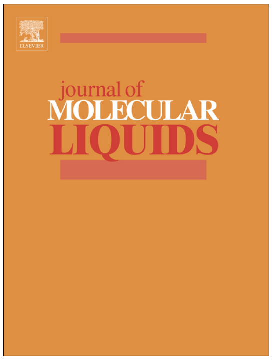

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Agricultural biomass/waste as adsorbents for toxic metal decontamination of aqueous solutions

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Abstract

Toxic metals can be present in the environment, causing negative effects on the ecosystem and human health. Although several technologies have been used for decontamination purposes, biosorption is an environmentally friendly and cost-effective alternative to remove toxic metals from wastewater. Agricultural biomasses are a class of biosorbents that offer several advantages, including their low cost, availability in nature, simplicity to be obtained and used as adsorbents. This review article is focused on the use of agricultural biomass materials for the removal of toxic metal(oid)s from contaminated aqueous matrices. In addition, raw and modified forms of these biosorbents are considered as precursors for the preparation of other adsorbents like biochar. Following agricultural biomasses are discussed: i) watermelon, ii) potato, iii) cucumber, iv) peanut, v) almond, vi) walnut and hazelnut, vii) pistachio, and viii) tea waste-based biosorbents. The adsorption potential of the biomasses is exhibited under the optimum experimental conditions, and their characterization and possibility to reuse is also considered. Moreover, isotherm and equilibrium parameters of the metal(oid) adsorption by the biomasses are discussed. Specifically, thermodynamic studies are described in order to better understand the nature of the biosorption process between contaminant and biomass. All these considerations reflect the high potential of agricultural waste-based adsorbents for toxic metal(oid)s removal related to wastewater treatment technologies.

Keywords: toxic metal(s), agricultural wastes, biosorption, thermodynamic studies, equilibrium modelling, isotherms

1. Introduction

Heavy metals are represented by those elements that have a specific density greater than 5 g/cm^3 [1]. This classification includes essential elements (e.g. iron, vanadium, cobalt, copper, manganese, zinc, strontium, molybdenum), which are essential for living organisms at trace concentrations. However, if the threshold level is exceeded, several damages can be observed in living systems [2]. Heavy metals comprise also non-essential elements, including arsenic, cadmium, nickel, lead, mercury, and antimony [3]. The International Agency for Research on Cancer has classified cadmium, arsenic, chromium, lead and mercury as known or probable carcinogenic elements [4]. Non-essential heavy metals are highly toxic even at trace concentrations. Thus, not only concentrations in the order of g/L or mg/L may lead to toxic effects, but also a few µg/L or ng/L can cause adverse effects on the ecosystem and human health [5]. Besides the heavy metal concentration, the toxicity is determined by chemical speciation, exposition route, and characteristics of the exposed organism such as genetic, age, gender and nutritional status [6].

The presence of heavy metals in man’s environment originates from both, natural (e.g. soil erosion, weathering of the earth´s crust, volcanic eruptions) and anthropogenic sources such as mining and mineral beneficiation, industrial effluents originated from cement, food, textile, paper, electronic activities, chemical formulations used for plague control, etc. [7]. Considering that heavy metals are not degraded under environmental conditions, their accumulation in environmental compartments (e.g. air, soil and waters) could in long-term lead to their migration in food and water intended for human consumption [8]. This is a major environmental concern and provokes researchers to work on new developments that enable the removal of toxic elements from contaminated environmental sources.

Several treatment technologies have been reported for remediation of heavy metals from effluents and wastewaters. These technologies are based on biological substrates, membrane filtration, reverse osmosis, oxidation, electrochemical oxidation, coagulation/ flocculation, chemical precipitation, and adsorption [9-11]. However, there is a current trend based on the need to generate alternative processes that are in line with the principles of “Green Chemistry” or “Sustainable Chemistry”. Some principles of Green chemistry are summarised as follows:

- reduce the consumption of toxic chemical reagents like conventional organic solvents;
- use other safer reagents;
- avoid the generation of wastes that cannot be recycled;
- reuse reagents
- decrease energy consumption;
- choose environmentally friendly analytical techniques for the detection of analytes
- use of automation and developments on a microscale level.

Biosorption is a branch of bioremediation that has arisen in response to the need of promoting processes that are friendly to the environment [12]. The use of biosorbents in water treatment technologies has several advantages compared to conventional chemical sorbents. These include biodegradability under natural/environmental conditions, high abundance in nature and simple collection and preparation procedures [13]. Biosorbents include bacteria (Gram positive, Gram negative and cyanobacteria), fungi (moulds, fungi, and yeasts), algae (microalgae, macroalgae, and seaweed), industrial, natural, agricultural residues, and other biomaterials (e.g. materials derived from chitosan) [14]. These systems offer a high surface area to volume ratio and have many active binding sites on their surface through which heavy metals can be efficiently retained under suitable conditions (e.g. -COOH, -NH_2, -OH, -SH groups) [15].

This review is focused on the use of agricultural biomass as biosorbents for heavy metal removal from wastewaters. Raw and modified forms of these biosorbents are considered, besides their use as substrates to obtain new adsorbent materials (e.g. biochar). Recently developed biosorption processes based on peanut, pistachio, walnut, hazelnut, almond, tea, watermelon, potato and cucumber waste-based biosorbents are presented and discussed in detail. Besides possible mechanisms involved in metal retention on biosorbents, the review includes also kinetic, equilibrium, and thermodynamic aspects of agricultural residues used as biosorbents. Finally, future perspectives on biosorbents applications for heavy metal removal in wastewater treatment are presented.

2. Agricultural waste biosorbents for heavy metal(oid)s adsorption

2.1 Watermelon-based biosorbents

Untreated watermelon rind (WMR), xanthate-modified WMR (X-WMR) and citric acid-modified WMR (CA-WMR) were used to remove As(III) and As(V) from aqueous solutions by Shakoor et al. [16]. For As(III), maximum uptake appeared at pH 8.2 for X-WMR and 7.2 for both CA-WMR and WMR. For As(V), highest adsorption was found at pH 4.6, 4.5 and 5.2 for X-WMR, CA-WMR and WMR, respectively. Xanthate watermelon rind gave the highest relative adsorption for arsenic (i.e. As(III) = 99% and As(V) = 98%) compared to other adsorbents. Desorption studies were performed by using 0.1 M NaOH and after the first adsorption/desorption cycle, the desorption rates were for As(III) 98% (X-WMR), 94% (CA-WMR) and 97% (WMR) and for As(V) were 96% (X-WMR), 93% (CA-WMR), and 98% (WMR), respectively. The estimated mean adsorption energy indicated that ion exchange and chemisorption might not be the only mechanisms for As adsorption.

The biosorption of Cr(III) by watermelon rind was tested by Reddy et al. [17]. The highest removal was established in a pH range between 2 and 3. Biosorption was found to be fast and the equilibrium was achieved within 30 min. Regeneration studies were carried out for 4 adsorption/desorption cycles. Among examined desorption eluents (water, 0.1 M NaOH, and 0.1 M HCl) 0.1 M NaOH presented the highest desorption efficiency (98.7% metal recovery for the first cycle) and there was no change in adsorption efficacy observed during four repeated adsorption–desorption cycles.

Husein et al. [18], examined the application of raw watermelon rind (WM) and watermelon rinds microwave-irradiated in deionised water (WMW), in NaOH (WMA) and in H_2O_2 (WMH), for the removal of Cd(II) from aqueous media. The pH was found to control the adsorption process and the highest uptake for all the adsorbents was observed at pH 9.12. Compared to WMA (q_{max} = 57.14 mg/g) and WM (q_{max} = 53.48 mg/g) adsorbents, WMH (q_{max} = 68.03 mg/g) and WMW (q_{max} = 68.97 mg/g) appeared to have higher maximum adsorption capacity. The mean energy of adsorption was estimated to be between 0.11 – 0.32 KJ/mol, suggesting a physisorption process.

Watermelon rind was also used to remove Co(II) and Ni(II) ions from waters [19]. The increase of pH from 2 to 7 led to an increment of the uptake capacity, and at pH values higher than 5 there was a slight decrease in adsorption capacity due to the formation of soluble hydroxyl complexes. The highest uptake capacity was noticed at 2.5 and 2 g/L of biosorbent dosage for Ni(II) and Co(II) ions, respectively. FTIR spectra before and after Ni(II) and Co(II) adsorption indicated that acidic groups and carboxyl and hydroxyl groups were involved in the process. Activated carbon obtained from watermelon rind was examined to remove also Ni(II) ions [20, 21]. Maximum removal capacity of 18.43 mg/g was observed at pH 6.69 (pH range 2.0–7.0), initial concentration of 100 mg/L (initial concentration ranged from 5 to 100 mg/L), 365.89 min of contact time (contact time ranged between 20 and 720 min) and 5 g of adsorbent dosage (adsorbent dosage ranged from 5 to 25 g/L) [20]. Mathangi and Kalavathy [21] concluded that a) the uptake capacity was found to decrease with the increment of adsorbent dosage from 0.1g/100 mL to 0.5 g/100 mL, b) the adsorption equilibrium was achieved at 60 min and c) the adsorbent was used for two adsorption-desorption cycles without significant loss of the efficiency against nickel.

