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Recent advances in the use of walnut (*Juglans regia* L.) shell as a valuable plant-based bio-sorbent for the removal of hazardous materials

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The effective use of agricultural by-products is definitely a major challenge in waste management. In the walnut fruit processing industry, large amounts of shells are produced as agricultural by-products and discarded or burned produced as fuel. Walnut (*Juglans regia* L.) is a valuable tree nut in the Juglandaceae family. The fruit is composed of four main parts: the kernel, the skin, the shell, and the husk. The importance of walnuts is mostly related to theirs valuable kernels. However, their shells are currently experiencing as much interest as their kernels due to the beneficial effects of the shells. In the past several years, walnut shell (WS) has been widely explored as a naturally inert plant-based biosorbent. In this review, we first highlight recent scientific literature regarding the development of adsorbents from WS in the form of carbon-based materials including unmodified/modified WS, and activated carbons (ACs). Next, we discuss the potential applications of WS-derived by-products as natural yet effective adsorbents for the removal of various hazardous materials including heavy metals (HMs), synthetic industrial dyes, and harmful chemicals.

1. Introduction

Currently, environmental contamination from various hazardous materials is a primary concern worldwide. It is a significant risk, and scientists believe that it endangers public health. For this reason, many recent studies have focused on the effective removal and elimination of such to reduce their harmful effects on living organisms.[1] Annually, large amounts of toxic materials resulting from human industrial activities are discharged into the environment. Different synthetic dyes, various HM ions, oils derived from crude and processed petroleum, and pharmaceuticals are known to be significant hazardous compounds.[2] Hazardous materials show carcinogenic and toxic effects, and thus is a growing interest worldwide for in the development of cost-effective, rapid, secure, regenerating and applicable biosorbents for the removal of such dangerous substances from industrial wastewaters before their discharge into terrestrial and aquatic ecosystems.[3] Accordingly, the removal of different hazardous materials that threaten human health and affect various forms of life in aquatic ecosystems is now an important topic of study among environmental scientists. Currently, agricultural by-products and carbon-based products derived from waste crops seem to be the most attractive materials for the removal of various toxic chemicals because of their abundance, renewability, and cost-effectiveness. In recent years, various plant-based waste residues have been considered as adsorbents.[4] Hazardous material separation using low-cost alternative adsorbents can be advantageous since provides a double advantage, *i.e.*, waste product management and water purification. Additionally, the low-cost ACs derived from biomass similar or better than non-renewable coal-based granular activated carbons (GACs) and may successfully replace GACs. Consequently, the material used to produce ACs is critical because considerably affects the adsorption capacity. Nutshells, as standard and inexpensive agricultural waste materials, are used for this purpose.[5]

Walnut is as a popular tree nut that has been widely cultivated across the world for its valuable kernel. Inside the walnut fruit, the kernel is surrounded by three distinct layers called the seed coat, the shell, and the green husk. Unlike the kernel, the remaining parts of the fruit are regarded as waste products and are discarded without being put to any practical use.[6] Recently, the walnut shell has gained increasing attention due to its high availability and several unique properties. One of the main and

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recently highlighted applications of WS by-products is the use of processed or unprocessed WS as biosorbent.[7] Accordingly, this review aims to summarize up-to-date developments in the preparation and application of unmodified and modified WS in the form of ACs, as well as chemically modified WS in adsorption procedures for the removal of HMs, dyes, oils, pharmaceuticals and other hazardous substances from aqueous solutions. Additionally, important parameters for obtaining optimal adsorption conditions for different hazardous materials are highlighted. Furthermore, the thermodynamics of the adsorption reactions are discussed. Building upon the information derived from the literature review, concluding remarks and suggestions for future research are provided.

2. Walnuts

The Persian, English, or common walnut is valuable tree nut in the family Juglandaceae. Due to its valuable kernel, walnut is commercially cultivated in most parts of the world. It is considered a high-density nutrient that is rich in protein and essential fatty acids.[8,9] In recent years, there has been a rapid increase in global walnut production, particularly in Asian countries, which appreciate these products for their high nutritional value and antioxidative potential.[10] It has been reported that walnut kernels have high amounts of phenolic compounds and that their consumption provide many beneficial effects for human health.[11–26] Black walnut (*Juglans nigra* L.) is another important species of this genus that is valuable for its wood.[27] The fruit and timber of the common walnut have been extensively used in human nutrition and industrial applications.[18] The shell and husk are the main by-products of the walnut fruit and are produced in high amounts upon processing the walnut fruit to obtain the kernel. Recent investigations of these by-products demonstrated that they contain valuable compounds including phenolics.[6,28–30] The green husk of the walnut fruit is available in high amounts. Recently, Oliveira, *et al.*[31] recognized the aqueous extract of the low-cost green husk as an excellent natural source of phenolic compounds with antimicrobial and antiradical activities. The leaves of walnut are also considered another source of beneficial medicinal compounds and have been comprehensively applied in folk medicine for the treatment of hyperhidrosis, skin inflammations, and ulcers. Additionally, its prepared extracts or identified constituents show anti-septic, anti-helminthic, anti-diarrheic, antioxidant and astringent properties.[20,32–38] The other parts of the walnut tree, such as the branches and shoots have recently been used for the extraction of useful compounds with antioxidant and antimicrobial properties.[39,40] Moreover, walnut kernels are valuable nutraceuticals considering that their regular consumption is reported to decrease the risk of human coronary heart disease.[15,17–19,22,24,25,41–44] The health benefits of walnut are commonly attributed to its chemical composition,[13,32,45] as it is known as a good source of tocopherols and tocotrienols, proteins, fibre, sterols, folate, essential fatty acids, melatonin, tannins, and other polyphenols.[11,13,16,28,36] Studies on different types of nuts have indicated that walnut has the highest content of antioxidant compounds, particularly tocopherols and polyphenols, and most of the walnut kernel phenolic compounds are concentrated in the pellicle or skin.[13,18,46,47] Recently, some valuable constituents such as pyrogallol and juglone (5-hydroxy-1,4-naphthoquinone) have gained considerable attention. Juglone is found in different parts of the walnut tree and shows excellent biological activities, in particular anticancer properties.[48,49]

3. Walnut fruit

From a nutritional standpoint, the fruit of walnut is the most crucial part of the tree because the seed inside the fruit is generally what is consumed by humans. It is a rounded, single-seeded stone fruit that has four distinct different parts (see Fig. 1 for more details). The green husk or hull is characterized as a thick an external thick layer of walnut fruit. This part is cracked when the fruit ripens fully on the tree. After its separation, the remaining part of the fruit is called the nut.[6] The woody and hard material that is the middle portion of the fruit is called the shell. In most walnut cultivars, the shell must be cracked mechanically to obtain the meat.[7] The internal portion of the fruit is the kernel or seed, which consumed as the nutritious part of the fruit.[50]

Similar to that in other tree nuts such as almonds, the kernel of the walnut is covered by a thin leathery light brown layer called the skin, seed coat, or pellicle. This part of the walnut fruit has not been comprehensively studied in comparison with those of other tree nuts.[30] The most critical and divergent antioxidants are concentrated in this part of the fruit and act as protective agents against harmful UV radiation effects, as well as microbial, fungal, and viral contamination.

4. Walnut by-products

As shown in Fig. 1, during walnut fruit processing to obtain the valuable kernel, large amounts of green husk and woody shell are produced and discarded without being put to any practical use. In some areas, both shells and husks are burned as fuel for heating purposes, which may cause environmental pollution.[7] The husk and the shell account for more than 60% of the walnut fruit by weight. The shell makes up a considerable percentage of the fruit by weight (∼40%) and is available as an abundant and low-cost agricultural by-product in walnut production centres. It is crucial point is to reconsider the value of the husk and the shell, not as agricultural waste products to be generated and discharged into the environment during the production of the walnut kernel, but as valuable by-products with applications in the pharmaceutical, nutritional and industrial fields.[30]

5. Walnut shell

The middle part of the walnut fruit surrounding the kernel is called the shell. It is considered a hard organic abrasive that is chemically inert, nontoxic, and biodegradable. It has multiple advantages, including cost-effectiveness, outstanding durability and elasticity. In addition, it leaves no scratches or pitting during cleaning and is environmentally friendly. Its availability

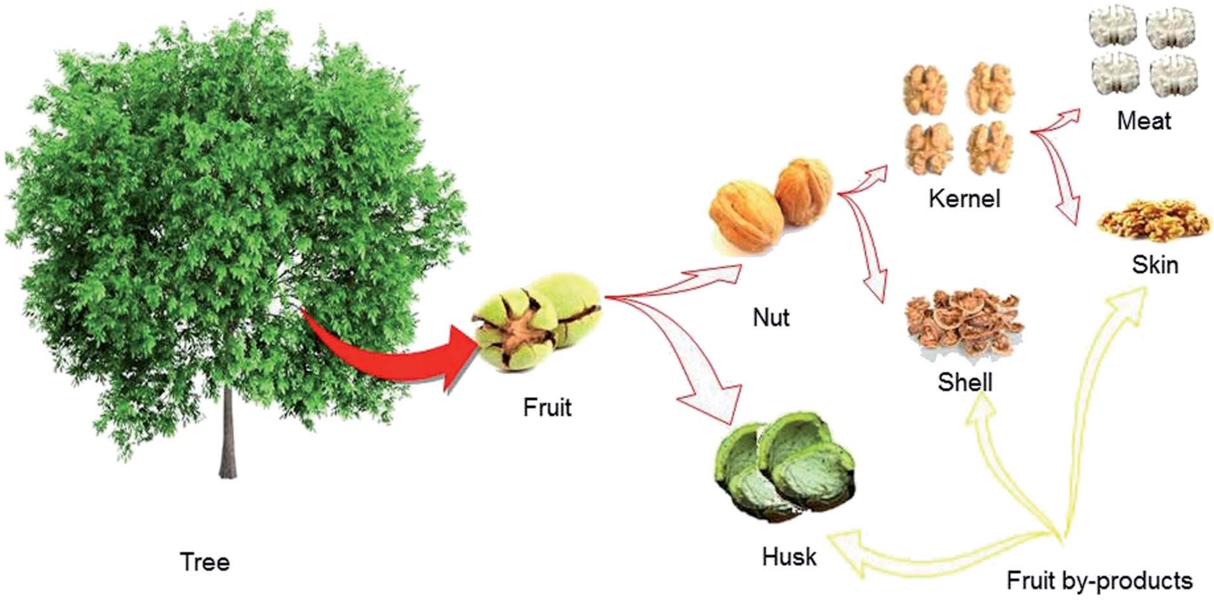

Fig. 1 Different parts of walnut fruit and the corresponding by-products. The walnut fruit mainly consists of the husk, shell, skin, and kernel. The husk, shell and skin, are the main agricultural waste products of walnut fruit.

as a renewable resource can be regarded as an additional advantage.[51] The shell portion of the walnut fruit is a lignocellulosic agricultural waste composed of cellulose (17.74%), hemicellulose (36.06%), and lignin (36.90%).[52]

WS is the primary waste material remaining after consumption of the edible part of walnut and has limited applications.[53] However, after powdering and sizing, it may be used as a medium in abrasive blasting for polishing and cleaning soft metals, plastics, wood, and stone. It may also be applied in the pre-treatment of some parts and devices before painting as well as for the effective deburring of electrical components, casting, moldings, *etc.* Furthermore, WS may be used for cleaning and polishing by barrel tumbling, as a filtration medium in hydration systems, as an extender for adhesives materials, as a loss circulation material in the oil industry, and as a filler in casting. The processing of WS enables its use as a scrub in the soap and cosmetic industries and as an abrasive suitable for polishing jewellery, gun casings, and some metal materials.

WS powder has also been found to have excellent adsorbency,[54] and it is also an excellent reinforcing material,[55] which allows its use as an efficient biosorbent. Considering its unique mechanical properties, low ash content, and bulk density, WS has also been used to produce ACs and to remove HM ions and oils.

