamy [77]

		0.596 mmol/g	–	–	Altun, Pehlivan [107]
		3.5 mg/g	–	–	Lu et al. [108]
		574 mg/g	–	–	Zbair et al. [113]
3	As^{3+}	200 μg/l	–	–	Saqib et al. [138]
		3.42 mg/g	–	–	Jafari-Mansoorian et al. [82]
4	Cd^{2+}	14.29 mg/g	–	–	Gondhalekar, Shukla [109]
		11.6 g/kg	–	–	Almasi et al. [139]
		70.78 mg/l	–	–	Saffari [111]
		345 mg/g	–	–	Zbair et al. [113]
5	Pb^{2+}	210.14 mg/g	–	–	Cheng et al. [140]
		81.96 mg/g	–	–	Yi et al. [112]
		32.362 mg/g	789	0.304	Moreno-Barbosa et al. [98]
		294.10 mg/g	738	–	Saadat et al. [141]
		32 g/kg	–	–	Almasi et al. [139]
		792 mg/g	–	–	Zbair et al. [113]
6	Zn^{2+}	6.079 mg/g	789	0.304	Moreno-Barbosa et al. [98]
		17.69 mg/g	890	–	Olafadehan et al. [117]
		89 mg/g	1388	1.6474	Davidi et al. [116]
7	Hg^{2+}	151.5 mg/g	780	0.426	Zabihi et al. [115]
		151.5 mg/g	803	0.387	Zabihi et al. [90]

–Not reported.

5.1.1. Removal of Cu ions

Cu is known as a toxic heavy metal that is capable of polluting the atmosphere and is possibly toxic to humans and living organisms. In order to evaluate the WS adsorption capacity for Cu ions, the adsorption characteristics of the granular activated carbon (GAC), produced from the waste WS, for the Cu^{2+} ion were comprehensively studied and reported [85]. The authors proposed that the AC adsorption capacity was compatible with commercial conditions and claimed to be superior to what is made of the coconut shell. In another research, the elimination of Pb, Cd, Zn, and Cu from the industrial wastewater has been tested by the AC produced from the walnut, almond, pistachio and hazelnut shells and the apricot stone [104]. The results of the study have revealed that the prepared AC from plant-based materials significantly removed the studied HMs.

The modified carbons were obtained from WS using acids or acid-based solutions. Then, the batch experiments were performed to assess the adsorption capacity for Cr^{6+} and Cu^{2+} ions [88]. According to the reported results, the authors demonstrated that the pH of the solution and the functional groups on the surface of the developed AC played more critical roles in the effective removal of Cu ions from water rather than the textural properties of the AC did.

The utilization of ultrasound technology (UST) for enhancing the Cu^{2+} adsorption capability of the GAC produced from WS [105] has also been reported. In one such investigation, the adsorption capacity of GAC was 1.7-3.86 mmol/g with the use of UST, and 0.66-2.7 mmol/g without the use of UST. Besides, the efficacy of adsorption was improved with the increase in the specific

surface area and initial concentration.

5.1.2. As ions removal

As is recognized as another toxic heavy metal that can pollute the environment and has potentially harmful effects on the human health. The adsorption process is one of the mechanisms used for the As elimination from aqueous solutions [106]. Only in one report, the removal of As using the carbon materials prepared from the WS fruit has been reported. In that study, the AC obtained from the WS with KOH as an activating reagent was successfully used for its removal. The results of that study showed that the increase in the adsorbent dosage and the reduction in pH enhanced the adsorption of As while the increase in pH and the initial concentration lowered the adsorption of As ions. The authors recommended that the WSAC could be considered as an inexpensive adsorbent for the As ion removal from wastewater [82].

5.1.3. Cr ions removal

Cr is also an HM described as a hazardous element. The Cr removal using the AC developed from WS has been reported in some studies. In an investigation, different ACs were prepared by changing the impregnation ratio of char:NaOH to 1:1 (AC1), 1:3 (AC2), and 1:5 (AC3) and the effect of impregnation ratios on the adsorption capacities of the generated AC for the removal of Cr^{6+} was studied. Overall, the produced AC with the maximum impregnation ratio (AC3) showed a higher removal capability compared to AC1 and AC2 [77]. In another research, the results of batch experiments for the modified types of carbon generated from WS, using acids and acid-based solutions, showed that the adsorption of Cr^{6+} mainly would depend on the pH of the solution and the textural properties of the modified carbon [88].