Watermelon-based biosorbents were also used to adsorb Pb(II) [22, 23]. Akkaya and Güzel [23] found that the optimum conditions using watermelon rind as an adsorbent, were obtained at pH 5, 80 min of contact time and 0.1 g/50 mL solid/liquid ratio. Lakshmipathy and Sarada [22] examined the application of watermelon rind treated with 0.1 M HCl, and maximum adsorption was estimated to be 116.2 mg/g at pH 5, 30 min of contact time, and 303 K.

The application of watermelon-based biosorbent was also investigated regarding the Cu(II) removal [22-25]. Using watermelon rind modified with 0.1 M HCl, the highest Cu(II) uptake appeared at pH 5 and equilibrium was attained within 30 min

[22]. Akkaya and Güzel also found that the highest uptake was at pH 5 using watermelon seed hulls as biosorbent [23]. The temperature has also positively affected the adsorption efficiency. More specifically, the rise of temperature from 293K to 333 K led to an increase of the maximum adsorption capacity from 27.03 to 33.90 mg/g. Banerjee et al. [24] also noticed that the increase of temperature from 303 K to 323 K led to an adsorption enhancement, using watermelon shell as adsorbent. However, in contrast to the previous work, they found that maximum adsorption was achieved at pH 8.0 [24]. Liu et al. [25] studied the effect of some pre-treatment procedures of watermelon rind for copper adsorption. They found that a) 120 °C was the appropriate drying temperature, b) the best drying time was 3 h and c) the material with particle size < 150 μm was the best fraction for Cu(II) uptake.

Liu et al. [26] studied the removal of Cu(II), Zn(II) and Pb(II) by watermelon rind in single and in multi-metal solution. It was concluded that in single metal solutions the maximum adsorption occurred at pH 6.8 for Pb(II) and Zn(II) and at pH 5 for Cu(II). In multi-metal solution, the selectivity order in the studied range was found to be Pb(II) > Cu(II) > Zn(II), indicating the increased affinity of watermelon rind particularly for lead. Regeneration studies were also conducted in three adsorption/desorption cycles. Among the tested desorption eluents (distilled water, 0.1 M NaOH, 0.5 M HNO_3, and 0.5 M HCl) 0.1 mol/L NaOH provided high desorption efficiency and affected positively the uptake capacity of the material.

In summary, Table 1 presents the list of biosorbents derived from watermelon with their isotherms, kinetics and the maximum sorption capacities.

Table 1. List of isotherm and kinetic models for the adsorption of potentially toxic metal(oids) on watermelon-based biosorbents.

Biosorbents	Heavy metal(oid)s	Isotherm models	Kinetic models	Maximum adsorption capacity (mg/g)	References
Watermelon-based adsorbents					
Water melon rind	As(III)	Langmuir	Pseudo-second order	4.81	[16]
Xanthated water melon rind	As(III)	Langmuir	Pseudo-second order	4.83	[16]
Citric acid modified water melon rind	As(III)	Langmuir	Pseudo-second order	4.72	[16]
Water melon rind	As(V)	Langmuir	Pseudo-second order	3.29	[16]
Xanthated water melon rind	As(V)	Langmuir	Pseudo-second order	1.5	[16]
Citric acid modified water melon rind	As(V)	Langmuir	Pseudo-second order	3.62	[16]
Raw watermelon rind	Cd(II)	Langmuir	Pseudo-second order	53.48	[18]
Microwave-radiated watermelon rind in the presence of H_2O_2	Cd(II)	Langmuir	Pseudo-second order	68.03	[18]
Microwave-radiated watermelon rind in the presence of NaOH	Cd(II)	Langmuir	Pseudo-second order	57.14	[18]
Microwave-radiated watermelon rind in the presence of deionized water	Cd(II)	Langmuir	Pseudo-second order	68.97	[18]
Watermelon rind	Co(II)	–	–	10.2[a]	[19]
Watermelon shell	Cu(II)	Langmuir	Pseudo-second order	111.1	[24]
Watermelon seed hulls	Cu(II)	Langmuir	Pseudo-first order	27.03	[23]
Watermelon rind treated with 0.1 M HCl	Cu(II)	Langmuir	Pseudo-second order	39.2	[22]
Watermelon rind	Cu(II)	Langmuir	Pseudo-second order	6.281	[26]
Watermelon rind	Cu(II)	–	–	5.73[a]	[25]
Watermelon rind	Cr(III)	Langmuir	Pseudo-second order	175.4	[17]
Watermelon rind	Ni(II)	–	–	11.9[a]	[19]
Watermelon rind activated carbon	Ni(II)	–	–	18.43[a]	[20]

Activated carbon from watermelon rind (H_3PO_4 activation)	Ni(II)	Langmuir	Pseudo-second order	38.98	[21]
Watermelon seed hulls	Pb(II)	Langmuir	Pseudo-first order	24.15	[23]
Watermelon rind treated with 0.1 M HCl	Pb(II)	Langmuir	Pseudo-second order	116.2	[22]
Watermelon rind	Pb(II)	Langmuir	Pseudo-second order	98.063	[26]
Watermelon rind	Zn(II)	Langmuir	Pseudo-second order	6.845	[26]

[a] Obtained from experimental results

2.1.1 Mechanism of adsorption on watermelon-based biosorbents

Generally, the adsorption by WR and modified WR is based on the interaction between the hydroxyl, amino and carboxylic groups present on the adsorbents surface and the metal such as Cu^{2+}, Pb^{2+} and Cr^{3+} anions [17, 22, 23] and metalloid species such as arsenite and arsenate [16]. The significant changes (Figures 1,2) in the position and the relative ratio of the peaks at 3400 cm^{-1}, 1600 cm^{-1}, 850 cm^{-1}, which are characteristic for hydroxy, carboxylic and amino moieties, respectively [16], indicate the formation of strong inner-sphere complexes. The adsorption mechanism is described as an ion exchange process, which could be true for metal ions (e.g. Cu^{2+}, Pb^{2+} and Cr^{3+}), and could be represented by following equations:

$$\text{WMR-OH} + M^{z+} \longrightarrow \text{WMR-O-}M^{(z-1)+} + H^{+}$$

$$\text{WMR-NH}_2 + M^{z+} \longrightarrow \text{WMR-NH-}M^{(z-1)+} + H^{+}$$

$$\text{WMR-COOH} + M^{z+} \longrightarrow \text{WMR-COO-}M^{(z-1)+} + H^{+}$$

However, in the case of As(III) and As(V), which exist in the form of arsenite and arsenate, respectively, ion exchange reactions [16] are not expected because both, arsenite and arsenate exist in aqueous solutions basically in the form of anions or neutral species. The adsorption is expected to occur rather through the formation of ester and amide bonds between the arsenic species and the surface hydroxy and amino groups, and is described for arsenite by following equations:

$\text{WMR-OH} + \text{As(OH)}_3 \longrightarrow \text{WMR-O-As(OH)}_2 + H_2O$

$\text{WMR-NH}_2 + \text{As(OH)}_3 \longrightarrow \text{WMR-NH-As(OH)}_2 + H_2O$

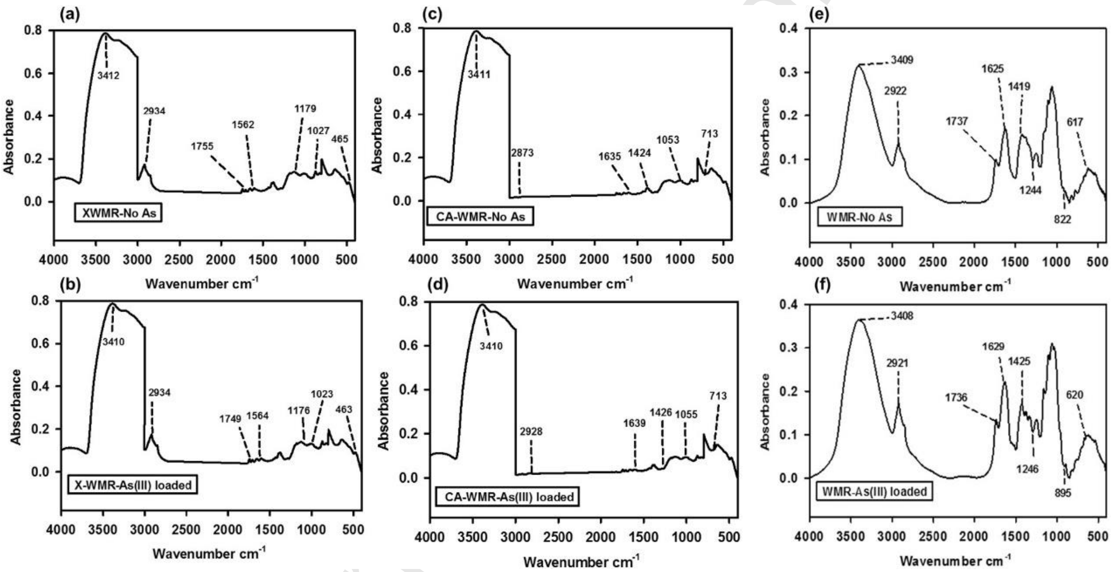

Figure 1. The FTIR absorbance spectra of xantahed water melon rind (X-WMR), citric acid modified water melon rind and water melon rind (WMR), (a, c, e) no As-loading and (b, d, f) As(III)-loaded. Reprinted with permission by Elsevier [16].