Since WS is considered an agricultural waste material, it has no commercial value. Thus, this cellulose-rich agro-waste material is suitable for the development of commercially biodegradable packaging films.[56] WS can be used as a carbonaceous sorbent to control various HMs from industrial liquid streams.[57] Additionally, it is a suitable medium for crude oil separation from water.[51] Finally, WS has some antioxidant compounds such as flavonoids,[28] and recently, in addition to ACs some valuable compounds, such as charcoal and pyroligneous acids have been obtained from WS.[58]

6. Carbon-based materials derived from walnut shell

6.1. Modified walnut shell

Lignin, cellulose, and hemicellulose are the primary components that make up agricultural crop residues. Lignin is known to be a relatively hydrophobic and aromatic natural polymer, whereas cellulose is a typical biopolymer that is present in plant cell walls. Hydroxyl (–OH), carbonyl (–C═O), and carboxyl (–COOH) groups are considered significant polar functional groups in natural sorbents derived from waste crops, and are potentially involved in the bonding of pollutants during the sorption process. Various agricultural waste products are good alternatives to expensive adsorbents because they naturally have large amounts of functional groups on their structure.[52] In their natural form, the binding of adsorbates to the adsorbents developed from agricultural waste residues is not significant because of the presence of methyl esters in the chemical constituents. However, the metal-binding potential of the adsorbent *ca.* be increased by treating the adsorbent with a base or by modifying the methyl esters to –COOH groups. For example, sodium hydroxide (NaOH) transforms cellulose I into cellulose II by penetrating into the structure of cellulose, thus reducing the crystallinity and increasing the porosity and surface area.[59] In chemically modified adsorbent, the –OH groups of cellulose macromolecules are more easily accessible, which induces the liberation of new adsorption sites on the adsorbent, in the end, the adsorption capacity of the adsorbent is improved. The untreated form of WS shows a low removal capability and its process kinetics are slow. Thus, chemical modification could be considered to enhance its adsorption capacity. The introduction of chemically functional groups may improve the efficiency of adsorption, for instance, amide ($CONH_2$), –COOH, and –OH groups. Among them, the addition of the –COOH group is the most commonly used procedure.[60] The effect of alkali pretreatment on the adsorption capability of WS has been reported. WS modified with citric acid contains phenolic compounds that are abundant in –OH and –COOH groups, which may serve as active sites for the successful removal of different hazardous materials.[52]

6.2. Activated carbons prepared from walnut shell

ACs are some of the most extensively accepted adsorbents for the purification of gaseous and aqueous solution systems on an industrial scale. ACs are prepared in three main steps: a raw material pretreatment process, a low-temperature carbonization process, and an activation procedure. The carbonized material is activated using two different methods: chemical activation (CA), and physical activation (PA). In the PA process, the raw material is activated after the carbonization of the porous structure developed on the surface and inside of the carbon material. Generally, for the reduction of carbon loss, activation is executed at temperatures between 800 and 1000 °C under anaerobic condition. In the CA method, chemical agents are added to the raw materials and then heated with an inert gas as a protectant. In this preparation method, the carbonization and activation processes progress are simultaneously. CA has some advantages compared to PA, such as a more easily controllable activation reaction, a larger specific surface area (SSA) of the product and a shorter activation time. Currently, it is the dominant process for producing high-performance ACs.[61] The price of ACs has increased over time. For this reason, to develop a sustainable method, it is essential to explore new methods for as alternatives to ACs production using non-conventional and low-cost methodologies. All materials with carbonaceous structures can be used for the preparation of ACs, but the raw materials used and the activation process determine the properties of the obtained ACs. Nutshells, fruit pits, paper mill waste (lignin), wood, charcoal, brown and bituminous coals, lignite, bone, and peat are the most commonly used starting materials for the production of ACs.[62] Walnut is an ordinarily accepted nutrient food but WS has no commercial value. Consequently, to turn the produced waste shell biomass into a valuable product, WS can be used to prepare ACs. WS has been considered as the raw material for the preparation of ACs *via* both PA and CA methods. For example, using potassium carbonate (K_2CO_3) as a chemical activator, ACs were prepared from five different types of nutshell.[63] Almond, coconut, oil palm, pistachio, and walnut shells were used as the starting materials. The ACs from all the samples had maximum SSAs at the preparation temperature of 800 °C. The authors found that K_2CO_3 is a useful activation reagent, but it worked differently at temperatures below 527 and above 27 °C. In addition, Kim, *et al.*[64] reported the use of WS as the raw material for the production of GACs *via* the CA process. It was shown that the iodine value increased with increasing activation temperature. However, at temperature above 400 °C, the iodine was thermally degraded. The microporous structure of the ACs was also destroyed at activation times longer more than 1 h and at 375 °C. The increasing concentration of the zinc chloride ($ZnCl_2$) solution improved the iodine value. However, it decreased with excessive $ZnCl_2$. The degree of activation by $ZnCl_2$ was compared with that by $CaCl_2$ and a high degree of activation was observed for WS activated by $ZnCl_2$. High contents of carbon and oxygen are associated with the presence of polysaccharides such as lignin, cellulose, and hemicellulose in the WS.[65] A high iodine number and specific surface area are reported for the ACs obtained from WS. These properties are associated with the low ash and high lignin contents of the shells and hard shells such as WS have relatively low ash contents.[66] Due to high carbon and low ash contents, WS is therefore a suitable material for the production of ACs.

7. Hazardous material removal with walnut shell

7.1. Removal of heavy metals

Due to human activities, natural water resources are polluted by discharged wastewater from public residual and industrial wastewater. Typical industrial wastewater contains poisonous substances such as acids, HMs, and dyes. To preserve water quality, it is essential for industries to treat their effluent before discharging it into the environment.[67] Agricultural by-products may be used as green adsorbents to resolve the problems concerning HM pollution, especially that from medium-sized and small industrial facilities.[68] Different processes such as ion exchange, electrocoagulation, chemical precipitation, membrane separation, biosorption, and adsorption have been developed to eliminate different metal ions from wastewater before inflow into water for human use.[69] Among these processes, adsorption is considered an economical and efficient technology because many adsorbents can be provided by forestry and agricultural residues (normally biomass) with is one method of "dealing with waste by waste".[70] The adsorption of HM ions from the aqueous phase on carbonaceous adsorbents is a diffusion-based process that includes two main steps: first the adsorbate is transferred from the aqueous phase to the external surface of the carbon through the liquid film that surrounds the carbon particle, and second, the HM ions move deeper into the pores and are adsorbed *via* chemical complexation and/or ion-exchange at the chemically active sites.[71,72]

At least 20 different HM ions have been determined to be toxic elements,[73] and thus, their release into fresh waters could have adverse outcomes for human health and aquatic organisms.[74] As a highly available agricultural by-product with a high SSA, excellent chemical stability, high mechanical strength, and easy regeneration, WS has proven effective as an adsorbent in the removal of HMs from wastewater.[54,75] Copper (Cu^{2+}), chromium (Cr^{6+}), arsenic (As^{3+}), cadmium (Cd^{2+}), lead (Pb^{2+}), caesium (Cs^{+}), nickel (Ni^{2+}), zinc (Zn^{2+}), manganese (Mn^{2+}), iron (Fe^{2+}), and mercury (Hg^{2+}) are 11 HM ions that are considered to be removable by WS. The optimized operational conditions, including solution pH, adsorbent dosage, temperature, agitation speed, and contact time are the main parameters considered in identifying the maximum removal efficiency (%) for HM ion removal by adsorption by WSACs (Table 1). Additionally, the corresponding maximum adsorption capacity (q_m), thermodynamics of the adsorption reaction, and fitting and kinetic models, are summarized in Table 2. Further discussion regarding each HM ion is presented in the following sections.

7.1.1. Zinc ions removal. Zn^{2+} is one of the most significant elements that is frequently detected in effluents released from manufacturing facilities in association with acid mine effluent, galvanization factories, natural minerals, and municipal wastewater processing plants. The World Health Organization (WHO) set the highest tolerable concentration in drinking water of Zn^{2+} as 5.0 mg l^{-1}.[94] Zn^{2+} is non-biodegradable and is bioaccumulated throughout the food chain, thus, its removal is of great importance. In a batch model study performed by Moreno-Barbosa, *et al.*,[88] they attempted to remove Pb^{2+} and Zn^{2+} ions from solution through adsorption onto synthesized watermelon shell activated carbons (WMSACs) and walnut shell activated carbons (WSACs) in a CA process using phosphoric acid (H_3PO_4) 40%. The production yields were 85 and 80% for the WMSACs and WSACs, respectively. The surface area and pore volume of WSACs were 10 and 13% higher than those of the WMSACs, respectively. Additionally, surface areas of 789 m^2 g^{-1} and 710 m^2 g^{-1} were reported for the WSACs and WMSACs, respectively. Moreover, the WSACs demonstrated a better resistance to high temperatures than the WMSACs. Likewise, the adsorption isotherm data were better fitted by the Langmuir model. According to the experimental results, 1 g of WMSACs adsorbed >1 mg of Pb^{2+} and Zn^{2+} more than 1 g of WSACs. This higher adsorption potential indicated the importance of pore distribution in the adsorption system, as WMSACs have a mesoporous and microporous composition, while WSACs only

Table 1 The optimal conditions for the removal of various HM ions by WS[a]

No	HM ions	pH	Adsorbent dosage	Temp. (°C)	Agitation speed (rpm)	Contact time (min)	Efficiency (%)	Ref.
1	Cu^{2+}	—	0.3 g l^{-1b}	30	Shaking	30	63	Kim, *et al.*[64]
		5.6	1 g l^{-1b}	40	180	60	—	Xie, *et al.*[76]
		7	2 g l^{-1c}	Room temp.	Shaking	80	90	Feizi and Jalali[77]
		7	0.1 g^b	Ambient temp.	—	—	97.5	Kazemipour, *et al.*[78]
2	Cr^{6+}	2	2 g l^{-1b}	40	200	—	99	Ghasemi, *et al.*[79]
		5	1 g l^{-1b}	40	180	60	—	Xie, *et al.*[76]
		2	1.5 g/0.15 l^b	27	150	1440	—	Nethaji and Sivasamy[80]
		3.5	0.5 g/0.02 l^c	25 ± 1	200	100	85.32	Pehlivan and Altun[75]
		2	0.1 g/0.02 l^b	25 ± 1	Shaking	120	75	Altun and Pehlivan[52]
		1	0.80 g^b	35	200	120	99.4	Lu, *et al.*[81]
3	As^{3+}	5.5	0.03 g l^{-1b}	24	120, 90	420, 1440	—	Jafari-Mansoorian, *et al.*[82]
		10	40 g l^{-1b}	20	60	40	88	Saqib, *et al.*[83]
4	Cd^{2+}	6	0.2 g l^{-1b}	30	150	240	41.96	Gondhalekar and Shukla[84]
		6–10	0.1 g^b	Ambient temp.	—	—	50.9	Kazemipour, *et al.*[78]
		7	2 g l^{-1c}	Room temp.	Shaking	200	90	Feizi and Jalali[77]
		5	20 g l^{-1b}	25	150	30	~90	Almasi, *et al.*[85]
		6.92	0.56 g l^{-1b}	25	Shaking	40.42	99.72	Saffari[86]
5	Pb^{2+}	5	0.18 g l^{-1b}	35	—	—	89.61	Cheng, *et al.*[60]
		6–10	0.1 g^b	Ambient temp.	—	—	96	Kazemipour, *et al.*[78]
		5.5	2 g l^{-1b}	25	140	150	94.12	Yi, *et al.*[87]
		4.5	0.5 g/0.05 l^b	25	Shaking	14 days	100	Moreno-Barbosa, *et al.*[88]
		5	1.0 g l^{-1b}	45	65	400	99	Saadat, *et al.*[89]
		6.3	13.5 g l^{-1b}	—	65	300	98.2	Saadat and Karimi-Jashni[90]
		5	20 g l^{-1b}	25	150	30	~90	Almasi, *et al.*[85]
		4	5 g l^{-1c}	25	120	60	62.9–83.7	Gala and Sanak-Rydlewska[91]
6	Cs^+	—	20 g l^{-1b}	Room temp.	200	2880	—	Ding, *et al.*[54]
		4	15 g l^{-1b}	25 ± 1	200	1440	99.8	Ding, *et al.*[92]
7	Ni^{2+}	8	10 g l^{-1b}	45	65	300	88.3	Karimi-Jashni and Saadat[59]
		6	2 g $l^{-1b,c}$	Room temp.	Shaking	120	90	Feizi and Jalali[77]
8	Zn^{2+}	8	2 g l^{-1c}	Room temp.	Shaking	200	90	Feizi and Jalali[77]
		6–10	0.1 g^b	Ambient temp.	—	—	71	Kazemipour, *et al.*[78]
		4.5	0.5 g/0.05 l^b	25	Shaking	14 days	98.4	Moreno-Barbosa, *et al.*[88]
9	Mn^{2+}	8	2 g l^{-1c}	Room temp.	Shaking	200	96.5	Feizi and Jalali[77]
10	Fe^{2+}	8	2 g l^{-1c}	Room temp.	Shaking	20	90	Feizi and Jalali[77]
		4.5	2 g l^{-1b}	40	200	—	96.2	Ghasemi, *et al.*[79]
11	Hg^{2+}	5	0.02 g/0.05 l^b	25	720	60	90	Zabihi, *et al.*[93]
		5	0.05 g^b	29	720	60	—	Zabihi, *et al.*[57]

[a] — not reported. [b] Modified WS. [c] Ordinary WS.