A two-step $ZnCl_2$ CA-thermal pyrolysis process was employed for the synthesis of a high-performance AC using the waste WS [81]. A porous structure with excellent textural properties such as a high total pore volume (0.85 cm^3/g) and a high BET surface area (1223 m^2/g) were demonstrated in characterization studies. The adsorption of Fe^{2+} and Cr^{6+} from an aqueous solution was investigated by the final adsorbent developed in the research. It was demonstrated that the maximum removal of Fe^{2+} and Cr^{6+} ions could be obtainable at the pH of 4.5 and 2 respectively. Finally, compared to other types of AC, the AC developed from WS showed a higher adsorption efficiency in similar conditions.

For the removal of Cr^{6+} ions from aqueous solution, WS after treatment with citric acid has been utilized as an adsorbent [107]. In all cases, the maximum adsorption of Cr^{6+} was reported to be at pH values between 2.0 and 3.0, showing a pH-dependent procedure for the Cr removal by the citric acid–modified WS. Under experimental conditions, the obtained maximum adsorption capacities were 0.596, and 0.154 mmol/g for Cr^{6+} ions by a citric acid-modified WS and an untreated WS respectively.

The adsorption properties of the ordinary and H_3PO_4-modified WS for the removal of Cr^{6+} were also compared in a study. The results of the investigation showed that the adsorption of the modified WS was more because of its larger surface void [108].

5.1.4. Removal of Cd ions

Cd is considered as one of the most critical pollutants in the terrestrial and aqueous environments [102]. WS has also been

reported to be a suitable adsorbent in the removal of Cd ions. For example, to enhance the adsorptive capacity for Cd^{2+} ions, WS was treated in alkali conditions[109]. Between the pH values of 2 and 6, the adsorption was reported to increase considerably. The biosorption capacity of the raw and modified WS for Cd^{2+} ions was found to be 4.20 and 14.29 mg/g respectively.

In recent years, biochar as a useful soil amendment has been considered for the remediation of Cd ions. In an investigation, the prepared biochar using WS was incubated in Cd $(NO_3)_2$ and kaolin for 15 days. Biochar is a charcoal-like substance that, in a controlled process called pyrolysis, is made by burning organic material from agricultural and forestry waste (also called biomass). While it looks a lot like common charcoal, biochar is produced using a particular method to reduce contamination and store carbon safely. It was found that the biochar derived from WS could reduce the mobility of Cd and improve the stability of biochar. It was also found that the improved biochar stability was related to the physical isolation and the formation of precipitates and complexes, created on the surface of or inside biochar [110].

The efficiency of contaminant removal can be increased using nanomaterials on the surface of biochar. Therefore, the efficiency of the walnut shell biochar (WSB) alone or supported by the nanoscale zero-valent iron (nZVI) on the Cd removal in an aqueous solution has been investigated [111]. The results of that study showed that WSB-nZVI had great potential in the removal of Cd ions. The presence of functional groups on the surface of WSB via adsorption and precipitation processes, as well as nZVI formed on the WSB-nZVI via generating complexation and adsorption processes increased its Cd removal ability more than that of the WSB raw adsorbent.

5.1.5. Pb ions removal

Pb is an extremely toxic element and its removal has also been considered using the AC prepared from WS. In an investigation, a Chinese WS-based AC was employed as an adsorbent for the separation of Pb^{2+} from an aqueous solution with a q_m of 81.96 mg/g [112]. Although the effect of temperature was not significant in the performed batch experiments, the adsorption of Pb^{2+} was strongly pH-dependent and at pH 5.5, the maximum removal was observed. The authors suggested that WSAC could be a potentially suitable adsorbent for the adsorption of Pb^{2+} from wastewater. The Watermelon shell-based activated carbon (WMSAC) and WSAC as alternative low-cost adsorbents were developed and H_3PO_4 40 % (w/w) was used as the chemical activation agent. Then, their capacities for the adsorption of Zn^{2+} and Pb^{2+} ions from aqueous solutions were tested. The results of the performed experiments indicated that the porosity could be an essential factor in the execution of the removal process because WMSAC had micropores and mesopores, but WSAC possessed only micropores. Furthermore, the active surface chemistry for the developed AC could be considered as another significant factor during the metal removal process because WMSAC showed a lower pH_{PZC} value than WSAC did (3.05 for WMSAC and 4.5 for WSAC respectively) [98].