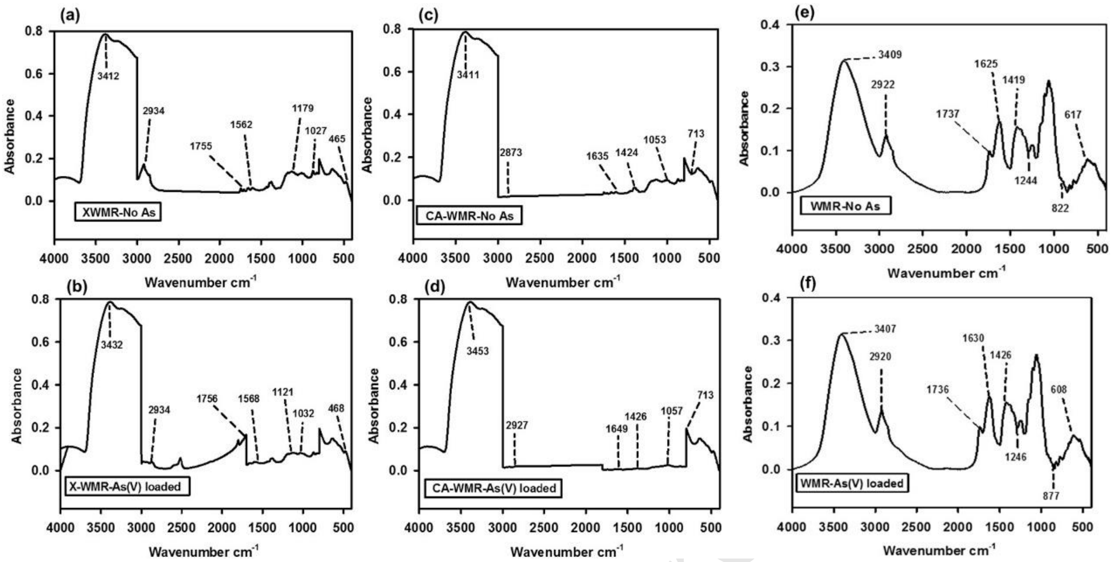

Figure 2. The FTIR absorbance spectra of xantahed water melon rind (X-WMR), citric acid modified water melon rind and water melon rind (WMR) (a, c, e) no As-loading, and (b, d, f) As(V)-loaded. Reprinted with permission by Elsevier [16].

2.2 Potato waste-based biosorbents

Another worldwide abundantly available solid waste, which could be utilized as biosorbent, are potato peels. Guechi et al. (2016) studied dried potato peels without further treatment for Cu(II) removal [27]. The optimal parameters were observed at an adsorbent dosage of 0.15 g/400 mL and particle size of 0.16-0.63 mm, 300 mg/L of copper solution, pH=5, temperature of 25 ^{o}C, stirring at 800 rpm, and no NaCl addition. The increment of the particle size, ionic strength, or temperature had a negative impact on the remediation efficiency. Fitting of the equilibrium data to Langmuir, Freundlich, Elovich, and Temkin isotherm models indicated that the former two models described better the adsorption process. The reported *Langmuir* adsorption capacity under the above conditions was 84.74 mg/g, a value significantly higher compared to other similar low-cost biosorbents. The adsorption followed better the pseudo-second order kinetic model, while interparticle diffusion was the rate determining step.

In 2008, Aman et al. used potato peels for the preparation of a charcoal and they studied the material's adsorptive capability towards Cu(II) in industrial wastewater samples [28]. After thoroughly washing and drying, the potato peels were thermally treated in a furnace for 2 hours at 700 ^{o}C (973 K). The resulted potato peels charcoal, abbreviated herein as PPC, was grounded and the particles of 0.2 mm were obtained after sieving. One gram of PPC was found capable of removing 99.8 % of Cu(II) (150 mg/L, 100 mL) at pH 6 after shaking for 20 minutes at 30 ^{o}C. Although, the *Langmuir* Q_o was very low (0.3877 mg/g) under these experimental conditions. The negative value of ΔG^{o} revealed that the adsorption was spontaneous and PPC showed the same sorption performance for up to 5 cycles.

Sabri et. al. [29] studied Fe(II) removal by the as above prepared potato peels charcoal. This material is referred to as PPC2. They went a step further by treating chemically the dried powder with HCl (PPC2-HCl) or H_3PO_4 (PPC2-HP). Temperature was found to be a significant factor affecting adsorption. The best adsorption efficiency was achieved at 20 °C (293 K), while the increase of temperature to 60 °C (333 K) led to a removal decrement due to enhanced desorption processes and the exothermic nature of the adsorption process. The untreated PPC2 showed a removal efficiency of 36.1% and 21.8 % towards 50 mg/L and 250 mg/L iron solution, respectively, at 20 °C. Treatment with hydrochloric acid led to more significant removal efficiencies of 90.4 and 78.0 % for 50 and 250 mg/L, respectively. The phosphoric acid modified samples revealed removal capabilities between those of the two above mentioned samples. Freundlich model did not show a good fitting, while the R^2 value of the *Langmuir* fitting was above 0.999 in all cases. The highest reported adsorption capacity based on the *Langmuir* fitting for PPC2 was 121.95 mg/g for an iron concentration of 250 mg/L. Pseudo-second order kinetic model was found to describe better the adsorption process for all samples, compared to the pseudo-first order.

Mahale et al. [30] studied the nickel removal by a powder (particle size of 0.147 mm) obtained after treating the potato peels with HCl followed by washing with distilled water, drying at 60 °C, and sieving. The removal efficiency revealed a strong pH dependence and the optimum adsorption efficiency took place at pH 9. At the optimum dosage of 1.4 g/L the material revealed a removal efficiency of about 90 % in 250 mg/L Ni(II) solution after 50 minutes contact time. Mutongo et. al. [31] studied potato peels after activation/protonation by HCl as a biosorbent (particle size < 75 μm) towards hexavalent chromium. The quantitative (100%) removal efficiency of Cr(VI) at low concentration (20 mg/L) was achieved only for high biosorbent amount (4 g/L) under acidic conditions (pH=2.5, 27 °C). However, the reported adsorption capacity based on the *Langmuir* model was only 3.28 mg/g.

The study of activated carbons obtained from biomass by-products as remediation media towards a broad spectrum of compounds like heavy metal(loid)s ions, dyes, toxic vapours, and pharmaceuticals continues to grow strongly [32-46]. Matis and co-workers [47] studied the removal of Co(II) by activated carbons obtained from potato peels after chemical activation by H_3PO_4, followed by pyrolysis under a nitrogen atmosphere at three different temperatures: 400° (PoP400), 600° (PoP600), and 800 °C (PoP800). An important aspect for the use of biomass and in general of raw precursors for the synthesis of porous carbons is the yield of the process. According to the present study, the highest reported yield was 55% in the case of pyrolysis at the lowest temperature (400 °C) and the lowest yield 49% in the case of PoP800. Another feature of the carbonaceous materials, especially regarding their remediation capability, is their textural features and their specific surface areas. The analysis of nitrogen adsorption isotherms revealed a specific surface area of 904.6 cm^2/g for PoP400, while the increase of the carbonisation temperature by 200 °C led to a 15% decrement. The material after pyrolysis at 800 °C showed a negligible porosity, and as a result, it was no further examined. On the contrary, carbonisation at 600 °C led to a higher total pore volume, compared to PoP400. PoP400 revealed a micro-mesoporous structure with a wide pore size distribution. In addition to its significant mesopore volume, PoP600 showed a similar distribution in pore sizes in this range but with a smaller volume of pores, especially in the micropore region. An enhanced surface functional group heterogeneity was revealed for both PoP400 and PoP600, with the latter having almost three times lower amount of oxygen-containing surface groups. Nevertheless, both samples found to be acidic. The optimum pH value for the removal capacity was 6, and for that reason, the rest of the adsorption experiments and data evaluation were performed at this pH. The kinetic and equilibrium data evaluation showed a better fitting to the pseudo-first order and *Langmuir* models, respectively for both carbons. PoP400 revealed Q_m=373 mg/g, while PoP600 Q_m=405 mg/g at 25 °C. The better performance of PoP600 suggests that the total pore volume or/and more particular the presence of macroporous area plays a key role in the adsorption process. The increment of the adsorption temperature had a positive impact on the adsorptive ability. At 65 ^oC, the Q_m values for PoP400 and PoP600 were 389 and 480 mg/g, respectively. The negative value of ΔG^o suggests a spontaneous nature of the adsorption, while the positive ΔH^o an endothermic process. Finally, based on FTIR measurements it was proposed that the high removal performances, greater comparing to other biomass-derived carbonaceous materials, is due to the interactions between Co(II) and the oxygen-containing surface functional groups, especially aliphatic ones. The phosphoric acid activation resulted in increment of these oxygen groups that can act as cobalt complexation sites. The latter together with electrostatic interactions and cation exchange are the major mechanism for the cobalt removal (Figure 3).