Table 2 The adsorption capacity, thermodynamic, fitting and kinetic models for the removal of different HM ions by the WS[a]

No	HM ions	q_m[b]	Fitting model	Kinetic model	Thermodynamic	Ref.
1	Cu^{2+}	30 mg l^{-1}[c]	Freundlich	—	Not spontaneous, exothermic	Kim, *et al.*[64]
		204.08 mg g^{-1}[c]	Langmuir	Pseudo-second order	Spontaneous, endothermic	Xie, *et al.*[76]
		38.8 mg g^{-1}[d]	Langmuir	Pseudo-second order	—	Feizi and Jalali[77]
		—	—	—	—	Kazemipour, *et al.*[78]
2	Cr^{6+}	43.12 mg g^{-1}[c]	Langmuir–Freundlich	Pseudo-second order	Spontaneous, endothermic	Ghasemi, *et al.*[79]
		51.28 mg g^{-1}[c]	Langmuir	Pseudo-second order	Spontaneous, endothermic	Xie, *et al.*[76]
		6.01 mg g^{-1}[c]	Langmuir	Pseudo-second order	Spontaneous, endothermic	Nethaji and Sivasamy[80]
		8.01 mg g^{-1}[d]	Langmuir	—	—	Pehlivan and Altun[75]
		154 mg g^{-1}[d] 596 mg g^{-1}[c]	Langmuir	—	Spontaneous, endothermic	Altun and Pehlivan[52]
		3.5 mg g^{-1}[c] 1 mg g^{-1}[d]	Langmuir	Pseudo-second order	—	Lu, *et al.*[81]
3	As^{3+}	0.2 mg l^{-1}[c]	Langmuir, Freundlich	—	—	Saqib, *et al.*[83]
		3.42 mg g^{-1}[c]	Langmuir	—	—	Jafari-Mansoorian, *et al.*[82]
4	Cd^{2+}	14.29 mg g^{-1}[c]	Langmuir	Pseudo-second order	Spontaneous, exothermic	Gondhalekar and Shukla[84]
		—	—	—	—	Kazemipour, *et al.*[78]
		76.9 mg g^{-1}[d]	Langmuir	Pseudo-second order	—	Feizi and Jalali[77]
		11.6 g kg^{-1}[c]	Langmuir	Pseudo-second order	—	Almasi, *et al.*[85]
		70.78 mg l^{-1}[c]	—	—	—	Saffari[86]
5	Pb^{2+}	210.14 mg g^{-1}[c]	Langmuir	—	Spontaneous, endothermic	Cheng, *et al.*[60]
		—	—	—	—	Kazemipour, *et al.*[78]
		81.96 mg g^{-1}[c]	Langmuir	Pseudo-first order	—	Yi, *et al.*[87]
		32.362 mg g^{-1}[c]	Langmuir	—	—	Moreno-Barbosa, *et al.*[88]
		294.10 mg g^{-1}[c]	Langmuir	Pseudo-second order	—	Saadat, *et al.*[89]
		—	—	—	—	Saadat and Karimi-Jashni[90]
		32 g kg^{-1}[c]	Langmuir	Pseudo-second order		Almasi, *et al.*[85]
		23.1 mg g^{-1}[d]	Langmuir–Freundlich	—	—	Gala and Sanak-Rydlewska[91]
6	Cs^{+}	14.6 μmol[c]	Freundlich	Pseudo-second order	Spontaneous, endothermic	Ding, *et al.*[54]
		6 ± 4.3[c]	Langmuir	Pseudo-second order	—	Ding, *et al.*[92]
7	Ni^{2+}	8.57 mg g^{-1}[c]	Langmuir	Pseudo-second order	Spontaneous	Karimi-Jashni and Saadat[59]
		29.4 mg g^{-1}[d] 38.9 mg g^{-1}[c]	Langmuir	Pseudo-second order	—	Feizi and Jalali[77]
8	Zn^{2+}	33.3 mg g^{-1}[d]	Langmuir	Pseudo-second order	—	Feizi and Jalali[77]
		—	—	—	—	Kazemipour, *et al.*[78]
		6.079 mg g^{-1}[c]	Langmuir	—	—	Moreno-Barbosa, *et al.*[88]
9	Mn^{2+}	28.6 mg g^{-1}[d]	Langmuir	Pseudo-second order	—	Feizi and Jalali[77]
10	Fe^{2+}	62.6 mg g^{-1}[d]	Langmuir	Pseudo-second order	—	Feizi and Jalali[77]
		39.25 mg g^{-1}[c]	Langmuir, Freundlich	Pseudo-second order	Spontaneous, endothermic	Ghasemi, *et al.*[79]
11	Hg^{2+}	151.5 mg g^{-1}[c]	Langmuir, Freundlich	Pseudo-second order	—	Zabihi, *et al.*[93]
		151.5 mg g^{-1}[c]	Langmuir, Freundlich	Pseudo-second order	Endothermic	Zabihi, *et al.*[57]

[a] — not reported. [b] Maximum adsorption capacity. [c] Modified WS. [d] Ordinary WS.

contain micropores. In addition, surface chemistry was reported to be an important variable in the adsorption process as the WMSACs had a lower point of zero charge pH (pH_{PZC}) than the WSACs (3.05 for WMSACs and 4.5 for WSACs) and the pH of each metal solution was adjusted in 4.5. This suggests that the electrostatic interactions between the ion and the carbon surface had increased. Further findings reported that orange peel, hazelnut shell, and WS can be appropriately employed as low-cost adsorbents for Zn^{2+} and Cd^{2+} removal from water, and their highest sorption abilities were 15.51 and 19.8 mg g^{-1}, 11.55 and 16.65 mg g^{-1}, and 26.60 and 21.10 mg g^{-1}, respectively. In addition, Zn^{2+} and Cd^{2+} ion biosorption from aqueous solution to organic wastes such as orange peel, hazelnut shell, and WS were investigated using batch adsorption studies.[95] Hazelnut shells had the highest removal efficiency for Zn^{2+} and Cd^{2+} ions. The method was reported to be quick and all the studied biosorbents were capable of removing 90% of HM ions. The sorption process can be performed on a heterogeneous surface with chemisorption. The raw material WS was also employed as regional agricultural biomass in Yasouj city, Iran. for the preparation of ACs.[96] Using the Taguchi experimental design, the optimum condition of the synthesis process was obtained and the adsorption ability of the generated ACs towards Zn^{2+} was considered as a response. The activation time and the impregnation ratio were found to be effective parameters for defining the optimum conditions, according to the data analysis. The ACs developed under optimum conditions had a mesopore structure with an SSA of 1388 m^2 g^{-1}. The adsorption capacity of the produced carbon for Zn^{2+} was 89 mg g^{-1}. Additionally, the composite biosorbents obtained from WS and snail shells were used to study the biosorption process of Zn^{2+} ions in industrial wastewater.[97] Composite adsorbents were provided by activating WS with H_3PO_4 to achieve acid-treated WS (AWS). Then, WS and AWS were separately impregnated on chitosan (CS) to prepare WS impregnated on CS (WSCS) and acid-treated WS impregnated on CS (AWSCS). A pH of 5, 1 g adsorbent dosage, Zn^{2+} ion initial concentration of 30 mg l^{-1}, contact time of 2 h, agitation speed of 150 rpm, particle size of 60 BSS and temperature of 30 °C resulted in the greatest adsorption capabilities 3.1104, 3.8052, 16.4474 and 17.6991 mg g^{-1} for WS, AWS, WSCS and AWSCS, respectively. Among the investigated kinetic models, the pseudo-second-order kinetic model gave the best fitting model. Zn^{2+} ions adsorption on the prepared adsorbents was film diffusion-controlled. According to the experimental results from this work, AWSCS has the high potential to be regarded as an alternative effective and inexpensive biosorbent in the remediation of HMs in wastewater. Zn^{2+} ion adsorption on the derived composite biosorbents was exothermic, endogenic, favourable, and non-spontaneous. Based on the q_m values presented in Table 2, WS adsorption capacity for Zn^{2+} is not sufficient with only 6–33.3 mg g^{-1} scavenging potential.

7.1.2. Iron ion removal.

Of the HMs, Fe^{2+} is an essential element in haemoglobin for carrying oxygen molecules in the blood circulatory system. However, it may cause adverse effects at high concentrations, and thus, excess amounts of Fe^{2+} must be removed from the environmental effectively. In comprehensive research by conducting batch experiments, the residues of sunflower, potato, canola, and WS were used as sorbents to sorb different HMs (Fe^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}) from aqueous solution. The highest sorption of HMs by the various sorbents was observed at approximately pH 4–8 and the optimal time for reaching equilibrium was in the range of 20–600 min. The authors observed that the ability of sorbents to sorb of HMs was as follows: sunflower residue > potato residue > canola residue > WS residue. The order of metal sorption in the competitive system for the WS was reported as $Ni^{2+} < Cu^{2+} < Zn^{2+} < Mn^{2+} < Cd^{2+} < Fe^{2+}$. The Langmuir isotherm model fit the sorption results well. The kinetics of HM sorption followed pseudo-second-order kinetic. In this study, electrostatic interaction and ion exchange, as well as complexation were reported to be the main sorption mechanisms in the adsorption of the studied HMs.[77]

WS is reported to be a suitable material for biochar development. Walnut shell biochar (WSB) is also recommended as a green reducing agent to reduce the iron phase in waste copper slag and to clean up hazardous waste. Biochar has been used as a reducing agent in research to reduce waste copper slag for iron recovery. The reduction of copper slag by WSB was theoretically evaluated, and the iron in the slag was effectively retrieved through reduction and magnetic separation techniques.[98] As presented in Table 2, the q_m values achieved for the removed Fe^{2+} ions (40–63 mg g^{-1}) indicated that WS could be considered a suitable biosorbent for the separation of this HM from contaminated wastewater.

7.1.3. Nickel ion removal.

At relatively low levels, Ni^{2+} is poisonous and cancerous. Ni^{2+} is resistant to degradation and accumulates in living organisms, causing respiratory failure, embolisms, lung cancer, pulmonary fibrosis, asthma, chronic bronchitis, congenital disabilities, heart disorders, allergic reactions and renal oedema. The maximum permitted Ni^{2+} discharge concentration is 2 mg l^{-1}. A practical and cost-effective technology is therefore required to remove Ni^{2+} from aqueous solution.[99] Using pre-treated WS, univariate studies with a factorial design were employed to study the different factors that influence Ni^{2+} removal.[59] The pH of the solution was noted to be the most critical parameter in Ni^{2+} removal. The highest pretreated WS adsorption capability for Ni^{2+} was 8.57 mg g^{-1}. The adsorption mechanism of Ni^{2+} on pre-treated WS obeyed pseudo-second-order kinetics. In another study, different agricultural residues of sunflower, potato, canola, and WS were used as sorbents to sorb HMs including Fe^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}. The plant residues showed considerable capacity for the removal of Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+} from aqueous solution, but the Ni^{2+} sorption by residues was negligible. The authors improved the capability of natural sorbents to remove Ni^{2+} from aqueous solution by using 0.5 M sodium hydroxide (NaOH) as the chemical activation agent.[77] The removal of Ni^{2+} ions from aqueous solutions containing 100 mg l^{-1} of Ni^{2+} using WS has also been described.[100] At a pH of 5.85 with a 5 min contact time for a 5 mg l^{-1} solid-to-liquid ratio and an initial HM concentration of 100 mg l^{-1}, a maximum removal efficiency of 43.23% was achieved. Moreover, the effects of pH, contact time, initial metal concentration, adsorbent concentration, and co-ions in synthetic solutions and mining waste leachate were considered for the removal of Zn^{2+}, Cd^{2+} and Ni^{2+} using WS.[101] Metal adsorption was found to be dependent on the solution's initial pH; since the adsorption rate improved as the pH increased, demonstrating the highest affinity at pH 5–7. Additionally, the quantity of the removed metal increased as the initial concentration increased. Increasing the adsorbent dosage increased the removal, but reduced the quantity adsorbed per WS unit mass. The presence of co-ions existence reduced HM adsorption, with divalent ions having a more adverse impact than monovalent ions. Zn^{2+}, Cd^{2+} and Ni^{2+} adsorption on WS was reported to match the Langmuir and Freundlich isotherms. According to the qm values obtained in some research (Table 2), only 8–38 mg g^{-1} of Ni^{2+} is a removable by WS, which is a considerable the amount compared to the amount of other HMs removed by WS.

7.1.4. Copper ion removal.

As an important wastewater contaminant, Cu^{2+} ions are principally discharged from plating manufactures, mines, and metal cleaning, chemical production, and metal-processing facilities. Cu^{2+} is considered a non-biodegradable pollutant and is a very toxic HM. It can lead to severe damage in the human body through bioaccumulation.[102] The results of several investigations show that adsorption is regarded as the most useful technique for removal of HMs such as Cu^{2+} ions. A study Kazemipour, *et al.*[78] reported the successful removal of Pb^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+} from industrial wastewater onto the carbon produced from walnut, hazelnut, almond, and pistachio shells as well as apricot stones. In this work, to achieve maximum removal efficiency, the heating time and temperature were optimized at 15 min and 800 °C, respectively. Maximum removal occured at pH 6–10, a 3 ml min^{-1} flow rate, and an adsorbent dosage of 0.1 g. In another investigation reported by Kim *et al.*,[64] they characterized the adsorption capacities of the prepared GACs developed from WS through CA by using $ZnCl_2$ as an activating agent. The ACs were tested as adsorbents in synthetic wastewater containing Cu^{2+} ions and the Freundlich model interpreted well the adsorption of Cu^{2+} ions well. It was suggested that the adsorption potential of the manufactured ACs reached commercialization quality since it was determined to be better than that obtained from coconut shells. Furthermore, in another work published by Xie *et al.*,[76] they developed acid and acid–base modified WSACs and carried out batch experiments to study their adsorption behaviours towards Cu^{2+} and Cr^{6+}. In this effort, the kinetics data matched excellently with pseudo-second-order kinetics. The results showed that the acid–base-prepared ACs presented adequate Cu^{2+} adsorption capacity, with a highest adsorption potential of 204.08 mg g^{-1}. Additionally, it was suggested that Cu^{2+} adsorption on acid–base ACs was a chemical ion-exchange procedure. Thermodynamically, Cu^{2+} adsorption was spontaneous and endothermic. The authors concluded that the pH and the surface chemistry of the ACs, rather than the carbon composition properties, had a critical function in the uptake of the Cu^{2+} ions from aqueous solution, while the Cr^{6+} adsorption was closely associated with the pH and textural characteristics.