Lastly, Zbair et al. [113] synthesized carbon microspheres from WS under an N_2 flow and then used them as adsorbent for the removal of Pb^{2+}, Cu^{2+}, Cr^{3+} and Cd^{2+} metal ions. SEM micrographs of the prepared material showed

a homogeneous sphere-like structure with an average diameter of 4.55 microns. A selective and rapid removal of hazardous metal ions from synthetic water samples were described for the prepared carbon microspheres. The effects of the pH of the solution, the contact time and temperature on the removal process have been systematically investigated. It has been claimed in that work that the used material for the elimination of Cr^{3+}, Pb^{2+}, $Cd^{2+}$and Cu^{2+} at an optimum pH of 5, presented the adsorption capacities of 792, 638, 574 and 345 mg/g respectively, the highest adsorption capacities ever reported. The binding ability of Cr^{3+} to the hydroxyl (–OH) or carboxyl (–COOH) functional groups was stronger and was followed by thoes of Pb, Cu, and Cd.

5.1.6. Hg ions removal

Hg is another toxic element in wastewater that has been tried to be eliminated using the WS [114]. The adsorption capability of the AC derived from the WS in the powdered form was also reported in two investigations to generate an effective and more commercial sorbent for the removal and elimination of Hg^{2+} ions present in the industrial liquid streams [115, 90]. The carbonaceous materials being resulted from the Iranian WS were produced using a CA method from $ZnCl_2$ as the chemical activator agent. The authors claimed that the developed adsorbent had not been used before for the adsorption of Hg^{2+} ions from water. The appropriate selection of optimum preparation conditions resulted in the development of the AC with the characteristics of microporous structures, and the adsorption value of this monolayer adsorbent for Hg^{2+} ions was obtained as 151.5 mg/g.

5.1.7. Removal of Zn ions

It is well-documented that the presence of Zn in the ecosystems has deleterious effects on living organisms. Thus, its removal is of great importance among environmental technologists. As a local agricultural biomass, the Iranian WS was used to prepare AC [116]. Using Taguchi experimental design and the adsorption ability of WS towards Zn^{2+} as a response, the optimum condition for the process of synthesizing AC was determined. The analysis of results showed that the activation time and impregnation ratio were the main affecting parameters. The AC synthesized under the optimum condition had a mesoporous structure and the specific surface area was 1388 m^2/g. The adsorption capacity of the produced AC for Zn ions was found to be 89 mg/g.

In another research study, the derived composite biosorbents from walnut and snail shells were used in Olafadehan et al. [117] study to investigate the removal process of Zn^{2+} ions from industrial wastewater. For the preparation of composite adsorbents, the walnut shell carbon (WSC) was activated by H_3PO_4 to obtain the acid-treated WSC (AWSC). In the next steps, for the generation of WSC impregnated on chitosan (CS) (WSCC) and AWSC impregnated on CS (AWSCC), WSC and AWSC were independently impregnated on CS separately. At the pH of 5 and the temperature of 30 °C, the maximum adsorption capacities of 3.1104, 3.8052, 16.4474, and 17.6991 mg/g were obtained for WSC, AWSC, WSCC, and AWSCC respectively. The adsorption of Zn^{2+} ions on the prepared adsorbents was film diffusion controlled. The results of this research explained that AWSCC had a high potential to be employed as a useful alternative low-priced biosorbent.

5.2. Dyes removal

Dyes are known as another group of toxic materials discharged into the environment and contaminating the fresh waters. Different agricultural waste products, nanomaterials [118], and nanocatalysts have been considered for the removal or degradation of industrial dyes. In this regard, there are some investigations in the literature demonstrating the application of the crude or unprocessed WS as an active and cheap plant-based sorbent for the elimination of different dyes [6]. The modified WS in the form of AC is considered for the adsorption of the methylene blue (MEB), reactive brilliant red K-2BP (RBR K-2BP), methyl bromide (MB), reactive red 2 (DR2), crystal violet (CV), brilliant green (BG), malachite green (MG) and congo red (CR) (see Table 7 for more details). For the removal of MEB, Yang, Qiu [89] produced AC from WS using the vacuum CA process. The results of this research showed that the MEB adsorption capacity was positively correlated with the BET surface area. For the obtained AC, the maximum MEB adsorption capacity was found to be 315 mg/g. In another investigation, the AC from some nuts and fruits produced in California (the shell of almond and walnut as well as the pit of prune and peach) were prepared as sorbents and then, it was used to remove MB in the ventilation effluent after a postharvest chamber fumigation [119].