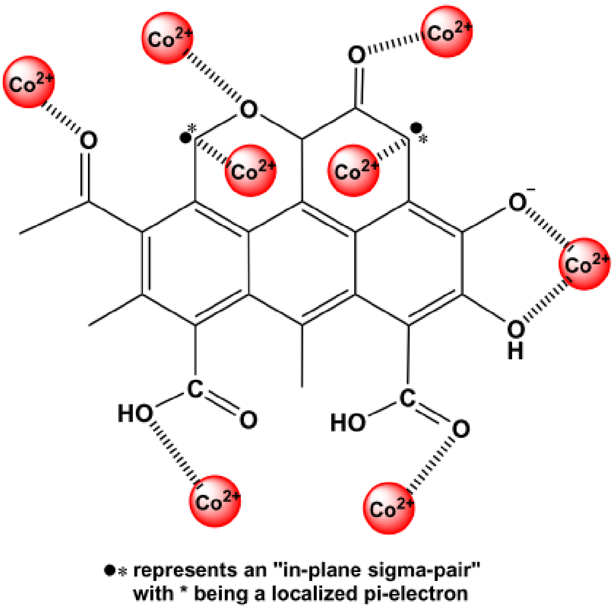

Figure 3. All the possible adsorptive interactions between Co(II) and the activated carbon. Reprinted with permission by Elsevier [47].

Removal of Co(II) by carbons synthesised via hydrothermal treatment of potato peels followed by chemical activation was published in 2018 by Kyzas et al **[48]**. Briefly, washed and dry potato peels underwent a hydrothermal treatment in an autoclave at 200 °C for 4 h (with a heating rate of 4 °C per min, a pressure of around 580 psi at 200 °C, and mixing at a rate of 150 rpm). The obtained hydrochar (solid phase) was washed with hot distilled water as well as with ethanol and was dried at 100 °C. The next step was the chemical activation by H_3PO_4 and after filtration, carbonisation took place at 400 °C, 600 °C, and 800 °C under nitrogen atmosphere. The final material obtained after Soxhlet washing, freeze-drying, and grounding/sieving was evaluated as lead removal adsorbent. The relative removal yield of the hydrochar was around 32.5%. Different durations of hydrothermal treatment (2, 4, 24 h) were studied and the authors analysed in detail the chemical and surface features, but these materials were not studied as adsorbents. The increase of the hydrothermal treatment resulted in higher elemental carbon content. All samples were found to be rich in surface functional groups, but treatment for 24 hours led to the degradation/transformation of the starch and cellulose content. The hydrochar obtained after 24 hours of carbonisation at 800 °C led to an almost non-porous material that was not evaluated. The porosity of HP400 was significantly higher compared to HP600. The former sample showed a specific surface area of 465.8 m^2/g, while the micropores volume was 0.142 cm^3/g, and the total pore volume 0.291 cm^3/g. The respective values for HP600 were 157.3 m^2/g, 0.011 cm^3/g, and 0.099 cm^3/g. The sample was found to possess a combination of micro- and mesopores. Regarding the Co(II) removal efficiency, it was found to continuingly increase from a pH of 2 and up to 6 and the pseudo-second order model found to fit better to the experimental data. The analysis of the equilibrium data with *Dubinin–Radushkevich*, *Freundlich*, and *Langmuir* models showed that a better fitting was achieved to the latter model (R^2= 0.982–0.994). HP400 has an approximately two times greater adsorption capacity of 479 mg/g compared to HP600 (217 mg/g). Considering the three times higher surface area of HP400 and that the FTIR analysis revealed an increase surface heterogeneity as a result of H_3PO_4 activation, the author concluded that cobalt was adsorbed by surface complexation and cation exchange mechanisms.

Another recent study regarding the usage of potato peels as a zero cost agricultural waste precursor for activated carbon as Pb(II) adsorbent was published by Kyzas and Mitropoulos [49]. They synthesized activated carbons following the above hydro carbonisation process. The specific surface area calculated based on N_2 sorption was 625 m^2/g, which is a satisfactory value for carbon materials obtained from biowastes and a relatively mild activation/carbonisation procedure. The optimum pH value was found to be six and evaluation of the equilibrium data revealed a better fitting to the *Langmuir* rather than to *Freundlich* isotherm model. The q_m was found to be 217 mg/g at 20 °C and 262 mg/g at 50 °C. The thermodynamics results suggested that the adsorption was a spontaneous and endothermic process. Interestingly, the authors presented also estimations regarding the real-life cost-effectiveness of the hydrothermal produced activated carbon.

In summary, Table 2 presents the list of adsorbents derived from potato with their isotherms, kinetics and the maximum sorption capacities.

Table 2. List of adsorption isotherms and kinetics models for the adsorption of potentially toxic metal(oids) on potato and cucumber peels derived biosorbents (q_m reported at 293-298 K).

Biosorbent	**Adsorbate**	**Maximum biosorption capacity; mg/g**	**Dominant isotherm / kinetic model**	**Reference**
Dried Potato Peels	Cu(II)	84.74	Several models (*Langmuir, Freundlich, Temkin, Elovish*, pseudo-first order, pseudo-second order)	[27]
Potato Peels Charcoal (PPC)	Cu(II)	0.3877	*Langmuir* and *Freundlich*	[28]
Potato Peels Charcoal	Fe(II)	121.95	Langmuir and pseudo-second order	[29]

Potato Peels HCl activated	Cr(VI)	3.28	Several models (*Langmuir*, *Freundlich*/ pseudo-first order, *Elovish*)	[31]
Carbons derived from Potato Peels (activated with H_3PO_4 and pyrolysis)	Co(II)	405	*Langmuir* and pseudo-first order	[47]
Hydrothermally and H_3PO_4 activated carbon derived from Potato Peels	Co(II)	479	*Langmuir* and pseudo-first order	[48]
Hydrothermally and H_3PO_4 activated carbon derived from Potato Peels	Pb(II)	217	*Langmuir*	[49]
Cucumis sativus (cucumber) peels	Cd(II)	7.142	*Freundlich* and pseudo-second order	[50]
Cucumis sativus (cucumber) peels	Pb(II)	28.25	*Langmuir* and pseudo-second order	[51]
Cucumis sativus (cucumber) peels HCl modified	Cd(II)	58.14	*Langmuir* and pseudo-second order	[52]
Cucumis sativus (cucumber) peels	Pb(II)	147.06	*Langmuir* and pseudo-second order	[53]
Cucumis sativus (cucumber) peels	Cu(II)	88.50	*Langmuir* and pseudo-second order	[53]
Cucumis sativus (cucumber) peels	Pb(II)	133.6	*Langmuir* and pseudo-second order	[54]

2.3 Cucumber waste-based biosorbents

Another agro-waste biomass that was utilized as a source of biosorbents are the peels of *Cucumis sativus* (CSP), widely known as a cucumber. Pandley et. al. [50] studied the removal of Cd(II) by the biosorbent/powder, of 1 -2 mm particle size, obtained after extensive washing with water (in order to remove particulate matters, like dust) and drying for 24 hours at 80 °C. The maximum removal determined by batch-type experiments using a 25 mg/L Cd(II) solution and 2 g/L material was reported to be 88.1% at pH=5 (25 °C, 160 rpm) after 150 min. The fivefold increase of the biosorbent amount (10 g/L) led to a slight increase of the removal efficiency to 90.2 %. The sorption equilibrium results revealed a good fitting by the Freundlich model for a wide temperature range (25-45 ^{o}C), while a barely acceptable R^2 value of 0.935 for the *Langmuir* model was obtained at 45 ^{o}C K. The *Langmuir* adsorption capacity at the latter case was 7.142 mg/g. Regarding the kinetics modelling, the pseudo-second order showed an almost 1 correlation coefficient, at high experimental temperatures. The increment of the temperature had a positive impact on removal efficiency suggesting a spontaneous and endothermic adsorption process. The analysis of the surface species by FTIR revealed a variety of functional groups, with the -OH, C=O, and -NH surface moieties to be the active surface species for the metal-ion adsorption.

The same research team studied the previously mentioned material towards Pb(II) [51]. The optimum pH was similar as in the case of Cd(II) ions by this biomaterial, while the best contact time was 90 minutes. The maximum removal efficiency of 87.12% was achieved at 5.0 g/L adsorbent dosage. The lesser removal efficient above this amount of biosorbent has linked to aggregation phenomena and/or overlay of the available active/binding sites. The removal was described better by the

Langmuir isotherm and kinetics by the pseudo-second order model, indicating a monolayer and chemical based sorption. The maximum *Langmuir* adsorption capacity was found to be 28.25 mg/g at 25 ^{o}C. The chemical nature of adsorption was investigated by FTIR analysis, revealing as binding sites for Pb(II) the –OH, –C=O, –COO–, –C–O–C–, and –COOH surface active groups.

The cucumber peels derived biosorbent biomass (CSP) was further treated with HCl for the enhancement of the negatively-charged binding/adsorptive sites [52]. Another aspect of the acidic treatment was to prevent tannin compounds elution that can lead to side-reactions and to increase of chemical oxygen demand (COD). Briefly, CSP powder was poured in HCl solution under stirring for 4 hours at room temperature and left overnight. The suspension was filtrated afterwards and washed until neutral pH of the filtrate. Finally, the obtained material was dried for 2 hours at 85 °C and was stored in a desiccator. This chemical modified material is referred to herein as CSP-Cl. This material achieved the maximum Cd(II) removal in the pH region between 4 and 6, compared to the unmodified counterpart that presented the maximum removal at pH 5. Based also on the fact that CSP-Cl had a pH_{zpc} 4.2, it can be concluded that the adsorptive removal is favourable above this value of pH_{zpc}, since the binding sites are negatively charged. The optimum biosorbent dosage was found to be 2 g/L and 10 g/L for the modified and unmodified sample, respectively. The equilibrium adsorption data were best fitted with the *Langmuir* isotherm model resulting in a value of q_m of 58.14 mg/g (at 25 ^{o}C and pH 5.0), which is more than eight times higher than that of the non-treated sample and other relevant biosorbents. A chemisorption removal process was suggested based on the fact the kinetics follow the pseudo-second order kinetic model, via electrons sharing or via covalent forces between adsorbate and adsorbent. The authors studied the effect of cations and anions on the removal efficiency, which revealed a relatively small effect, with sulfate anions to have the greatest negative effect (-15 %). On the other hand, the cations affected stronger the removal performance. The Na^+ and K^+ ions had smaller effect compared to Ca^{2+} and Mg^{2+} ions. This was linked to competition reactions between Cd(II) and Ca(II) regarding the adsorption, which caused a relative decrease in the removal efficiency of 39%.