Ultrasound technology is currently applied in various ways in different fields. The effects of ultrasound technology (UST) on the adsorption process of Cu^{2+} into GACs obtained from WS were recently studied. The GAC adsorption rates of 1.7–3.86 mmol g^{-1} Cu^{2+} using UST, and 0.66 to 2.7 mmol g^{-1} Cu^{2+} without UST were reported. Furthermore, the adsorption efficiency was enhanced with increases in the initial concentration and SSA.[103] Ultrafine water mist (UWM)-plasma alteration is a new approach for promoting the adsorption potential of raw materials. It has been suggested that nonthermal plasma in UWM can enhance the content of –COOH groups on the surface of raw WS which increases its efficiency in the extraction of Cu^{2+} from wastewater.[104] Characterization studies using techniques including Brunner–Emmett–Teller (BET) measurements, scanning electron microscopy-/energy-dispersive X-ray analysis (SEM-EDX), and X-ray photoelectron spectroscopy (XPS) showed that more –COOH groups were created on the surface of modified WS (MWS). In the introduced technology, the dis-associated oxygen atoms in water mists with plasma bonded to the WS and formed active sites containing –COOH groups. After the chemisorption of Cu^{2+} by the –COOH groups, the COOH groups' content in the WS diminished because several groups were changed into –C=O groups. For the raw WS, the efficiency of Cu^{2+} removal was 33.5%; however, after plasma modification for 15 min under 3 g min^{-1} water mist, the efficiency increased considerably (98%). The highest Cu^{2+} adsorption potential of the UWM-plasma-modified WS was 39.4 mg g^{-1} at pH 5.3 and 25 °C, approximately 8 times higher than that of the raw WS. Based on the q_m values obtained in different studies for the removal of Cu^{2+} ions (see Table 2 for more details), the WS adsorption capacity for such metal ions is in the range of 30–204 mg g^{-1}. This adsorption capacity is reasonable for the practical application of WS when compared to its adsorption of other HMs such as Ni^{2+}, Zn^{2+} and Mn^{2+}.

7.1.5. Chromium ion removal.

Cr^{6+} ion is another hazardous HM ion, and its removal using WS has been reported in several investigations. For example, an attempt to remove Cr^{6+} from an aqueous solution using ACs derived from WS biomass through alkali impregnation with NaOH.[80] The authors impregnated WS with NaOH, and different ACs were created by varying the impregnation ratio of char: NaOH to 1 : 1 (AC1), 1 : 3 (AC2), and 1 : 5 (AC3). The adsorption of Cr^{6+} onto the ACs fit well with the Langmuir isotherm model, and the data followed the pseudo-second-order kinetic model. Film diffusion and intraparticle diffusion were the main mechanisms of the adsorption reaction. The ACs with the highest impregnation ratio (AC3) had better adsorption characteristics compared to AC2 and AC1. Ghasemi *et al.*[79] synthesized highly effective ACs from WS through a two-step CA process and thermal pyrolysis using $ZnCl_2$ to facilitate Cr^{6+} and Fe^{2+} removal from an aqueous solution and studied their single and binary solute adsorption. It was demonstrated that the developed ACs had a porous structure with excellent textural characteristics such as high BET surface area (1223 m^2 g^{-1}) and high total pore volume (0.85 cm^3 g^{-1}). The results of adsorption experiments showed that at both pH levels of 4.5 and 2, the maximum removals were 96.2 and 99% at 40 °C for Fe^{2+} and Cr^{6+} ions, respectively. Conclusively, it was claimed that under similar conditions, the developed WSACs showed better adsorption performance than other ACs.

Other studies reported Cr^{6+} adsorption in water using WS modified by H_3PO_4.[81] Cr^{6+} ion biosorption from aqueous solution was also investigated in batch experiments with the use of shells from walnut, hazelnut, and almond shell.[75] In this study, kinetic experiments showed that the dilute Cr^{6+} solutions attained equilibrium in 100 min. The biosorption potential of all the investigated shells was dependent on the pH which was optimized at 3.5. The adsorption data suited the Langmuir isotherm model well. The maximum sorption capacity conformed to the Langmuir isotherm and was reported to be 8.01 mg g^{-1} for WS. At a concentration of 0.5 mM, removal percentage by WS was obtained to be 85.32%. The same research group,[52] used MWS as an adsorbent to remove Cr^{6+} ions from aqueous solution after treatment with citric acid in batch experiments. The rate of adsorption was studied under various conditions, including different amounts of adsorbent (0.02–0.20 g), pH (2–9), contact times (10–240 min), temperatures and initial Cr^{6+} concentrations (0.1–1.0 mM). In all cases, Cr^{6+} adsorption was pH-dependent and for the citric acid modified walnut shell (CAMWS), a maximum equilibrium was obtained at pH values between 2 and 3. Under experimental conditions, the highest adsorption capabilities of CAMWS and untreated WS for Cr^{6+} ions were 596 and 154 mg g^{-1}, respectively. The column studies performed under different operating conditions showed that WS is an efficient and cost-effective adsorbent for Cr^{6+} removal and can be a solution for industries that discharge Cr^{6+}. In this study, better adsorption results were obtained with low influent flow rate, a low influent Cr^{6+} concentration, and a high bed depth. The Cr^{6+} adsorption equilibrium (Langmuir isotherm constant = 0.6754 l mg^{-1}) fit well with the Langmuir isotherm model.[105] According to the q_m values reported in the literature (Table 2), WS and in particular MWS have high potential to be used as an effective biosorbent for Cr^{6+} ion elimination. Additionally, of all the examined HMs, WS has the highest adsorption capacity for Cr^{6+} (in the range of 1–596 mg g^{-1}).

7.1.6. Arsenic ions removal. As^{3+} is an HM that is considered a toxic pollutant because of the hazard it poses to both human health and the environment. One of the most popular methods for As^{3+} removal from an aqueous solution is the adsorption process. For example, Jafari-Mansoorian *et al.*,[82] evaluated As^{3+} adsorption from aqueous solutions using ACs derived from WS. According to the Langmuir model, a q_m of 3.15 mg g^{-1} was achieved using the WSACs. Additionally, the q_m of the provided WSACs was reported to be 2.05 mg g^{-1} by the Freundlich model. The results of this work showed that an increase in the adsorbent dosage and a reduction in the pH improved As^{3+} adsorption. Adsorption decreased with increasing pH and initial As^{3+} concentration. In another study, Saqib *et al.*[83] studied As^{3+} bioremediation from aqueous solutions by low-cost materials derived from blue pine wood shavings (*Pinus wallichiana*), WS, and chickpea testa. It has been shown that blue pine wood shavings have great potential as a remediation substance for the removal of As^{3+}. Considerable biosorption capacity (88%) was also achieved for WS. However, the biosorption capacity of chickpea testa was not sufficient. As^{3+} biosorption in this study fit well to both the Langmuir and Freundlich isotherms. In total, the results of the adsorption studies summarized in Table 2 indicate tha WS could only adsorb low amounts of As^{3+} ions from contaminated aqueous solutions (0.2–3.42 mg g^{-1}).

7.1.7. Caesium ion removal. Due to its relatively long half-life and varied sources, Cs^+ an abundant element that is thought to be very dangerous. Because of its similar chemical properties to potassium ion (K^+), it can easily be taken up by aquatic and terrestrial organisms.[106] Thus, its separation and elimination from waste solutions is necessary. Ding *et al.*,[54] conducted equilibrium, kinetic, and thermodynamic modelling studies of Cs^+ adsorption from aqueous solution using WS. They incorporated nickel hexacyanoferrate (NiHCF) into the prepared biosorbent, which served as a high selectivity trapping agent for Cs^+. It was indicated that the adsorption of Cs^+ by NiHCF-WS is an endothermic and spontaneous process. In another investigation by the same research group,[92] the prepared novel NiHCF functionalized-WS was developed to enable the selective removal of Cs^+ ions from aqueous solution. Their results showed that the removal of Cs^+ was fast and reached equilibrium in 2 h. Acidic conditions were favoured for Cs^+ removal because of the unique features of NiHCF-WS. Additionally, the fabricated NiHCF-WS could selectively eliminate Cs^+ in the presence of other ions (Na^+ and K^+). Using NiHCF-WS, it was demonstrated that approximately 99.8% of the liquid waste was reduced. Based on the q_m values (see Table 2 for more details) extracted from the Cs^+ ion adsorption studies, the WS adsorption capacity of Cs^+ ions is not significant (6–14.6 mg g^{-1}), thus, additional treatment procedures should be tested to enhanced its adsorption capacity.

7.1.8. Mercury ion removal. Hg^{2+} is one of the key pollutants on the United States Environmental Protection Agency (US EPA) pollutants list, as it can easily pass the blood–brain barrier and influence the brains of foetuses. High Hg^{2+} concentrations trigger lung and kidney function impairment, chest pain and dyspnoea. The reasonable Hg^{2+} discharge thresholds for inland and drinking water are 10 and 1 μg l^{-1}, respectively. While the discharge of Hg^{2+} into aquatic systems has decreased in recent years, there is still a shortage of efficient, inexpensive means to treat wastewater that contains Hg^{2+}.[107] In pursuit of producing a more economical and effective carbonaceous sorbent to enable the control of Hg^{2+} ions from industrial liquid streams, Zabihi *et al.*[93] evaluated the adsorption ability of a powdered carbonaceous sorbent derived from the Iranian WS and prepared by CA method using $ZnCl_2$ as an activating reagent. This adsorbent had not been previously used to remove Hg^{2+} from water to the best of the authors' knowledge. Hg^{2+} adsorption from aqueous solution was performed under various experimental conditions such as different treatment, times, concentrations of metal ions, adsorbent quantities, pH values and solution temperatures. Hg^{2+} uptake was shown to decrease with increasing solution pH. The selection of the proper procedure resulted in the preparation of a microporous AC with 0.45 g cm^{-3} density, 737 mg g^{-1} iodine number, and 780 m^2 g^{-1} BET surface area. The optimum monolayer sorption capability of the adsorbent was 151.5 mg g^{-1}. The same research group,[57] studied the adsorption of Hg^{2+} ions from industrial liquid streams on ACs prepared from WS. In this study, carbonaceous sorbents derived from the local WS were also prepared by the CA process with $ZnCl_2$. Microporous ACs with distinct BET values of 780 (ACs A, 1 : 0.5 $ZnCl_2$) and 803 (ACs B, 1 : 1 $ZnCl_2$) m^2 g^{-1} were the result of an appropriate selection of preparation processes. For ACs A and B, the monolayer adsorption capacities of the adsorbents were 151.5 and 100.9 mg g^{-1}, respectively. Based on the corresponding q_m values shown in Table 2, it can be concluded, that compared the adsorption potential of WS for other HMs such as Cr^{2+} and Pb^{2+}, the adsorption potential of WS of the removal of Hg metal ions is moderate (151 mg g^{-1}).