Table 7
The adsorption capacity of the AC prepared from WS for the removal of various dyes.

No.	Dyes	q_m	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Ref.
1	MEB	315 mg/g	1800	1.176	Yang, Qiu [89]
2	RBR K–2BP	568.18 mg/g	–	–	Cao et al. [142]
3	MB	–	–	–	Hall et al. [119]
4	RR2	0.04 mg/g	–	–	Almasi et al. [120]
5	CV	96.01-123.2 mg/g	2.095	0.0171	Ashrafi et al. [143]
6	BG	79.07-146.40 mg/g	2.095	0.0171	Ashrafi et al. [143]
7	MG	11.76 mg/g	420.5	–	Hajialigol, Masoum [121]
8	CR	40.00 mg/g	–	–	Ojo et al. [122]

–Not reported.

An investigation has also been conducted on the preparation of a natural-based adsorbent AC from the waste WS for the removal of the RR2 in an aqueous solution [120]. In this study, a glass column with the diameter of 1 cm and the height of 25 cm filled with different dosages of carbon was used to study the adsorption of RR2. It was found that the adsorption of RR2 on the prepared activated charcoal steam had a direct relationship with the increase of the dye concentration and an inverse association with the increase of adsorbent amount.

In another study reported by Hajialigol, Masoum [121], they synthesized and successfully applied AC based on the WS for the removal of MG in an aqueous solution. The response surface methodology (RSM) was utilized in batch experiments to optimize operating parameters by considering the removal efficiency of AC as a response. It was shown that at the initial MG concentration of 33.3 mg/l, nano biomass dose of 33.3 mg and contact time of 20.0 min,

approximately a 100 % elimination was attained.

Additionally, it has been shown that for the treatment of the CR dye in aqueous solutions, the WS could be used as an excellent adsorbent. In that batch process study, Ojo et al. [122] investigated the adsorption of the CR dye on the AC prepared from WS powder. The carbonized powder of WS was achieved through an H_3PO_4 treatment. It was reported that the adsorption uptake increased with the increase in the initial concentration of the dye and contact time. The optimum condition of the dye adsorption was detected at pH 3.12, with 94.53 % uptake. The adsorption data well fitted using the Langmuir model with the maximum monolayer coverage of 40 mg/g.

5.3. Removal of pharmaceuticals

Currently, the overuse of antibiotics is a public concern and thus, different materials have been considered for the effective removal of pharmaceuticals. It has been shown that the AC obtained from the WS is a useful material in the removal of pharmaceutical products. Cephalexin (CFX), metronidazole (MET) and sulfamethoxazole (SUL) are tried to get removed using the WSAC. Table 8 summarizes the q_m values obtained for the removed pharmaceuticals. The effective elimination of the CFX antibiotic has been comprehensively evaluated by WS in several studies compared to others. For example, Nazari et al. [123] investigated the adsorption of CFX antibiotics on WSAC by batch adsorption experiments. The CA method in the presence of $ZnCl_2$ was used for the development of the adsorbent. Based on the Langmuir model, the maximum adsorption capacity was obtained as 233.1 mg/g. In another research, the constant wave propagation theory was employed for the calculation of the mass transfer coefficients for the CFX adsorption onto WSAC. Moreover, three models were developed to predict the mass transfer coefficient [124]. In another study reported by the same research group, the AC was prepared from WS by the CA using $ZnCl_2$, and then, it was examined in a fixed-bed column for the adsorption of CFX from the aqueous phase [125]. The highest bed capacity of 211.78 mg/g, using the inlet drug concentration of 100 mg/l, 2 cm bed height and 4.5 ml/min flow rate at optimum pH 6.5, was obtained in that study. Furthermore, both mathematical and experimental studies of the CFX adsorption by WSAC in batch experiments were also investigated by the same research group [126]. The used adsorbent was synthesized in the presence of $ZnCl_2$ using the CA process. The developed model revealed good agreement with the experiments. The effective diffusivity of 0.47×10^{-9} m^2/s for CFX in the WSAC was reported.

Table 8
The adsorption capacity of the AC prepared from WS for the removal of pharmaceuticals.