Removal of Cu(II) and Pb(II) by cucumber peels derived biosorbent was also studied by Akkaya and Guzel [53]. The material was prepared with extensive washing and drying for 24 hours at 70 ^oC, and grounding to 500 μm particle size. The FTIR analysis showed the presence of similar functional groups as above, the reported pH_{pzc} was 6.42, while maximum uptake was observed at pH 5 for both Cu(II) and Pb(II) ions. The equilibrium data were analysed by applying the *Langmuir* and *Freundlich* isotherm models and better correlation coefficients were obtained for the former model. In the case of Pb(II), the q_{m} value was increased from 121.95 at 293 K to 147.06 mg/g at 60 ^oC. For Cu(II), the q_{m} was evaluated to be 64.10 mg/g at 293 K and 88.50 mg/g at 60 ^oC. The increase of q_{m} by a temperature increment indicated the endothermic nature of the adsorption. The analysis of the biosorption kinetic data corresponding to 20 ^oC and 60 ^oC revealed high R^2 values, with the pseudo-second order model to have values slightly closer to unity. A spontaneous and endothermic (positive ΔH^0 value) nature of the biosorption was concluded by thermodynamic parameters analysis for both Cu(II) and Pb(II). The application of the intraparticle diffusion model revealed a three steps process. The first one is assigned to an instantaneous adsorption stage or/and external surface adsorption, the second one to intraparticle diffusion, which is the rate determine step, and the third one to the equilibrium stage. Scanning electron microscopy analysis revealed that the structure of the material was altered after the interactions with Cu(II) or Pb(II).

Basu et al. [54] studied also the lead removal by cucumber peels, and the conclusions were in a good correlation with the ones mentioned above. The authors studied the lead removal by various other peel-derived sorbents like orange, mango, pea, and sweet lemon peels (Figure 4) with the biosorbent derived from cucumber peels (CP) to be the best-performing. The main constituents of the latter were reported to be around 61% hemicellulose, 8% lignin, and 19% cellulose. The XRD pattern revealed the amorphous structure of the material. A monolayer pattern of adsorption was concluded since the fitting of the equilibrium data to the *Langmuir* model showed a R^2 value of 0.999 and the calculated q_m was equal to 133.6 mg/g.

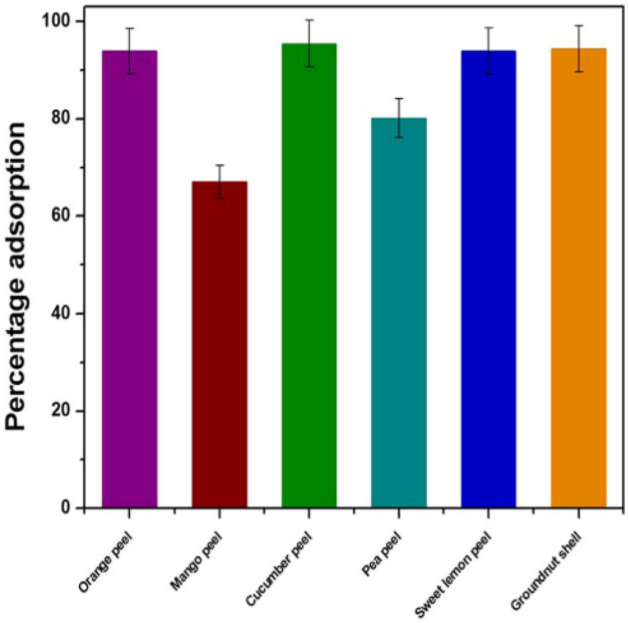

Figure 4. The Pb(II) adsorption capability of various peel-derived materials (at 30 ^{o}C, initial concentration of 50 mg L-1). Reprinted with permission by Elsevier [54].

In order to determine which functional groups in between carboxyl, hydroxyl, phosphate, and amino play a key role on the removal capability, the CP was chemically modified in a variety of ways in order to eliminate each time a specific functional group. The most pronounced decrease was found after the modification of carboxyl group by esterification (-42.79 %), followed by modification of phosphate groups (-22.51 %). Acetylation of the hydroxyl groups and methylation of the amino groups led to less pronounced decrease of the removal capability, by around -12 and –5 %, respectively. Based on these results, the authors stated that the carboxyl and phosphate groups are the more important ones for the lead removal.

SEM and EDX analysis of the biosorbent after the adsorption tests showed the formation of lead containing micro-particles on the surface (Figure 5). However, the most interesting outcome came from the EDX analysis of the spend sample. The EDX data revealed the absence of nutrient elements (Na, Ca, Mg, or K) detected on the pristine sample, fact linked to the involvement of ion exchange adsorption mechanisms. Additionally, the removal of Pb(II) was found to be favoured by the presence of cadmium in the binary adsorption system. The desorption efficiency tests revealed HCl as the best eluent, with relative desorption value around 97%. Nitric acid and a chelating agent (EDTA) showed also elevated desorption capability of around 93%. On the contrary, H_2SO_4 and Na_2CO_3 showed regeneration values of less than 40 %. In summary, Table 2 presents the list of biosorbents derived from cucumber with their isotherms, kinetics and the maximum sorption capacities.

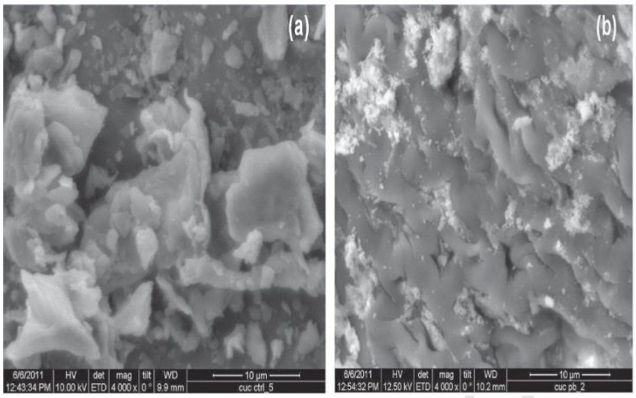

Figure 5. SEM micrograph of pristine (a) and after Pb adsorption cucumber peels derived material. Reprinted with permission by Elsevier [54].

2.3 Peanut waste-based adsorbents

According to the *Scopus* database more than 180 research articles, investigating the adsorption of the metal and metalloid ions using peanut plant-based materials (including activated carbon, biochar and ashes), have been published since 1972, when the use of peanut skins and shells, among other materials, were tested for the removal of mercury [55].

Based on the published results, peanut shells (also called husks by some authors, although this term could also mean peanut skins) can be used as an efficient and environmentally friendly biosorbent for the removal of metal ions. For example, Witek-Krowiak and her research group [56] determined that the maximum adsorption capacity of peanut shells was 25.39 mg/g and 27.86 mg/g for Cu(II) ions and Cr(III) ions, respectively. The equilibrium was reached within 20 minutes and the uptake of metal ions increased with the increase of the temperature up to 50°C. However, the sorption capacity decreased at 60°C and it was attributed to the probable damage of active binding sites of the biomass. Moreover, this research group used four kinetic models to determine the kinetic parameters and five adsorption isotherm models to describe the biosorption equilibrium – a unique approach compared to the routinely used approach of using only *Langmuir*/ *Freundlich* adsorption and pseudo-first/ pseudo-second order kinetic models.

Abdelfattah and co-workers [57] have correctly stated that *"the major disadvantage of the previously published adsorption research is that most of the research works are still in the lab-scale",* therefore they have used industrial wastewater to investigate the use of peanut husks (i.e., shells) for the removal of different metal ions. The removal efficiency was 100%, 41%, 38%, 30%, and 24% for Pb(II), Cd(II), Mn(II), Co(II) and Ni(II) ions, respectively. Based on the calculated construction and running costs of the constructed pilot scale treatment plant it was also concluded that peanut shells are a cost-effective adsorbent.

The costs of the biosorbent (peanut shells) have also been reported by Ali and co-workers [58]. They estimated that the total cost (including electrical energy, handling, transportation, chemicals, drying) would be approximately 10 EUR (11.35 USD) per ton. In general, this research work is a good example of a well-planned biosorption study. Beyond the sorption experiments at standard laboratory scale and application of well-known adsorption equilibrium and kinetic models, the biosorbent was also characterized using a variety of techniques (i.e., FTIR, SEM, XRD, TGA and BET). In addition, thermodynamic studies were conducted, in-depth explanation of the adsorption mechanism was given and the importance of cost-analysis was highlighted in this work [58].