7.1.9. Lead ion removal. Pb^{2+}, a well-known prestigious HM, poses a significant danger to organisms and the environment; in the recent years, Pb^{2+} removal has attracted increasing attention. The release of large amounts of Pb^{2+}' into terrestrial and aquatic ecosystems has raised public concern. Because of its toxicity, accumulation in food chains and persistence in nature, Pb^{2+} can threaten human lives. It is a strong metabolic poison and enzyme inhibitor and can accumulate in the brain, bones, muscles, and kidneys. The WHO recommends that the highest tolerable concentration of Pb^{2+} in drinking water is 0.1–0.05 mg l^{-1}.[108] Thus, as a toxic and hazardous metal ion, its removal by WS *via* adsorption has been comprehensively studied. Using single-walled carbon nanotubes (SWCNTs) Saadat *et al.*,[89] synthesized a novel SWCNT-doped walnut shell composite (SWCNTs/WSC), and characterized its ability to adsorb Pb^{2+} from aqueous solution. First, they determined the Pb^{2+} removal capacity of different synthesized carbon nanostructures, including SWCNTs, multiwalled carbon nanotubes (MWCNTs), SWCNTs doped with iron (SWCNTs/Fe), and carbon nanofibres (CNFs). The SWCNTs had highest sorption capability for Pb^{2+} ions. Further, the authors prepared a novel adsorbent, SWCNTs/WSC, with 99% through the immobilization of SWCNT particles on the WS surface. The developed adsorbent was tested for its potential to remove Pb^{2+} ions from aqueous solution. The prepared SWCNTs/WSC showed effective removal of Pb^{2+} ions from aqueous solution. The adsorption followed the equation of the Langmuir isotherm well, with an expected maximum uptake of 185.2 mg g^{-1}. The removal of Pb^{2+} by adsorption onto Chinese WSACs was also explored,[87] and the results showed that they might be successfully applied to remove Pb^{2+} from wastewater. By varying the contact time, temperature, pH, adsorbent dose and initial concentration of Pb^{2+}, the authors performed batch experiments, and the adsorption equilibrium was obtained within 150 min. Although the effect of temperature was not notable, the adsorption of Pb^{2+} was mostly pH-dependent, and the greatest elimination was obtained at pH 5.5. The efficiency of Pb^{2+} removal was improved by increasing the dosage of ACs to 2.0 g l^{-1} which produced a maximum removal potential of 94.12%. The findings proposed that the Langmuir isotherm model with a q_m of 81.96 mg g^{-1} described the equilibrium conditions well. The results showed that the adsorption kinetic data were described well by the pseudo-first-order model. Saadat and Karimi-Jashni[90] used a factorial design and simplex methodologies to analyse the separation of Pb^{2+} ions and the optimized Pb^{2+} adsorption onto the MWS. They attempted to remove Pb^{2+} ions from aqueous solution using chemically modified WS in a batch system. The adsorbent dosage of 13.5 g l^{-1}, solution pH of 6.3, and initial metal concentration of 45.3 mg l^{-1}, with an efficiency of 98.2% were recommended as the optimum conditions for Pb^{2+} removal. A comparative study of Pb^{2+} sorption from aqueous solution onto WS and plum stones was also performed, and the maximum sorption capacity obtained for WS was 23.1 mg g^{-1}. The Pb^{2+} depletion percentage in the solution was reported to be in the range of 62.9–83.7.[91] The adsorption equilibrium and the kinetics of Pb^{2+} removal from aqueous solution by MWS with acrylic acid were also investigated in the temperature range of 15–35 °C.[60] MWS samples with distinct graft yields (3.65, 10.45, 18.49, and 19.66 wt%) were prepared by reactions with acrylic acid and WS. The effects of the adsorbent dose, graft yield, contact time, temperature, and pH on the adsorption of Pb^{2+} were analysed. Both WS and MWS-4 (19.66 wt%) were characterized, and the Langmuir isotherm model interpreted the isotherm adsorption data better. The maximum adsorption capacity obtained for Pb^{2+} was 210.14 mg g^{-1} at 35 °C.

In very recent the work, a novel carboxylate-functionalized walnut shell (CFWS) has been prepared with malonate through the esterification of WS.[109] The characterization of CFWS characterization by various methods suggested the introduction of –COOH groups on the WS surface. The efficiency of the modified adsorbent at removing Pb^{2+} ions from aqueous solutions. The investigation data showed that the Langmuir isotherm could thoroughly describe the equilibrium data, and the best adsorption ability for Pb^{2+} ions was determined to be 192.3 mg g^{-1} with 0.8 g l^{-1} of the adsorbent, pH 5.5, and a temperature of 25 °C. Under various experimental conditions, two methods, namely multiple linear regression (MLR) and an artificial neural network (ANN), were adopted to build a practical model for the prediction of the removal of Pb^{2+} ions. A comparison between the created models demonstrated that the ANN model could more correctly predict the percentage of Pb^{2+} ions removal. Therefore, an automated wastewater remediation plan could be designed using this ANN model. It should also be noted that the CFWS was obtained from aqueous solution using EDTA-2Na and used to remove Pb^{2+} ions. Additionally, in a newly published study, an amino-modified walnut shell (AMWS) was developed as an environmentally friendly, green, easy-to-use and sustainable HM trapping agent and its adsorption of Pb^{2+} ions in aqueous solution was studied.[110] The adsorption ability of AMWS for Pb^{2+} was examined in pH 2–9 and various doses of adsorbents (0.5–2.0 g l^{-1}). The results showed that at pH 7, the q_m of AMWS on Pb^{2+} ions was reasonable. The highest predicted adsorption capacity of Pb^{2+} ions was achieved with the Langmuir fitting model at 25 °C (56.81 mg g^{-1}). The pseudo-second-order equation represented the adsorption kinetics well. Thermodynamic investigations confirmed that the adsorption process of AMWS for Pb^{2+} ions was endothermic and spontaneous. In addition, the results showed that AMWS possessed remarkable recovery capacity. In Lu and Guo,[111] a low-cost biosorbent for the removal of Pb^{2+} in aqueous solution was synthesized by grafting sulfur-functionalized WS (SFWS) using xanthate. The synthesized adsorbent was characterized by XPS, Fourier-transform infrared spectroscopy (FT-IR), BET and SEM. This study showed that the adsorption efficiency of SFWS was significantly higher than that of unmodified WS due to ion exchange and complexation by the sulfur-containing functional groups. The adsorption process was exothermic and spontaneous. Additionally, it was found that the Pb^{2+} adsorption on SFWS followed the Temkin isotherm model which had a high correlation with pseudo-second-order kinetics. Ashrafi, *et al.*[112] investigated WS modification using a solvent-free reaction in which WS was blended with malonic acid cyclic isopropylidene ester, forming carboxylic acid-functionalized WS. The ability of the modified adsorbent simultaneously eliminate Pb^{2+} and methylene blue (MB) was considered. A high removal percentage, 97.14%, was obtained under the optimum experimental conditions. The FT-IR spectra showed that electrostatic interactions were the main forces driving Pb^{2+} adsorption.

In another technique, carbon microspheres are produced under N_2 flux from WS and then applied as an adsorbent for the elimination of Pb^{2+}, Cu^{2+}, Cr^{3+} and Cd^{2+} ions.[113] The prepared material was characterized using XPS, SEM, BET, FT-IR and Raman spectroscopy. SEM images revealed an average diameter of 4.55 μm in a uniform sphere-like structure. The removal of hazardous HMs from the synthetic aqueous samples by the prepared carbon microspheres was reported to be selective and rapid. The carbon microspheres in this work were reported to have the highest adsorption capacities ever observed for Cr^{3+}, Pb^{2+}, Cd^{2+} and Cu^{2+} at an optimal pH 5, with adsorption capacities of 792, 638, 574 and 345 mg g^{-1}, respectively. Good agreement with the results of adsorption studies was reported using density functional theory predictions, in which Cr^{3+} had the highest binding affinity to the –OH and –COOH functional groups followed by those of Cu^{2+}, Pb^{2+}, and Cd^{2+}. The results reported for Pb^{2+} ion removal indicated that WS could be used use as an inexpensive adsorbent for Pb^{2+}. Based on the q_m values in Table 2, more than 300 mg g^{-1} of Pb^{2+} could be removed using WS. In addition, the highest amounts of adsorption were achieved (>600 mg g^{-1}) ACs in the form of carbon microsphere was used. Such an approach may be applicable for increasing the adsorption capacity of WS for ther HMs.

7.1.10. Cadmium ion removal. It has been well documented that Cd^{2+} has adverse impact on the atmosphere and poses a serious threat to human health through accumulation in the food chain. Cd^{2+} is a toxic, carcinogenic, element that tends to accumulate in the body. Of the total Cd^{2+} discharged from different companies, 50% of the Cd^{2+} is released by electroplating facilities.[114] The biosorption of Cd^{2+} metal ions on raw and chemically MWS has been reported.[84] In this work, WS was treated with 0.1 N aqueous NaOH at 558 °C for 2 h to enhance its adsorptive capacity for Cd^{2+} ions. Using FT-IR and SEM analysis, the raw WS and alkali-treated WS were characterized by their morphological features and functional groups. Between pH 2 and 6, the adsorption increased drastically and the Langmuir isotherm model presented a better fit for the experimental data than the Freundlich isotherms, as determined by the providing high correlation coefficients. The biosorption capacity of raw WS and treated WS for Cd^{2+} ions was determined to be 4.20 and 14.29 mg g^{-1}, respectively. The adsorption conformed to pseudo-second-order kinetics, suggesting a chemisorption process and monolayer coverage. There was no observable reduction in the desorption performance until the third cycle of the treatment.

The use of different biochars to eliminate HMs from aqueous solution has progressed in recent years. Biochar is also known as an effective soil amendment for Cd^{2+} remediation. It is recommended that WSB be applied as a Cd^{2+} sorbent for soil remediation. Biochar prepared using WS was incubated in $Cd(NO_3)_2$ and kaolin for 15 days. The authors found that WSB could diminish the mobility of Cd^{2+}. The biochar R_{50} value increased from 61.31 to 69.57–72.24% after incubation, indicating an increase in biochar stability. Their results explained that the improved biochar stability was possibly due to mechanical separation and the development of complexes and precipitates, created on the biochar surface or its inside.[115]

The application of nanomaterials to biochar surface may improve their ability to eliminate metal ions elimination. Accordingly, the effectiveness of WSB alone in combination with nanoscale zero-valent iron (WSB-nZVI) in Cd^{2+} removal in aqueous solution was examined. The results of this study revealed that in aqueous solution, WSB-nZVI provided a notable advantage to the performance of WSB for Cd^{2+} removal. The presence of functional groups on the WSB surface *via* adsorption and precipitation processes, as well as the nZVI developed on the WSB-nZVI from complexation and adsorption processes, resulted in an improved Cd^{2+} removal capacity compared to that of the raw WSB adsorbent. The predicted q_m for the Cd^{2+} removal based on the recommended model was 99.72%, with initial Cd^{2+} concentration of 70.78 mg l^{-1}, pH 6.92, adsorbent dose of 0.56 g l^{-1} and contact time of 40.42 min.[86] A study of the kinetic and equilibrium of Pb^{2+} and Cd^{2+} removal from aqueous solution using processed WS was also undertaken by Almasi *et al.*[85] In this study, the structural characterization by FT-IR spectroscopy of the adsorbent prepared from WS confirmed that –OH, –COOH, and –C=O groups were involved in Pb^{2+} and Cd^{2+} ions sorption. The highest adsorption was obtained within the pH range of 4–6. The Langmuir isotherm model was well adapted to the equilibrium kinetics. The highest monolayer adsorption potentials were determined to be 32 g kg^{-1} and 11.6 g kg^{-1} for Pb^{2+} and Cd^{2+} ions, respectively. The adsorption isotherms of the various HM ions removed by the WS were well fitted by the Langmuir and Freundlich models, and the kinetic data for the adsorption of the investigated HM by WS followed pseudo-second-order kinetic models. Furthermore, the sorption process was mostly spontaneous due to the negative values reported for ΔG. Additionally, in most studies, the reaction was enthalpy driven and endothermic. Thus, WS and its derivatives are suitable materials for use in the development of adsorption processes to eliminate HMs from industrial wastewater. Unprocessed WS an MWS presented high adsorption capacities for Cr^{6+}, Pb^{2+} and Cu^{2+} ion removal (more than 200 mg g^{-1}). The elimination Hg^{2+}, Cd^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+} by WS and MWS is reported to be moderate (<200 mg g^{-1}), and WS can only adsorb low levels of Cs^{+} and As^{3+} ions.

As shown in Table 1, considerable increases in the elimination of HM ions using WS were observed upon increasing the solution pH to 7, after which a reduction was observed. Accordingly, the highest HM removal values were achieved at pH values between 4 and 7. The reduced metal removal obtained at low pH values can be attributed to the mobility of H^{+} ions and their higher concentration; H^{+} ions have a higher adsorption affinity than HM ions. The lower H^{+} at higher pH values with a negatively charged adsorbent surface results in a greater attraction of metal cations. Nonetheless, a decrease in adsorption was observed under alkaline conditions, which may be due to the formation of several HM specific hydroxides that are precipitated and contribute to a decrease in the free metal ions in solution. In addition, more oxygen-containing groups on the adsorbent surface are ionized and adsorb more water at higher pH values. The development of water clusters on adsorbents blocks access to adsorption for of metal ions and results in a low adsorption capacity.

7.2. Dye removal

Colorants and pigments are essential in the textile industry and approximately 10 000 colorants are used in the textile industry, as well as in industrial chemistry.[116] More than seven million tons of dye are generated worldwide each year and dyes are commonly used in various industries, including the paper, plastics, leather, pharmaceuticals, food, cosmetics, paint manufacturing and textile industries.[117] Discharging up to 10% of these colorants during their manufacturing ad consumption can generate numerous issues for water supplies. They may influence of food and water, as well as trigger allergic dermatitis and skin sensitivities. In addition, these dyes can be toxic and dangerous and cause mutation in aquatic. Dyes can be cationic (basic), anionic (direct, acid, and reactive) or nonionic (dispersive). For the industry and the environment, the treatment of these pigmented wastewaters is a primary issue.[118] Dye removal with the use of agricultural wastes and forestry residues has recently attracted considerable attention due to their abundance and low price of these by-products.[4] WS is used for the removal of different dyes such as reactive brilliant red K-2BP (RBR K-2BP), C. I. Acid Red 97 (AR97), maxilon red (MR GRL), crystal violet (CV), methylene blue (MEB), rhodamine B (RB), reactive red 2 (RR2), malachite green (MG), methyl bromide (MB), and brilliant green (BG). The chemical structures of some basic dyes are shown in Fig. 2.