No.	Antibiotics	q_m	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Ref.
1	CFX	233.1 mg/g	1.452e+03	7.151e–01	Nazari et al. [123]
		211.78 mg/g	–	–	Nazari et al. [125]
		233.1 mg/g	–	–	Nazari et al. [126]
2	MET	107.4 mg/g	934	0.457	Teixeira et al. [127]
3	SUL	93.5 mg/g	934	0.457	Teixeira et al. [127]

–Not reported.

In an investigation reported by another research group, the removal of MET and SUL antibiotics by the WSAC was also studied [127]. In that investigation, the response surface methodology (RSM) was combined with a three-level Box-Behnken experimental design with three factors, including pH, temperature and the initial concentration of antibiotics. It was determined that the pH factor had a significant and distinct effect on the removal efficiency of both antibiotics. Increasing pH values was favorable for the removal of MET with the maximum value registered at pH 8, while SUL showed a maximum adsorption value at around 5.5, and it decreased as the pH increased. The initial concentration of 40 mg/l and pH 5.5 were achieved as the best conditions for the removal of the antibiotic SUL (106.9 mg/g) at a temperature of 30 °C as predicted by the model. For the antibiotic MET, the highest removal (127 mg/g) was estimated at pH of 8 and the same initial concentration and temperature. The results of isotherm experiments (at 20 °C and pH 6) displayed good agreement with the predicted models. In that investigation, the q_m of 107.4 and 93.5 mg/g for MET and SUL were reported respectively.

5.4. Other hazardous materials removal

Not only is the AC obtained from the WS a useful sorbent in the removal of different HM ions and dyes, but it has also been comprehensively studied in the separation and elimination of some other dangerous materials such as 2–dimethylaminoethylazide (DMAZ), benzene, methanol, phosphine (PH_3), nitrate (NO_3), ammonia nitrogen (NH_3-N), nitrogen dioxide (NO_2), phenanthrene (PHE) and fusicoccin. The q_m values for the above-mentioned materials tried to be removed by the WSAC are summarized in Table 9.

Table 9
The adsorption capacity of the AC prepared from WS for the removal of other hazardous materials.

No.	Materials	q_m	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Ref.
1	DMAZ	166.67 mg/g	1480	0.805	Ghanbari Pakdehi, Rezaei [128]
2	Naphthalene	7210 µg/g	4.32	–	Zhu et al. [91]
3	NOMs	37.93 mg/g	–	–	Naghizadeh et al. [144]
4	Methanol	248.02 mg/g	1636	0.641	Yu et al. [99]
5	Benzene	61.22 mg/g			Mataji, Khoshandam [129]
6	PH_3	284.12 mg/g	1636	0.641	Yu et al. [131]
		595.56 mg/g	1636	0.782	Yu et al. [132]
7	NO_3^-	–	–	–	Taghizadeh, Vahdati [134]
		10 mg/g	1434.6	0.747	Alighardashi, Shahali [79]
8	NH_3–N	9.79 mg/g	–	–	Ding et al. [135]
9	NO_2	66 mg/g	2305	1.15	Nowicki et al. [100]
10	DIA	34.98 mg/g	–	–	Bayat et al. [133]
11	PHE	247.54 mg/g	410.84	0.61	Zheng et al. [136]

–Not reported.

In a study, it was revealed that the developed WSAC could be used as a suitable adsorbent for the DMAZ elimination from dilute aqueous solutions. In that investigation, the WSAC was produced using $ZnCl_2$ as a chemical activator, and after the

characterization studies, its adsorption capacity was evaluated to remove DMAZ from aqueous solutions. The removal percentage of 85.95 % was reported at the optimized conditions [128]. The Iranian WS was also employed to prepare carbonaceous materials. Following the CA method and using H_3PO_4 and $ZnCl_2$ as the activating reagents, the obtained AC was applied to separate and eliminate benzene present in the stream of amine-rich gas sweetening systems. The authors reported a higher BET surface area for the AC prepared by H_3PO_4 and better ability for the benzene removal (about 61.22 mg/g in an initial concentration of 300 mg/l). The uptake of benzene increased with the increase in the initial concentration and contact time [129]. Also, the produced WSAC via the CA process using KOH as the chemical activator was characterized and was then, used for the adsorption of methanol. The results showed that the WSAC prepared under the optimized condition was favorable for the methanol adsorption. The equilibrium adsorption capacity of the WSAC was 248.02 mg/g which was almost equivalent to that of the conventional AC [99].