Interestingly, some researchers have chosen to use solely the term *"groundnut"* instead of the more common term *"peanut",* and it should be remembered when searching for relevant publications. This has been done, for example, by Gupta and Sen [59], who compared the sorption performance of raw groundnut husks (i.e., shells) and citric acid modified groundnut husks. The maximum adsorption capacity of Cu(II) ions calculated by the *Langmuir* isotherm was 33.49 and 15.36 mg/g for raw and modified husks, respectively. Citric acid has also been used in the modification of peanut shells for the simultaneous removal of lead(II) and methylene blue [60].

A comparison of the adsorption capacity between raw and chemically modified peanut shells was carried out by Liu, Sun and Li [61]. Although, the maximum adsorption capacity of epichlorohydrin/ ethylenediamine modified shells was significantly higher than that of the raw shells – 14.17 mg/g versus 6.00 mg/g for Cd(II) ions and 30.72 mg/g versus 1.90 mg/g for Hg(II) ions, the potential health and environmental hazards associated with the use of these toxic substances was not mentioned. In general, the motivation to use hazardous chemicals (e.g., methanol, acrylic acid, dimethylformamide) in the modification of peanut shells is seldom, if ever, discussed by the researchers. An example of an environmentally-friendly modification method includes the use of weak acids and base solutions, where peanut shells and sugarcane bagasse was used for the removal of Sr(II) ions [62]. It was suggested that complexation of metals with oxygen-containing functional groups of the biomass was the major removal mechanism.

2.4 Almond, walnut and hazelnut waste-based adsorbents

A study comparing adsorption of Cu(II) ions in a continuous column mode showed that the maximum adsorption capacity of peanut shells is approximately 2.4 times higher than the sorption capacity of almond shells – 30.59 and 12.88 mg/g, respectively, although the specific surface area of peanut shells was 1.83 m^2/g and that of almond shells – 11.27 m^2/g [63]. Slightly lower maximum adsorption capacity (i.e., 10.53 mg/g) towards Cu(II) ions was observed by another research group [64], which studied biosorption of Cu(II) and Pb(II) ions by almond shells from both a single metal solution and a binary metal mixture.

A recent work by Cataldo et al. [65] demonstrated the use of differential pulse anodic stripping voltammetry (DPASV) technique in the determination of the amount of Pb(II) and Cd(II) ions removed by ground almond and hazelnut shells. They also accentuated the importance of metal speciation studies to explain the metal adsorption data, because each metal species is expected to interact differently with the binding sites of the adsorbent. In another study [66], several adsorbents based on almond shells, namely bleached almond shell, lyophilised-bleached almond shell, and TEMPO ((2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl) oxidised cellulose was used for the removal of Cu(II) ions.

Walnut shells and the residues of sunflower, potato, canola have been used as biosorbents to adsorb heavy metal ions from aqueous solutions using batch experiments [67]. The maximum adsorption capacity of walnut shells followed this order: Cd (76.9 mg/g) > Fe (62.6 mg/g) > Cu (38.8 mg/g) > Zn (33.3 mg/g) > Ni (29.4 mg/g) > Mn (28.6 mg/g). In general, these values are relatively high. However, it must be pointed out that both adsorption and precipitation reactions took place, which was confirmed by the SEM micrographs.

Similar results regarding adsorption of Fe(III) ions were obtained by Halysh et al. [68] and the maximum adsorption capacity was evaluated to be 61.1 mg/g. The maximum adsorption capacity of Cu(II) ions was 63.3 mg/g, and the *Langmuir* isotherm model was used for the calculation of both values. However, in the same study the results obtained from batch isotherm investigations were lower - 49.0 mg/g and 34.0 mg/g for Fe(III) and Cu(II) ions, respectively. It must be noted that the pH was not adjusted within the mentioned study and it is not known, whether precipitation of the metal ions took place. Much lower adsorption capacity (i.e., 5.02 mg/g) of Cu(II) ions has been observed by Wu et al. [69]. Adsorption capacity of raw walnut shells was enhanced to 39.4 mg/g by applying a method of non-thermal plasma in ultrafine water mist, which increased the content of carboxyl groups on the surface of walnut shells. The removal of Cu(II) ions was ensured by chemisorption (ion exchange and/or complexation).

Safinejad and co-workers [70] modified walnut shells with Fe_3O_4 nanoparticles creating a low-cost magnetic adsorbent, which could be separated from the aqueous solution within 20 seconds in the presence of an external magnetic field. FT-IR spectra of modified adsorbent and adsorbent saturated with Pb(II) ions was analyzed and compared. As no differences were observed, it was concluded that physisorption is the main removal mechanism. In another study, almond shells were activated by agitating them with H_2SO_4 at room temperature for 30 min. Afterwards, the material was washed with distilled water and soaked in 1% $NaHCO_3$ solution to remove any remaining acid. Authors stated that activated almond shell contains lignin, cellulose, pentosan, organic acids and tannins which can bind metal ions [71].

Modified pecan nut (belonging to *Juglandaceae* (walnut) family) shells have been used to adsorb Zn(II) ions [72]. It was concluded that by modifying shells with citric acid the maximum adsorption capacity increased 2.5 times (reaching 27.86 mg/g) due to the incorporation of carboxylic groups, and that the intraparticle diffusion controlled the overall adsorption rate of Zn(II) ions.

In summary, Table 3 presents the list of biosorbents derived from peanut, almond, and walnut, with their isotherms, kinetics and the maximum sorption capacities.

Table 3. List of adsorption isotherm and kinetic models for the adsorption of toxic metal(oids) on peanut, almond and walnut waste-based biosorbents.

Biosorbent	Adsorbate	Maximum biosorption capacity; mg/g	Dominant isotherm / kinetic model	Reference
Peanut skins	Hg(II)	820	n/a	[55]
Peanut shells	Hg(II)	220	n/a	[55]
Peanut shells	Cu(II)	25.39	Several models (Langmuir, Sips and Redlich–Peterson)/ pseudo-second order	[56]
Peanut shells	Cr(III)	27.86	Several models (Langmuir, Sips and Redlich–Peterson)/ pseudo-second order	[56]
Peanut shells	Pb(II)	27.03	*Langmuir* / n/a	[57]
Peanut shells	Cd(II)	11.36	*Langmuir* / n/a	[57]
Peanut shells	Mn(II)	14.29	*Langmuir* / n/a	[57]
Peanut shells	Co(II)	6.10	*Langmuir* / n/a	[57]
Peanut shells	Ni(II)	56.82	*Langmuir* / n/a	[57]
Peanut hulls	Cu(II)	14.13	*Langmuir*/ pseudo-second order and intra-particle diffusion	[58]
Peanut shells	Cu(II)	15.36	*Langmuir*/ pseudo-second order	[59]
Citric acid modified peanut shells	Cu(II)	33.49	*Langmuir*/ pseudo-second order	[59]
Peanut shells	Cd(II)	6.00	*Langmuir*/ pseudo-second order	[61]
Epichlorohydrin/ ethylenediamine modified peanut shells	Cd(II)	14.17	*Langmuir*/ pseudo-second order	[61]
Peanut shells	Hg(II)	1.90	*Langmuir*/ pseudo-second	[61]

			order	
Epichlorohydrin/ ethylenediamine modified peanut shells	Hg(II)	30.72	*Langmuir*/ pseudo-second order	[61]
Peanut shells	Sr(II)	9.4	*Redlich-Peterson* / pseudo-second order	[62]
NaOH-treated peanut shells	Sr(II)	17.6	*Redlich-Peterson* / pseudo-second order	[62]
Immobilized peanut shells	Sr(II)	38.0	*Redlich-Peterson* / pseudo-second order	[62]
Peanut shells	Cu(II)	30.59	*Langmuir*/ modified dose response model	[63]
Almond shells	Cu(II)	12.88	*Langmuir*/ *Thomas*	[63]
Almond shells	Pb(II)	26.55	Extended *Sips* / n/a	[64]
Almond shells	Cu(II)	9.44	Extended *Sips* / n/a	[64]
Bleached almond shells	Cu(II)	18.71	*Temkin*/ pseudo-first order	[66]
Lyophilized-bleached almond shells	Cu(II)	28.27	*Langmuir*/ pseudo-second order	[66]
Walnut shells	Cd(II)	76.9	*Langmuir*/ pseudo-second order	[67]
Walnut shells	Fe(III)	62.6	*Langmuir*/ pseudo-second order	[67]
Walnut shells	Cu(II)	38.8	*Langmuir*/ pseudo-second order	[67]
Walnut shells	Zn(II)	33.3	*Langmuir*/ pseudo-second order	[67]
Walnut shells	Ni(II)	29.4	*Langmuir*/ pseudo-second order	[67]
Walnut shells	Mn(II)	28.6	*Langmuir*/ pseudo-second order	[67]
Walnut shells	Cu(II)	63.3	*Freundlich*/ pseudo-second order	[68]
Walnut shells	Cu(II)	5.02	*Langmuir*/ pseudo-second order	[69]