The obtained optimal operational conditions, including pH, adsorbent dosage, temperature, agitation speed, and contact time for the maximum efficiency (%) of the adsorption process are shown in Table 3. Additionally, Table 4 tabulates the values of q_m obtained in the optimum experimental conditions, and the fitting and kinetic models, as well as the thermodynamics of the reaction for the different dyes removed by WS. In an investigation conducted by Ghazi Mokri *et al.*,[119] the authors considered the kinetics, thermodynamic parameters, and isotherms of AR97 dye adsorption from an aqueous solution onto WS and recommended that WS could be used in the removal of AR97 dye. In this study, the effect of the operational parameters, including the adsorbent dosage, agitation speed, contact time, pH and temperature, were analysed in a batch method. The results showed that 73.33% of AR97 (50 mg $\mathrm{l^{-1}}$) was decolorized with 12 g $\mathrm{l^{-1}}$ of adsorbent at 60 min of contact time, and an agitation rate of 140 rpm at 18 °C. The adsorption rate followed pseudo-second-order kinetics. The SSA of WS was calculated to be 1.28 $\mathrm{m^2\ g^{-1}}$ by the BET technique. The thermodynamic values indicated that the nature of the adsorption process was spontaneous, exothermic and principally physical. The equilibrium data were in good agreement with the Freundlich isotherm model.

Accordingly, the preparation of a new, low-cost and easy-to-use regeneration adsorbent by chemically MWS and an investigation of the kinetics and thermodynamics of the removal of anionic dye RBR K-2BP by this adsorbent was reported by Cao *et al.*[120] In this study, epichlorohydrin and diethylenetriamine as an etherifying agent and crosslinking agent, respectively, were used in the synthesis of chemically MWS, and they were characterized by FT-IR, SEM, electron dispersive spectroscopy and thermogravimetric (TG) analysis. They evaluated the effects of adsorbent dosage (0.1–6 g $\mathrm{l^{-1}}$) and pH (0.5–11) on the adsorption capacity of chemically MWS. The highest adsorption capacity for RBR K-2BP was calculated to be 568.18 mg $\mathrm{g^{-1}}$ at 40 °C, which was nearly 10 times the adsorption capacity of the raw material, with Langmuir isotherm as the best-fitting model. The kinetics of adsorption were also well fitted with pseudo-second-order kinetics. According to thermodynamic characterization, the adsorption mechanism was spontaneous and endothermic. In addition, the chemically MWS was inexpensive, showed excellent recovery capacity and was promising for RBR K-2BP removal. The treatment of wastewater-contaminated CV using WS suggested that it is an effective adsorbent for the removal of this dye, and it is also inexpensive.[123] Moreover, the removal of BG and CV from mono- and bi-component aqueous solutions using NaOH-modified WS has been studied.[124]

The possibility of using WS as a biosorbent for the removal of MR GRL dye from aqueous media was evaluated by Deniz *et al.*[122] The authors determined the nonlinear kinetic and equilibrium models and then concluded that WS might offer an efficient and cost-effective technology for MR GRL removal from aqueous solution. In turn, to remove MEB as a cationic dye, ACs were prepared from the WS *via* the vacuum CA process.[125] In another study, the efficiency of WS powder as a low-cost adsorbent for MB removal from aqueous solution was investigated in batch-scale experiments.[126] The authors showed that MB can be removed from dye-bearing effluent in an ecofriendly way using WS powder. Kinetic, equilibrium, and thermodynamic studies were conducted on the removal of RB from aqueous solution and wastewater by WS.[127] It was shown that WS, as a natural adsorbent, could be used for the removal of RR2 from aqueous solution.[128] Equilibrium, kinetic, thermodynamic, and regeneration studies were also carried out to investigate water remediation with the use of WS as a low-cost adsorbent of MG.[129] Hall *et al.*[130] considered the end-products of tree nut and tree fruit production from walnut and almond shells as well as peach and prune pits that were grown in California, US for the preparation of ACs and used them as sorbents to remove MB in ventilation effluent from postharvest fumigation chamber. AC sorbents were prepared using different methods of pyrolysis, activation, and quenching.

By employing a solvent-free reaction, Ashrafi, *et al.*[112] examined the modification of WS and obtained –COOH–functionalized WS. This material was mixed with malonic acid cyclic isopropylidene ester. The modified adsorbent efficiency for the simultaneous removal of $\mathrm{Pb^{2+}}$ and MEB was investigated. A high removal percentage, 92.61%, was obtained for MEB under the optimum experimental conditions. The FT-IR spectra revealed that π–π interactions and hydrogen bonding (H-bonding) were the main driving forces of MB adsorption on the developed adsorbent. It can be deduced from the available literature that the adsorption isotherm of various dyes removed by the WS was well fitted by the Langmuir and Freundlich models, and the kinetic data for the adsorption generally followed the pseudo-second-order kinetic model. The reaction was enthalpy driven, and it was endothermic. Furthermore, the sorption process of different dyes eliminated by WS was mostly spontaneous and favourable due to the negative values obtained for ΔG. Thus, WS can be considered in the adsorption processes for the removal of different industrial dyes. Additionally, the data presented in Table 4 show that high amounts of dyes (more than 500 mg $\mathrm{g^{-1}}$ of RBR K-2BP, CV and >300 mg $\mathrm{g^{-1}}$ of MEB) can be removed by the WS. Furthermore, the adsorption capacity of WS for other dyes, including DAEA, MEB (>150 mg $\mathrm{g^{-1}}$) and MR GRL, MG and BG is moderate. For dyes RB and RR2, the obtained q_m values are below 5 mg $\mathrm{g^{-1}}$. For various dyes removed by WS, the optimum pH values were reported at neutral or alkaline conditions, which could be attributed to the increase in the negative charge on the surface of the adsorbent with increasing pH and the H^+ ion reduction competing with the dye cations for the same positions on the biosorbent. For the anionic dyes removed by WS, the acidic pH supported the adsorption of the negatively-charged dye on the WS when the surface change of the WS was positive.

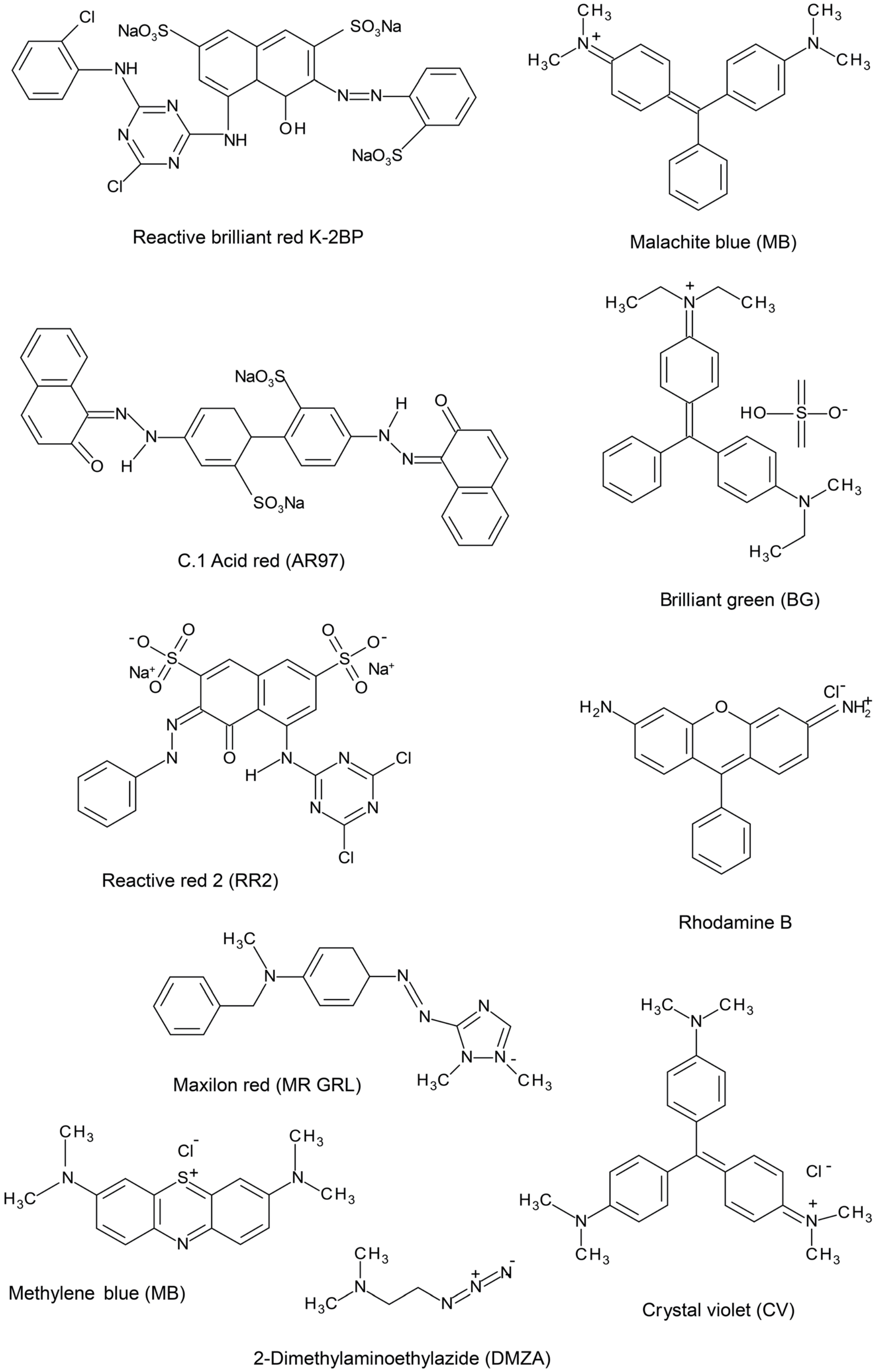

Fig. 2 The chemical structures of several dyes removed by WS: RBR K-2BP, AR97, DAEA, MR GRL, CV, MEB, RB, RR2, MG, MB, and BG.

Table 3 The optimal conditions for the removal of different dyes by WS[a]

No	Dye	pH	Adsorbent dosage	Temp.(°C)	Agitation speed (rpm)	Contact time (min)	Efficiency (%)	Ref.
1	RBR K-2BP	0.5–11	0.1–6 g l^{-1b}	40	180	—	—	Cao, *et al.*[120]
2	AR97	—	12 g l^{-1c}	18	140	60	73.33	Ghazi Mokri, *et al.*[119]
3	DAEA	10	0.29 g^{b}	—	100	—	85.95	Ghanbari Pakdehi and Rezaei[121]
4	MR GRL	8	5 g l^{-1c}	45	—	50	72.95	Deniz[122]
5	CV	6	0.2 g l^{-1c}	45	150	360	83.7	Song, *et al.*[123]
		7	0.8 g l^{-1b}	Room temp.	200	13	—	Ashrafi, *et al.*[124]
6	MEB	7	0.75 g l^{-1b}	25	270	1440	—	Yang and Qiu[125]
		6.8	0.5 g l^{-1c}	20	4000	15	—	Miyah, *et al.*[126]
7	RB	3	0.05 g^{c}	—	—	30	100	Shah, *et al.*[127]
8	RR2	6.7	0.5 g^{c}	25 ± 3	—	—	—	Almasi, *et al.*[128]
9	MG	5	0.03 g/0.02 l^{c}	Room temp.	250	120	87	Dahri, *et al.*[129]
10	MB	—	—	—	—	—	—	Hall, *et al.*[130]
11	BG	7	0.8 g l^{-1b}	25 ± 2	200	13	—	Ashrafi, *et al.*[124]

[a] — not reported. [b] Modified WS. [c] Ordinary WS.

Table 4 The adsorption capacity, thermodynamic, and fitting and kinetic models for the removal of various dyes by the WS[a]

No	Dye	q_m[b]	Fitting model	Kinetic model	Thermodynamic	Ref.
1	RBR K-2BP	568.18 mg g^{-1c}	Langmuir	Pseudo-second order	Spontaneous, endothermic	Cao, *et al.*[120]
2	AR97	—	Freundlich	Pseudo-second order	Spontaneous, exothermic	Ghazi Mokri, *et al.*[119]
3	DAEA	166.67 mg g^{-1c}	Freundlich	Pseudo-second order	Spontaneous, endothermic	Ghanbari Pakdehi and Rezaei[121]
4	MR GRL	58.21 mg g^{-1d}	Hill	Logistic	Endothermic	Deniz[122]
5	CV	714.3 mg g^{-1d}	Langmuir–Freundlich	Pseudo-second order	Spontaneous, endothermic	Song, *et al.*[123]
		96.01–123.2 mg g^{-1c}	Langmuir	Pseudo-second order	—	Ashrafi, *et al.*[124]
6	MEB	315 mg g^{-1c}	Redlich–Peterson Langmuir–Freundlich	—	—	Yang and Qiu[125]
		178.9 mg g^{-1d}	Langmuir	Pseudo-second order	Spontaneous, exothermic	Miyah, *et al.*[126]
7	RB	2.292 mg g^{-1d}	Langmuir	Pseudo-second order	Spontaneous, endothermic	Shah, *et al.*[127]
8	RR2	1 mg l^{-1d}	Langmuir	—	—	Almasi, *et al.*[128]
9	MG	90.8 mg g^{-1d}	Langmuir	Pseudo-second order	Spontaneous, endothermic	Dahri, *et al.*[129]
10	MB	—	—	—	—	Hall, *et al.*[130]
11	BG	79.07–146.40 mg g^{-1c}	Langmuir	Pseudo-second order	—	

[a] — not reported. [b] Maximum adsorption capacity. [c] Modified WS. [d] Ordinary WS.