It was reported that the use of metal oxides during the AC preparation and the degree of the pore development in the structure of AC could affect the desulfurization performance of catalysts. In another research, Guo et al. [130] considered the desulfurization activity of metal oxides mixed with the AC derived from the WS. The developed carbonized powder was blended with titanium ore (TO), titanium oxide (TiO_2), or iron oxide (Fe_2O_3) and activated using atmospheric CO_2. A fixed bed flow microreactor was designed for evaluating the desulfurization activity of activated carbon-blended titanium ore (ACTO), activated carbon-blended titanium oxide (ACT), and activated carbon-blended iron oxide (ACF) samples under a simulated gaseous mixture from the coal combustion. A surface area of 401.2 m^2/g was reported for the WSAC. In contrast, the surface area of ACTO, ACT, and ACF_2 increased to 937.1, 661.8 and 791.0 m^2/g respectively when TO, TiO_2, or Fe_2O_3 were incorporated in the structure of the prepared AC. Still other authors have reported the preparation of the AC obtained from the shell of the walnut fruit with predominant microporous development and the larger surface area in the structure by the CA process. KOH was used as a chemical activation agent, and then, the PH_3 adsorption of the produced AC was evaluated. It was suggested that the high surface area of WSAC with a microporous architecture was suitable for the effective removal of PH_3 [131]. In another research recently reported by the same group, different types of metal oxides ($Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and $La(NO_3)_3{\cdot}nH_2O$) were examined in the development of the modified walnut shell activated carbon (MWSAC) by the CA process using KOH as a chemical activator and then, it was used for PH_3 adsorption [132]. The results indicated that the maximum PH_3 equilibrium adsorption capacity was 595.56 mg/g. The authors proposed that an excellent removal performance and a high adsorption potential of MWSAC for the PH_3 adsorption were associated with its large surface area and high oxidation activity in the PH_3 adsorption-oxidation to H_3PO_4 and P_2O_5. Furthermore, MWSAC was successfully used to remove the diazinon (DIA) pesticide [133]. In that report, the adsorption of the DIA pesticide was evaluated by using the fixed-bed column and batch method on MWSAC from an aqueous solution. The results of continuous fixed-bed column studies showed

that the increase in the inlet concentration and bed height could lead to improving the bed capacity. The highest bed capacity for the considered pesticide was reported to be 34.98 mg/g.

The GAC made from the WS was also used in a continuous fixed bed pilot study for the NO_3 removal from an aqueous solution and a natural groundwater [79]. The BET surface area number and average pore size were 1434.6 m^2/g and 2.08 nm before the NO_3 adsorption and 633.28 m^2/g and 2.04 nm, respectively after the NO_3 removal. The contact time of 2 min, pH 6.5, and an NO_3 concentration of 200 mg/l were achieved as an optimum condition for the NO_3 removal, and the recorded q_m was reported to be 10 mg NO_3/g. In another comparative research, the characteristics of the AC prepared from pistachio, walnut, and almond shells in the removal of NO_3 from aqueous solutions were investigated [134]. In that research, the CA process was carried out by $ZnCl_2$. The results showed that the efficiency of the NO_3 removal for three nutshells, including pistachio, walnut, and almond shells were 45.74 %, 41.7 %, and 43.49 % respectively. The maximum NO_3 removal was reported at PH 8 for pistachio and PH 2 for walnut and almond shells. Carbonization of the WS by the activating agent $ZnCl_2$ and an investigation had been conducted to examine the possibility of the NH_3-N removal from the liquid phase [135]. At initial pH values between 6.6 and 6.8, the adsorption capacity for NH_3-N was 9.79 mg/g. It was found that the adsorption process was conducted through a combination of the chemical and physical adsorptions. In addition, the sorption characteristics of the prepared AC derived from WS were determined by the analysis of the NO_2 adsorption capacity under dry conditions [100]. It was demonstrated that a proper selection of the activation method could provide the AC with the highest potential for adsorbing NO_2, giving 66 mg NO_2/g. That investigation also explained that the adsorption capacity of carbonaceous sorbents depended on the process and method of activation as well as on their textural parameters and acid-based features on their surface.

The AC prepared and characterized by WS was also used to remove phenanthrene (PHE) dissolved in a Tween 80 solution [136]. It was shown that PHE was effectively removed by the prepared AC and the Tween 80 could be economically recovered after the adsorption process. The functional groups on the AC and π-π interactions played essential roles in the PHE adsorption process. The PHE removal and Tween 80 recovery reached 95 % and 90 % respectively under optimal conditions. The results also revealed that after adsorption, AC could be regenerated with ethanol.