Modified walnut shells	Cu(II)	39.4	*Langmuir*/ pseudo-second order	[69]
Magnetic walnut shell biosorbent	Pb(II)	28.57	*Langmuir*/ pseudo-second order	[70]
Activated almond shells	Zn(II)	5.54	*Freundlich*/ n/a	[71]
Pecan shells	Zn(II)	17.21	*Prausnitz-Radke* / n/a	[72]
Citric acid modified pecan shells	Zn(II)	27.86	*Prausnitz-Radke* / n/a	[72]

n/a: not available

2.4 Pistachio waste-based adsorbents

Pistachio is one of the widely-accessible agricultural wastes and its role in adsorption has been demonstrated for many metal(oid) ions including Cr(VI) [73], Cu [74], Hg(II) [75], Pb(II) [76, 77], Zn(II) [78] (Table 4). For example, Moussavi and Barikbin [73] investigated the adsorption potential of pistachio hull powder to remove Cr(VI) from aqueous solution under different experimental conditions like pH (2–8), temperature (5–50 °C), reaction time (1–60 min), concentration of pistachio shell powder (0.5–8 g/L) and that of Cr(VI) (50–200 mg/L). It was found that adsorption was pH dependent as 99% of Cr was removed after 60 minutes of equilibrium at pH 2 however its efficiency decreased to 52% when pH was increased to 8. Cr(VI) adsorption increased with an increase in temperature indicating the endothermic nature of this process. Turan and Mesci [78] reported that adsorption of Zn(II) increased with an increase in pH and reached a maximum (97% removal) at pH 6 with 1 g/L pistachio shells. Optimum contact time was found to be 10 minutes and the obtained adsorption data followed the pseudo-second order kinetic model ($R^2 = 0.999$).

Siddiqui and Ahmad [76] obtained pistachio shell carbon by pyrolysis of pistachio green shell waste for one hour in furnace at 750 °C. Removal of Pb(II) was up to 24 mg/g at pH 6 (at an initial concentration of 50 mg/L Pb(II) which was associated to the formation of soluble hydroxylated complexes of Pb(II) at this pH. Existence of hydroxyl groups on the surface of adsorbent could lead to the complexation between Pb(II) and surface of adsorbent. The adsorption process followed the pseudo-second order kinetic model and the Pb(II) adsorption data were best fitted by the *Langmuir* isotherm model compared to the *Freundlich* and *Temkin* models. Similarly, Sajjadi et al. [75] reported that activation of pistachio wood waste-derived carbon can improve its adsorption capacity. They investigated the Hg(II) adsorption potential of pistachio wood waste-derived carbon, which was obtained by pyrolysis and activated with ammonium nitrate. They reported that optimal synthesis conditions to synthesize activated carbon with high adsorption efficiency were pyrolysis at 800 °C for 2 h with impregnation of 5 wt% ammonium nitrate/precursor ratio. The obtained activated carbon showed much higher maximum adsorption capacity (202 mg/g) compared to that of a commercial activated carbon (66 mg/g). They observed that adsorption mechanism is mainly controlled by adsorbate-adsorbent dispersion interactions (physisorption) while pore filling and reduction mechanism played a minor role in adsorption.

Pistachio derived biochar has been used for Pb(II) and Cd(II) removal from aqueous solution by Komnitsas et al. [79]. Almost complete removal of both metals (15 mg/L of initial concentration) was observed by 10 g/L of biochar obtained by pyrolysis at 550 °C. Recently, Jalayeri and Pepe [74] investigated the development of biochar from pistachio green hull biomass for the efficient removal of Cu(II) from aqueous solutions. A maximum adsorption of 20 mg/g (at initial concentration of 70-270) was evaluated, and the adsorption kinetic and isotherm data were better fitted by the pseudo second order and *Langmuir* models, respectively. These findings indicate that in addition to the non-modified pistachio waste, biochar or activated carbon derived from it can serve as efficient adsorbents. Moreover, composite adsorbents of pistachio waste with other effective adsorbents can further improve their adsorption efficiency. For example, Asasian et al. [80] developed a composite adsorbent based on activated carbon derived from a mixture of pistachio-nut shells and licorice residues impregnated with zinc chloride. The resulted activated carbon showed strong adsorption capacity (q_m = 147 mg/g) for Hg(II). They reported that adsorption process mainly involved ion exchange and physical adsorption in micro- and meso-pores of adsorbent and filling of these pores by Hg(II) species has been confirmed by SEM characterization (Figure 6). It should, however, be noted that very few studies exist on the use of pistachio in composite adsorbents.

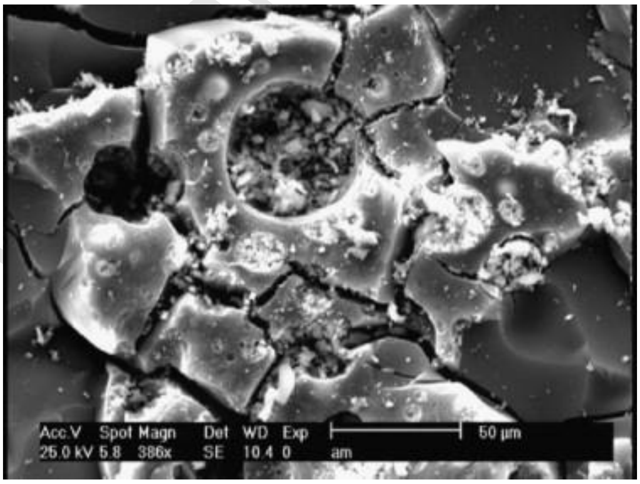

Figure 6. SEM characterization of pores of composite adsorbent filled by Hg(II) species. Reprinted with permission by Elsevier [80].

2.5 Tea waste waste-based adsorbents

Because of the higher content of aromatic, carboxylate, hydroxyl and phenolic groups in tea leaves, the associated biowaste shows an extended ion exchange behaviour which in turn improves its adsorption capacity as highlighted in a recent comprehensive review [81]. Tea waste has shown strong adsorption potential for variety of metals (Table 4) which are discussed in this section. For example, approximately 99% of Zn(II) (50 mg/dm^3 initial concentration) were adsorbed at pH 4.2 onto tea factory waste under batch conditions [82]. Recently, mixed waste tea resulted in comparatively higher Cr(VI) removal (adsorption capacity of 94 mg/g) than coffee ground (adsorption capacity of 87 mg/g) under similar experimental conditions (Cr(VI) concentration of 250 mg/L, pH 2) [83]. Malkoc and Nuhoglu [84] performed column experiments to evaluate the efficiency of tea waste to adsorb Ni(II). Highest Ni(II) adsorption and longest breakthrough time was noted at pH 4. Adsorption decreased with the increase in flow rate as adsorption of 11, 10 and 7 mg/g was noted at 5, 10 and 20 mL/min, respectively. Moreover, adsorption increased with a decrease in particle size (from 1–3 to 0.15–0.25 mm). It should be noted that batch experiments are usually performed to optimize the experimental conditions and to identify the affecting parameters. On the other hand, column experiments are aimed at evaluating the practical applicability of treatment by getting closer to in-situ conditions [85, 86]. Treatment efficiency often decreases in column tests as compared to batch experiments. For example, adsorption of Cu and Pb onto tea waste in column decreased by 40 and 20% compared to corresponding batch data (48 and 65 mg/g, respectively) [85].

Different strategies have been explored to improve the adsorption capacity of tea waste including pre-treatment by *Trichoderma reesei* cellulases [87], *Bacillus* sp. [88], alkali [89, 90], $Ca(OH)_2$ [91], magnetite [92, 93], sulfonation [94]. For example, *Trichoderma reesei* cellulases improved the efficiency of agricultural tea waste to adsorb Cr(VI) highlighting the role of cellulosic material to provide more accessible area for metal adsorption [87]. Hydrolysis by cellulases resulted in a fine structure, more attacked carbon sites and intensive change in the composition of tea waste. Use of tea waste biomass loaded with *Bacillus* sp. (at 15 g/L) adsorbed Cr(VI) (up to 741 mg/g) and phenol (up to 7.8 mg/g) in a co-contaminated solution (with an initial concentration of 100 mg/L and 50 mg/L of Cr(VI) and phenol, respectively) [88]. Yang et al. [91] soaked green tea waste in boiled water followed by its immersion in 0.05 mol/L $Ca(OH)_2$ solution. The obtained product was used for the adsorption of As(III) and Ni(II) in single and binary systems. The maximum adsorption efficiency was observed at pH 3 (for As) and at 7 (for Ni), while the estimated values of the maximum adsorption capacity were 0.42 and 0.31 mg/g for As(III) and Ni(II), respectively [91]. They attributed the adsorption mechanism to ion exchange (mainly by –OH and –COOH functional groups) and interactions between target pollutants and secondary amino groups.

Yang and Cui [89] treated tea residues by soaking them in 0.5 mol/L NaOH for 0.5 h and the obtained product showed significantly higher Pb(II) adsorption efficiency (98%) than non-treated green tea (64%) or green tea residue (70%) at Pb(II) concentration of 50 mg/L. They ascribed this higher adsorption to the removal of impurities by alkali treatment, which results in the exposure of additional adsorption sites [89]. Similarly, Weng et al. [90] subjected black tea waste (BTW) to different pre-treatments for its ultimate use in Cu(II) removal from aqueous solution. The observed order of Cu(II) adsorption efficiency was as following: alkali-treated BTW (0.1 M NaOH) > formaldehyde (10%) washed BTW > ultrasound BTW (47 kHz for 1 h) > pressure steam BTW > untreated BTW > acid washed BTW (0.1 M HNO_3 for 1 h). It should be noted, that all tea wastes were subjected to pressure steam (70 kPa at 100 °C for 20 min) before applying another treatment. They also observed that increase in temperature improves the adsorption efficiency in alkaline medium. Analysis of the associated FTIR data indicated that $^{-}$OH is among the key functional groups responsible for higher adsorption of Cu(II) [90], whereas acid pre-treatment reduced the adsorption efficiency of tea waste. However, Ahsan et al. [94] reported that extensively sulfonated tea waste (formed by pre-treatment with concentrated H_2SO_4 at 70 °C) can adsorb Cr(VI) to an exceptionally high level (438 mg/g). This difference can be associated to the treatment conditions, which may result in the reduction of Cr(VI) to Cr(III) and/or the nature of acid.