7.3. Oil separation

At various stages of production, transportation, refining, and use, oils can cause environmental pollution. Cutting liquids, fats, lubricants, heavy hydrocarbons such as tars, grease, crude oils (COs), diesel oil, and light hydrocarbons such as kerosene, jet fuel, and gasoline are the main oils found in contaminated waters.[1] Petroleum refineries, metal manufacturing and machining, and food processors are the primary industrial sources of oily waste. Kitchen and human wastes are the main sources of oil in municipal wastewater.[131] The capability of WS, as a low-cost and effective biosorbent, to remove different oils has also been studied. Standard mineral oil (SMO), vegetable oils (VOs), DoALL bright-edge 80 (DBE80), COs, refinery wastewater (RWW), and sunflower oils (SOs) were the main oils tested for removal by WS. Table 5 summarizes the values obtained under the optimal operational conditions, including the pH, adsorbent dosage, temperature, agitation speed, and contact time for maximum removal efficiency (%). Furthermore, to facilitate for better comparison, the q_m or biofiltration capacity values along with the fitting and kinetic models, and the thermodynamics of the adsorption process for the separated oils using WS are summarized in Table 6. Batch kinetic studies were conducted by Srinivasan and Viraraghavan[51] to evaluate the oil sorption capacities of WS media in pure oil and oil in an aqueous medium. They investigated SMO, VOs, and DBE80, found that the separated oil could be recovered from the WS media by applying pressure and showed that WS media was a suitable sorbent for oil removal. In 2010, the same authors[132] conducted another batch study to evaluate the efficiencies of four biomaterials, *i.e.*, fungal biomasses of *Mucor rouxii* and *Absidia coerulea* as well as CS and WS media, to remove the SMO, VOs and cutting oil from water. They demonstrated that *M. rouxii* had a better oil adsorption capacity than *A. coerulea* biomass, but the capacity of *M. rouxii* was still lower than those of CS and WS media. To compare the effectiveness of WS and polymeric resins at removing oil from water, two cross-linked polymeric resins based on glycidyl methacrylate-divinylbenzene

Table 5 The optimal conditions for the removal of different oils, drugs and other materials by WS[a]

No	Materials			pH	Adsorbent dosage	Temp (°C)	Agitation speed (rpm)	Contact time (min)	Efficiency (%)	Ref.
1	Oils	SMO		7.5^{d}	3g^{c}	10^{e}	No agitation	15^{e}	—	Srinivasan and Viraraghavan[51]
						20^{f}		140^{f}		
				5	0.2 g^{c}	20	175	360	83	Srinivasan and Viraraghavan[132]
				7.6					38	
		VOs		7.5^{d}	3 g^{c}	10^{e}	No agitation	15^{e}	—	Srinivasan and Viraraghavan[51]
						20^{f}		90^{f}		
				5	0.2 g^{c}	20	175	360	96	Srinivasan and Viraraghavan[132]
				7.6					60	
		DBE80		7.5^{d}	3g^{c}	10^{e}	No agitation	15^{e}	—	Srinivasan and Viraraghavan[51]
						20^{f}		90^{f}		
				5	0.2 g^{c}	20	175	360	96	Srinivasan and Viraraghavan[132]
				7.6					73	
		COs		—	—	—	—	—	~94.2	Aversa, *et al.*[133]
		RWW		—	4 g^{c}	25 ± 2	Shaking	2880	75	Ziad Ismail[134]
		SOs		—	4 g^{c}	25 ± 2	Shaking	2880	96	Ziad Ismail[134]
2	CFX			6.5	0.03 g^{b}	30	200	1200	100	Nazari, *et al.*[135]
				—	—	30	—	—	—	Nazari, *et al.*[136]
				6.5	0.03 g^{b}	30	200	—	—	Nazari, *et al.*[137]
				6.5	0.6 g l^{-1b}	30	Fixed-bed column	—	—	Nazari, *et al.*[138]
3	EA			6.3–7.2	—	30	Packed bio-filter	44 days	>80	Zare, *et al.*[139]
4	Naphthalene			7	1.0 g l^{-1b}	25	200	2400	—	Zhu, *et al.*[140]
5	NOMs			3	0.03 g l^{-1b}	—	180	5	—	Naghizadeh, *et al.*[141]
6	Methanol			—	—	30	—	120	—	Yu, *et al.*[142]
7	Benzene			12	0.3 g l^{-1b}	Ambient	190	60	—	Mataji and Khoshandam[143]
8	PH_3			—	—	—	—	—	—	Yu, *et al.*[142]
9	NO_3^-			6.5	200 g^{b}	25	—	2	80	Alighardashi and Shahali[144]
				2	1 g^{b}	20	Shaking	15	41.7	Taghizadeh and Vahdati[145]
10	NH_3–N			6.8	15 g l^{-1b}	32	160	390	~60	Ding, *et al.*[146]
11	SO_2			—	—	90	Fixed-bed	—	—	Guo, *et al.*[147]
12	MCPs		2-CP	2–4	1 g/0.04 l^{c}	—	—	240	~75	Kuśmierek and Świątkowski[148]
			3-CP	2–4	1 g/0.04 l^{c}	—	—	240	~75	Kuśmierek and Świątkowski[148]
			4-CP	2–4	1 g/0.04 l^{c}	—	—	240	~75	Kuśmierek and Świątkowski[148]

[a] — not reported. [b] Modified WS. [c] Ordinary WS. [d] WS media. [e] Pure oil medium. [f] Oil in aqueous medium.

Table 6 The adsorption capacity, thermodynamic, fitting and kinetic models for the removal of different oils, drugs and other materials by WS[a]

No	Materials		q_m[b]	Fitting model	Kinetic model	Thermodynamic	Ref.
1	Oils	SMO	300 mg g^{-1}[e] 560 mg g^{-1}[f]	—	—	—	Srinivasan and Viraraghavan[51]
			~80 mg g^{-1}[g] ~40 mg g^{-1}[h]	—	—	—	Srinivasan and Viraraghavan[132]
		VOs	510 mg g^{-1}[e] 580 mg g^{-1}[f]	—	—	—	Srinivasan and Viraraghavan[51]
			~90 mg g^{-1}[g] ~60 mg g^{-1}[h]	—	—	—	Srinivasan and Viraraghavan[132]
		DBE80	580 mg g^{-1}[e] 740 mg g^{-1}[f]	—	—	—	Srinivasan and Viraraghavan[51]
			~90 mg g^{-1}[g] ~70 mg g^{-1}[h]	—	—	—	Srinivasan and Viraraghavan[132]
		COs	—	—	—	—	Aversa, *et al.*[133]
		RWW	~3 mg[d]	Langmuir	—	—	Ziad Ismail[134]
		SOs	~9 mg[d]	Langmuir	—	—	Ziad Ismail[134]
2	CFX		233.1 mg g^{-1}[c]	Freundlich, Toth	Pseudo-second order	Spontaneous, endothermic	Nazari, *et al.*[135]
			—	Freundlich	—	—	Nazari, *et al.*[136]
			233.10 mg g^{-1}[c]	Freundlich, Toth	—	—	Nazari, *et al.*[137]
			233.1 mg g^{-1}[c]	Freundlich	—	—	Nazari, *et al.*[138]
3	EA		—	Michaelis–Menten	Zero-order	—	Zare, *et al.*[139]
4	Naphthalene		7.21 mg g^{-1}[c]	Freundlich	Pseudo-second order	—	Zhu, *et al.*[140]
5	NOMs		37.93 mg g^{-1}[c]	—	—	—	Naghizadeh, *et al.*[141]
6	Methanol		248.02 mg g^{-1}[c]	—	—	—	Yu, *et al.*[142]
7	Benzene		61.22 mg g^{-1}[c]	Langmuir Freundlich	Pseudo-second order	—	Mataji and Khoshandam[143]
8	PH_3		284.12 mg g^{-1}[c]	—	—	—	Yu, *et al.*[142]
9	NO_3^-		10 mg g^{-1}[c]	Langmuir	—	—	Alighardashi and Shahali[144]
			—	Freundlich	—	—	Taghizadeh and Vahdati[145]
10	NH_3–N		9.79 mg g^{-1}[c]	Langmuir	Pseudo-second order	Spontaneous, endothermic	Ding, *et al.*[146]
11	SO_2		—	—	—	—	Guo, *et al.*[147]
12	MCPs	2-CP	—	Freundlich	Pseudo-second order	—	Kuśmierek and Świątkowski[148]
		3-CP	—	Freundlich	Pseudo-second order	—	Kuśmierek and Świątkowski[148]
		4-CP	—	Freundlich	Pseudo-second order	—	Kuśmierek and Świątkowski[148]

[a] — not reported. [b] Maximum adsorption or bio-filtration capacity. [c] Modified WS. [d] Ordinary WS. [e] Pure oil medium. [f] Oil in aqueous medium. [g] pH = 5. [h] pH = 7.6.

(GMA-DVB) and styrene-divinylbenzene (STY-DVB) were synthesized, characterized and evaluated. The authors assumed that unlike WS, polymeric resins did not lose weight during processes that require interruption. They showed that WS HAD high REMOVAL efficiency (~94%) but STY-DVB showed even better removal efficiency (~100%) and additionally presented better mechanical resistance. Moreover, it was suggested that polymeric resins, mainly those based on GMA, can be chemically modified to remove specific contaminants that remain in the water after conventional treatment.[133] The ability of pulverized WS to remove oil from aqueous solution has also been examined and demonstrated. The study involved a two-phase process in which the WS was used as a filtering bed for the accumulation and adsorption of oil onto its surface. The efficiency of oil removal from synthetic wastewater samples reached 96%, while the test results showed 75% efficiency of oil removal from the actual RWW discharged from the Al-Daura refinery in southern Baghdad.[134] The q_m values in the Table 4 show that, of the different oils that were tested with WS, SMO (>300 mg g^{-1}), VOs (>500 mg g^{-1}) and DBE80 (>500 mg g^{-1}) could be effectively removed. Additionally, the capacity of WS to remove the mentioned oils is higher in an aqueous medium than in pure oil medium.

7.4. Removal of pharmaceuticals

Municipal sewage and industrial wastewater are the primary effluents the release different pharmaceuticals into the environment. Drugs are known as extremely resistant chemicals and are not-biodegradable. They remain in the environment for a long time and are discharged continuously, especially antibiotics. Thus, the disposal and presence of pharmaceuticals in the environment has caused public concern over their long-term effects on human health and has highlighted the need for their removal from wastewater before discharging it into the environment.[2] Research on the removal of pharmaceuticals using WS is very scarce, and it is limited to the removal of cephalexin (CFX), the chemical structure of which is shown in Fig. 3. This drug is the most widely used cephalosporin antibiotic with an annual use of 3000 tons and annual sales revenue of $850 000 000 at the beginning of the 21st century. The operational considerations reported under the optimized conditions including

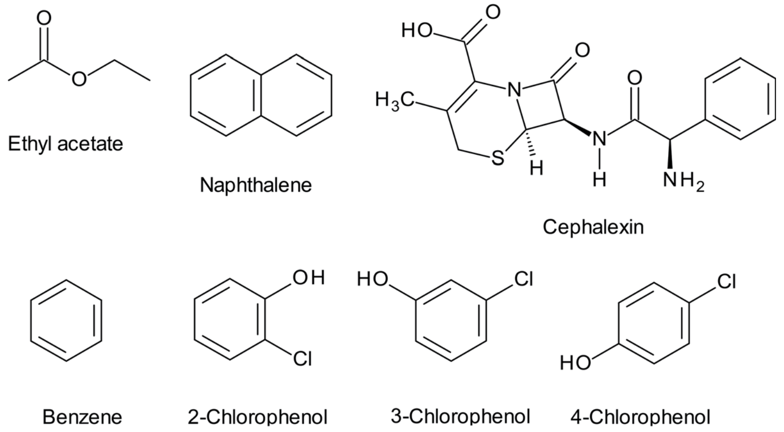

Fig. 3 The chemical structures of some hazardous materials removed by the WS including CFX, EA, naphthalene, benzene, and MCP derivatives (2-CP, 3-CP, and 4-CP).

the pH, adsorbent dosage, temperature, agitation speed, contact time, efficiency (%), q_m, fitting model, kinetic model, and thermodynamics for the CFX removal by WS, are summarized in Tables 5 and 6. Nazari *et al.*[135] prepared an adsorbent by the CA method using $ZnCl_2$ as the chemical activator agent. In this investigation, batch adsorption experiments were undertaken to investigate the adsorption of CFX antibiotics on WSACs. In another investigation performed by the same research group,[136] a fixed-bed column study was carried out to study the mass transfer coefficient of CFX adsorption onto WSACs. They calculated the mass transfer coefficients by employing the constant wave propagation theory. They also considered the effect of different conditions on the mass transfer coefficient and developed three models to predict the mass transfer coefficient. The same researchers[137] conducted batch adsorption studies of CFX by WSACs both experimentally and mathematically. The adsorbent was prepared *via* the CA method using the chemical activator $ZnCl_2$. The model revealed good agreement with the experimental data, and the effective diffusivity of CFX in the WSACs was estimated at 0.47×10^{-9} m^2 s^{-1}. The same authors also considered the aqueous phase adsorption of CFX by WSACs in a fixed-bed column.[138] This investigation showed that the ACs prepared from WS by the CA procedure were an effective and promising adsorbent for removing CFX from aqueous solution in a fixed-bed adsorption column. In the case of pharmaceuticals removed by WS, Table 6 shows that the adsorption isotherm was well fitted with the Toth and Freundlich isotherms, and the kinetic data for the adsorption by WS mostly followed the pseudo-second-order kinetic model. Additionally, the negative values of ΔG indicate that the sorption process was enthalpy driven, endothermic and spontaneous. The adsorption reaction of CFX by WS is highly favorable. Unfortunately, the information regarding pharmaceuticals removal using WS is limited to the elimination of CFX antibiotics. WS exhibits an acceptable adsorption capacity for CFX (233 mg g^{-1}). Thus, it could be used as an effective sorbent in the elimination of other pharmaceuticals.