Finally, different agricultural crop wastes, including the apricot kernels, rice husks, and Greek WSs were carbonized, and a large specific active surface area and good porous structure have been reported for the prepared carbon nanomaterials. The authors demonstrated that fusicoccin and similar biostimulators were separated effectively, and the lipopolysaccharides (LPS)–endotoxins from the blood plasma were selectively removed. On the surface of the synthesized sorbents, different functional groups such as –COOH, –OH, and carbonyl (–C=O) , which were essential for a sorbent in the adsorption process, were detected. Thus, it has been suggested that the carbonized products have the potential to be used as carriers for the delivery of probiotics into the intestine [8].

6. Conclusions

WS is a crucial agricultural waste product that is readily available in large amounts. This apparently waste material constitutes a considerable part (more than 40 %) of the walnut fruit. However, and up to now, it has not been effectively utilized. The recent trends in the application of WS for the preparation of AC have indicated that this agricultural byproduct has a high potential to be considered as a low-cost and renewable resource in the generation of the inexpensive AC. Moreover, the performed investigations have suggested that the generated AC from the shell of the walnut fruit could be used as an effective adsorbent in different areas, including the separation of hazardous materials from wastewater. It seems that more studies are needed to make a successful use of the AC derived from WS. In the future, these efforts could focus on improving AC preparation methods, testing other chemical activation agents, and combining other materials and AC to enhance the physical and chemical properties.

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Nomenclature

AC	activated carbon.
ACF	activated carbon–blended iron oxide.
ACT	activated carbon–blended titanium oxide.
ACTO	activated carbon–blended titanium ore.
Al	Aluminum.
As^{3+}	Arsenic.
AWSC	acid–treated walnut shell carbon.
AWSCC	acid–treated walnut shell carbon impregnated on chitosan.
BET	Brunaeur–Emmet–Teller.
BG	brilliant green.
C	Carbon.
–C=O	carbonyl.
Ca	Calcium.
CA	chemical activation.
$CaCl_2$	calcium chloride.
Cd^{2+}	Cadmium.
CFX	cephalexin.
Cl	Chlorine.
CO_2	carbon dioxide.
–COOH	carboxyl.
CR	congo red.
Cr^{6+}	Chromium.
CS	chitosan.
Cu^{2+}	Copper.
CV	crystal violet.
DIA	diazinon.
DMAZ	2–Dimethylaminoethylazide.
Fe_2O_3	iron oxide.
FT-IR	Fourier transform infrared spectroscopy.
GAC	granular activated carbon.
H	Hydrogen.
H_2SO_4	sulfuric acid.
H_3PO_4	phosphoric acid.
Hg^{2+}	Mercury.
HMs	heavy metals.
I	Iodine.
K	Potassium.
KOH	potassium hydroxide.
LPS	lipopolysaccharides.
MB	methyl bromide.
MEB	methylene blue.
MET	metronidazole.
Mg	Magnesium.
MG	malachite green.
MWSAC	modified walnut shell activated carbon.
N_2	Nitrogen.
Na	Sodium.
NaOH	sodium hydroxide.
NH_3-N	ammonia nitrogen.
NO_2	nitrogen dioxide.
NO_3	Nitrate.
NOMs	natural organic matters.
nZVI	nanoscale zero–valent iron.
O	Oxygen.
–OH	hydroxyl.
P	Phosphorous.
PA	physical activation.
Pb^{2+}	Lead.
PH_3	Phosphine.
PHE	phenanthrene.
PZC	point of zero charge.

q_m	maximum adsorption capacity.
RR2	reactive red 2.
RSM	response surface methodology.
S	Sulfur.
S_{BET}	surface BET.
SEM	scanning electron microscopy.
Si	Silicon.
SUL	sulfamethoxazole.
TEM	transmission electron microscopy.
TG	thermogravimetric.
TiO_2	titanium oxide.
TO	titanium ore.
UST	ultrasound technology.
WMSAC	watermelon shell–based activated carbon.
WS	walnut shell.
WSAC	walnut shell–based activated carbon.
WSB	walnut shell biochar.
WSC	walnut shell carbon.
WSCC	walnut shell carbon impregnated on chitosan.
Zn	Zinc.
$ZnCl_2$	zinc chloride.

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