7.5. Separation of other hazardous materials

Different HMs, dyes, and oils can be removed from wastewaters using WS, and various hazardous materials are also reported to be effectively eliminated from contaminated systems using WS. Ethyl acetate (EA), naphthalene, natural organic matter (NOM), methanol, benzene, phosphine (PH_3), nitrate (NO_3^-), ammonia nitrogen (NH_3–N), sulfur dioxide (SO_2), dimethyl aminoethyl azide (DAEA), monochlorophenols (MCPs) including 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), and 4-chlorophenol (4-CP) (see also Fig. 3), are dangerous chemicals that were tested for removal using WS. Table 5 gives an overview of the adsorbent dosage, pH, temperature, agitation speed, and contact time values obtained as the optimal operational conditions for the maximum removal efficiency (%). Moreover, the q_m values, thermodynamics, and fitting and kinetic models for different hazardous materials separated by WS are summarized in Table 6. A biofilter packed with WS served to remove EA from an air stream; in turn, NaOH-treated WS were used as a medium for *Pseudomonas putida* PTCC 1694 (*P. putida*) immobilization. The authors concluded that *P. putida* immobilized on WS has the potential to remove EA from air streams.[139] The adsorption of the liquid fuel DAEA, a noncarcinogenic liquid fuel used in space programmes, from dilute aqueous solution on ACs made of WS was considered by Ghanbari Pakdehi and Rezaei,[121] who demonstrated the feasibility of using WS for DAEA removal. They concluded that low concentrations of DAEA should be separated from dilute aqueous solutions to prevent environmental pollution. The adsorption of naphthalene from aqueous solution onto fatty acid-modified WS was also reported by Zhu *et al.*[140] Different fatty acids, including capric acid, lauric acid, palmitic acid, and oleic acid were tested in this work to develop a low-cost biosorbent for hydrophobic organic compounds. The authors recommended that, compared with other modified sorbents, oleic acid-grafted WS showed the maximum partition coefficient (4330 ± 8.8 l kg^{-1}) because it showed the lowest polarity and the highest aromaticity. The ACs derived from WS were also investigated for their ability to adsorb benzene from a rich amine stream of gas sweetening systems.[143]

There have also been attempts to use WS with zinc oxide nanoparticles (ZnO NPs) to remove NOMs from aqueous solution.[141] In this study, the authors used humic acid. NOMs are a group of linear and cyclic organic materials, including humic substances, hydrophilic and hydrophobic acids, and amino acids, and represent a mixture of chemically complex polyelectrolytes produced mainly from the decomposition of plant and animal residues. They occur in surface and groundwater resources, and their high concentrations in raw water and municipal water utilities create serious problems. Methanol adsorption by WSACs prepared *via* KOH activation has also been investigated[142] to analyse its adsorption performance under refrigerated conditions.

WS was also used to prepare ACs for desulfurization.[147] Titanium ore (TO), TiO_2, or Fe_2O_3 was blended into the carbonized powders, which were extruded into cylinders and activated under the atmospheric CO_2. The desulfurization of the samples was evaluated in a fixed bed under a simulated gaseous mixture from coal combustion. The authors found that WS was a useful material for preparation ACs for desulfurization. They observed that the addition of TO, TiO_2, or Fe_2O_3 into the WSACs increased the SSA and concluded that pore structure and metal oxides are the main factors affecting the desulfurization performance. To study the adsorption of phosphine (PH_3), ACs were prepared from WS by the KOH and CA processes.[149] The adsorption of NH_3–N in wastewater by MWS has also reported. An adsorbent was prepared by carbonizing WS using $ZnCl_2$ as the activating agent and was studied to its potential for liquid-phase adsorptive removal of NH_3–N.[146] The removal of NO_3^- from aqueous solution has been examined by comparing the characteristics of various samples of ACs made of walnut, pistachio, and almond shells using $ZnCl_2$ as the chemical activator.[145] Another study aimed to determine the potential chemical ACs derived from WS to remove NO_3^- from synthetic aqueous solution and groundwater in a continuous pilot system.[144]

Walnut, pistachio, and hazelnut shells were also investigated for their ability to remove three MCPs (2-CP, 3-CP, and 4-CP) from aqueous solution.[148] The authors concluded that the effectiveness of the MCPs removal from the water on the walnut, pistachio and hazelnut shells for MCP removal from the water was comparable and that the individual differences in the sorption of MCPs were also negligible. According to this study and the data on the optimized conditions summarized in Table 6, it can be observed that the adsorption isotherms of the different considered materials were well fitted with Langmuir and Freundlich models, and the kinetic data for the adsorption by WS usually followed the pseudo-second-order kinetics. Additionally, due to the negative values of ΔG, and the enthalpy-driven, endothermic removal process, the sorption process of the removed hazardous materials was mostly spontaneous. Subsequently, as for the HMs, dyes and oils discussed in earlier sections, WS has high potential to be used as an inexpensive biosorbent for the removal of other hazardous materials. Finally, as shown in the obtained q_m values summarized in Table 6, WS could adsorb significant amounts of methanol (>200 mg g^{-1}) and PH_3 (>250 mg g^{-1}). Consequently, WS can be considered as an inexpensive and cost-effective adsorbent for the removal of methanol and PH_3.

8. Conclusions

The waste by-products of walnut fruit constitute approximately 40–60% of the weight of the fruit and are readily available in walnut production centres as a source of valuable compounds such as phenolics. These by-products are generated in high quantities upon processing the walnut fruit to obtain its kernel, and they are typical discarded or used as fuel. Recent investigations on different parts of the walnut fruit have shown that its waste products could be used effectively due to their many beneficial properties and valuable compounds, with opens new possibilities for enhancing the value of walnut fruit coproducts. This review presented a wide range of hazardous materials such as various HM ions, various dyes, different oils, and various other toxic compounds that could be removed from aqueous solution by ordinary or chemically-modified WS. The ACs from the WS is an appropriate adsorbent for the removal of hazardous chemicals from aqueous solution. Inexpensive, locally available, and effective raw and treated plant-based waste products such as WS could be utilized as alternative materials, rather than expensive commercial ACs for the removal of different dangerous materials. From the large number of investigations reviewed here, it can be inferred that the adsorption mechanism and the adsorption kinetics on various hazardous substances by WS depend on the chemical nature of the investigated materials and various physicochemical experimental conditions such as the solution pH, the initial adsorbate concentration, the adsorbent dosage, and the temperature of the system. Consequently, these factors must be taken into account when the adsorption capacities of different forms of WS are considered.

An additional point is that raw or chemically activated low-cost plant products, such as WS powder, have high potential for applications in the removal of different hazardous materials including HM ions, dyes, oils, and other chemicals from aqueous solution. The biosorption of the different considered substances onto ordinary or processed WS was well described by the Langmuir and Freundlich isotherm models, demonstrating the chemisorption as the dominating mechanism of biosorption. The kinetic data reported for the various investigated HMs, dyes, oils and other hazardous indicated that those reactions mostly followed the pseudo-second-order model. According to the obtained thermodynamic parameters, the adsorption processes for the different studied hazardous materials removed by WS were enthalpy driven, endothermic, and spontaneous. It follows that raw or processed WS is a promising biosorbent for the removal of diverse hazardous substances from industrial wastewaters. This low-cost material is cost-effective and can be used as a bioremediation method for detoxification purposes.

The comprehensive review of the literature also shows the existing gap in the current knowledge and indicates a need for more studies to be performed to: (I) predict the performance of the adsorption process for the removal of various adsorbates by WS from real effluents under a wide range of operating conditions, (II) investigate the adsorbate removal from mixed wastewater, (III) better understand the adsorption mechanism of different hazardous materials on WS, (IV) verify the feasibility of various chemically modified WS types at an industrial scale, and (V) enhance the adsorption rate, shorten the reaction time, and include composite nanomaterial adsorbents during the adsorption process using WS. With these studies, more effective modifications can be made to improve the of WS in treating industrial wastewater.

Conflicts of interest

The authors declare no conflicts of interest.

Abbreviations

2-CP	2-Chlorophenol
3-CP	3-Chlorophenol
4-CP	4-Chlorophenol
ACs	Activated carbons
AMWS	Amino-modified walnut shell
ANN	Artificial neural network
AR97	C. I. acid red 97
As	Arsenic
AWS	Acid-treated walnut shell
AWSCS	Acid-treated walnut shell impregnated on chitosan
BET	Brunner–Emmett–Teller
BG	Brilliant green
–C═O	Carbonyl
CA	Chemical activation
CAMWS	Citric acid-modified walnut shell
Cd	Cadmium
CFWS	Carboxylate-functionalized walnut shell
CFX	Cephalexin
CNFs	Carbon nanofibre
–CONH$_2$	Amide
–COOH	Carboxyl
COs	Crude oils
Cr	Chromium
CS	Chitosan
Cs	Caesium
Cu	Copper
CV	Crystal violet
DAEA	Dimethyl amino ethyl azide
DBE80	DoALL bright-edge 80
EA	Ethyl acetate
Fe	Iron
FT-IR	Fourier transform infrared spectroscopy
GACs	Granular activated carbons
GMA-DVB	Glycidyl methacrylate-divinylbenzene
H$_3$PO$_4$	Phosphoric acid
H-bonding	Hydrogen bonding
Hg	Mercury
HMs	Heavy metals
K	Potassium
K$_2$CO$_3$	Potassium carbonate
MB	Methyl bromide
MCPs	Monochlorophenols
MEB	Methylene blue
MG	Malachite green
MLR	Multiple linear regression
Mn	Manganese
MR GRL	Maxilon red GRL
MWCNTs	Multi-walled carbon nanotubes
MWS	Modified walnut shell
NaOH	Sodium hydroxide
NH$_3$–N	Ammonia nitrogen
Ni	Nickel
NiHCF	Nickel hexacyanoferrate
NO$_3^-$	Nitrate
NOMs	Natural organic matters
–OH	Hydroxyl
P. putida	*Pseudomonas putida*
PA	Physical activation
Pb	Lead
PH$_3$	Phosphine
PZC	Lower point of zero charge
q_m	Maximum adsorption capacity
RB	Rhodamine B
RBR K-2BP	Reactive brilliant red K-2BP
RR2	Reactive red 2
RWW	Refinery wastewater
SEM-EDX	Scanning electron microscopy-energy-dispersive X-ray spectroscopy
SFWS	Sulfur functionalized walnut shell
SMO	Standard mineral oil
SO$_2$	Sulfur dioxide
SOs	Sunflower oils
SSA	Specific surface area
STY-DVB	Styrene-divinylbenzene
SWCNTs	Single-walled carbon nanotubes
SWCNTs/Fe	Single-walled carbon nanotubes-doped iron
SWCNTs/WSC	Single-walled carbon nanotubes-doped walnut shell composite
Temp	Temperature
TG	Thermogravimetric
TO	Titanium ore
US	United States
US EPA	United States Environmental Protection Agency
UST	Ultrasound technology
UWM	Ultrafine water mist
VOs	Vegetable oils
WHO	World health organization
WMSACS	Watermelon activated carbons
WS	Walnut shell
WSACs	Walnut shell activated carbons
WSB	Walnut shell biochar
WSB-nZVI	Walnut shell biochar-nanoscale zero-valent iron
WSC	Walnut shell composite
WSCS	Walnut shell impregnated on chitosan
XPS	X-ray photoelectron spectroscopy
Zn	Zinc
ZnCl$_2$	Zinc chloride
ZnO NPs	Zinc oxide nanoparticles

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