Wen et al. [92] reported the adsorption of Cu(II) and Zn(II) by magnetite decorated tea waste. Magnetite is a mixed-valent iron mineral (Fe(II) $Fe(III)_2$ O_4) which has shown strong adsorption potential towards a variety of pollutants [95-98]. Wen et al. [92] decorated magnetite nanoparticles by chemical co-precipitation of Fe(III)/Fe(II) on green tea waste. The obtained product demonstrated high adsorption efficiency with *Langmuir's* estimated maximum adsorption capacities of 95.44 and 68.78 mg/g for Cu(II) and Zn(II), respectively, at pH 6, compared to the maximum adsorption capacities of 68.35 and 54.11 mg/g by magnetite alone. In a binary system, Cu(II) greatly inhibited the Zn(II) adsorption suggesting higher affinity for Cu(II) because of its facile penetration in smaller spaces. They attributed the adsorption to electrostatic attractions and stable complexation between the hydroxyl groups on adsorbent (–OH, –COOH and –NH groups) and Cu(II) or Zn(II). Similar material (nano-magnetite loaded onto tea waste) attained strong adsorption efficiency for Cr(VI) that reached 75.76 mg/g according to the *Langmuir* model [93]. It should be noted that magnetic adsorbents are gaining particular attention due to their quick recovery by magnetic separation and reuse in next treatment cycles. Fan et al. [93] also highlighted the high reusability of magnetic tea waste as >70% Cr(VI) was removed after 5 treatment cycles. They proposed adsorption-coupled reduction as the most plausible mechanism for Cr(VI) removal by magnetic tea waste referring to physical adsorption, electrostatic interaction, reduction, ion exchange, surface complexation but further research is needed to illustrate the conclusive mechanism. In addition to the direct applications, tea waste has also been used to activate carbon electrode for simultaneous removal of Cr(VI) and fluoride [99] and to develop biochar for efficient Cd removal from aqueous solution [100] for efficient metal removal.

Table 4. List of isotherm and kinetic models for the adsorption of toxic metal(oids) on pistachio and tea waste-based biosorbents.

Biosorbents	**Target metals**	**Isotherm models**	**Kinetic models**	**Maximum adsorption capacity (mg/g)**	**References**
Pistachio hull powder	Cr(VI)	*Langmuir*	pseudo-second order	116	[73]
Mixture of pistachio-nut shells and licorice residues impregnated with zinc chloride	Hg(II)	*Langmuir*	pseudo-second order	147.1	[80]
Pistachio shell biochar	Pb(II) and Cu(II)	*Freundlich*	pseudo-second order	1.22 and 1.17 for Pb and Cu	[79]
Pistachio Shell Carbon	Pb(II)	*Langmuir*	pseudo-second order	24	[76]
activated carbon derived from pistachio wood wastes	Hg(II)	*Langmuir, Sips, Redlich-Peterson,* and *Toth*	pseudo-second order	202	[75]
Pistachio green hull	Cu(II)	*Langmuir*	pseudo-second	19.84	[74]

biochar			order		
Tea waste	Cu(II) and Cd(II)	*Freundlich*	Not reported	8.64 for Cu(II) and 11.29 for Cd(II)	[101]
Black tea waste	Cu(II) and Pb(II)	*Langmuir and Freundlich*	Pseudo-second order	48 for Cu(II) and 65 for Pb(II)	[85]
Tea waste hydrolyzed by *Trichoderma reesei* cellulases	Cr(VI)	Not reported	Kinetic model was derived on the basis of redox reaction between Cr(VI) and biomaterial	47	[87]
Alkali treated tea residue	Pb(II)	*Langmuir*	Pseudo-second order	64.10	[89]
Alkali treated tea residue	Cu(II)	*Langmuir*	Pseudo-second order	43.18	[90]
Tea waste biomass loaded with Bacillus sp.	Cr(VI)	*Redlich–Peterson*	Pseudo-second order	741.38	[88]
$Ca(OH)_2$ modified tea waste	Ni(II) and As(III)	*Freundlich* for Ni(II)) and *Langmuir* for As(III)	Pseudo-second order	0.3116 for Ni(II) and 0.4212 for As(III)	[91]
Magnetite-decorated tea waste	Cu(II) and Zn(II)	*Langmuir*	Pseudo-second order	95.44 for Cu(II) and 68.78 for Zn(II)	[92]
Magnetite-decorated tea waste	Cr(VI)	*Langmuir*	Pseudo-second order	75.76	[93]
Sulfonated tea waste	Cr(VI)	*Langmuir*	Pseudo-second order	438	[94]
Mixed tea waste	Cr(VI)	Freundlich	Pseudo-second order	94.34	[83]

3. Thermodynamic studies

In all adsorption studies, the estimation of the thermodynamic parameters (Gibbs energy change: ΔG^0, enthalpy change: ΔH^0, and entropy change: ΔS^0) is essential and indispensable. The thermodynamic parameters not only predict the adsorption mechanism (e.g., physical and chemical) [102], but also provide information about the spontaneity of the adsorption process and examine the temperature range in which the adsorption is favorable or not [103]. The magnitude of $\Delta \mathrm{H}^0$ may also help to identify the type of adsorption. The heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, *i.e.*, 2.1–20.9 kJ/mol, while the heats of chemisorption generally fall into a range of 80–200 kJ/mol [104].

Generally, van’t Hoff approach is used in almost all studies relevant to adsorption of pollutants from contaminated liquid phases, which is a an easy and suitable alternative to calorimetric measurements [105]. The ΔG^0 can be computed from equation 1 (van't Hoff equation), and it is connected with ΔH^0 and ΔS^0 through equation 2.

$$\Delta G^0 = -RT \ln K \tag{1}$$

$$\Delta G^0 = \Delta H^0 - \mathrm{T}\Delta S^0 \tag{2}$$

The constant R is the universal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin and K is the thermodynamic equilibrium constant.

Tables 5 contains the calculated thermodynamic parameters for adsorption of heavy metals onto various agricultural adsorbents. The process of pollutants from aqueous solutions onto adsorbent should be spontaneous to be considered as a suitable economic process. The spontaneity and feasibility properties of an adsorption system are proved by the negative sign of $\Delta G^{\mathbf{o}}$ values. The data summarized in Table 5 show that the removal process of heavy metals ion on all the tabulated adsorbents happens spontaneously and naturally. On the other hand, the sign of ΔH^{o} value is positive for 17 adsorption systems in Table 5, out of total 29 cases. The positive values of ΔH^{o} reflect endothermic nature of the adsorption process, which is associated by an increase in the adsorption capacity of the adsorbent at higher temperatures. Conversely, the negative values of ΔH^{o} exhibit the exothermic nature of the adsorption process, which is associated by a decrease in the adsorption capacity of the adsorbent at higher temperatures. In addition, the sign of $\Delta S°$ shows that whether the organization of the adsorbate at the solid/solution interface during the adsorption process becomes less ($\Delta S° < 0$) or more ($\Delta S° > 0$) random. The data exhibited in Table 5 shows that, out of the adsorption systems tabulated, only 9 systems (31%) exhibited a negative entropy change. These results reveal that, for a large percentage of adsorption system, the organization of the adsorbate ions at the solid/solution interface becomes more random during the adsorption process, which is usually attributed to the liberation of water of hydration during the adsorption process [106].

Nevertheless, it should be concerned that the values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ reported in Table 5 might be wrongly calculated, using incorrect constants as thermodynamic equilibrium constant.

A literature survey indicates that, unfortunately, van't Hoff equation is used in different manners without any consideration on the concept of physical-chemistry of equilibrium. In the past decades, the researchers have faced with some struggles in calculation of thermodynamic parameters for adsorption processes [107]. In fact, suggesting different procedures like using $K_c = \frac{(C_o - C_e)}{C_e}$, $K_d = \frac{q_e}{C_e}$, K_g (the constant of the best fitted isotherm model), etc. as thermodynamic equilibrium constant for calculation of thermodynamic parameters has misled the researchers involved in the field of adsorption science and technology. Frankly speaking, using wrong constant as thermodynamic equilibrium constant in van't Hoff equation has caused many researchers to report erroneous thermodynamic parameters. To be used in van't Hoff equation for calculation of thermodynamic parameters, the derived thermodynamic equilibrium constant for any adsorption system should have these two properties [108]: (i) it should be dimensionless and (ii) its derivation manner should be consistent with the concepts of physical-chemistry of equilibrium. From this point of view, the value of K_g (the constant obtained from the best isotherm model fitted) has no parallel for deriving the correct thermodynamic equilibrium constant for using in van't Hoff equation [108].

The correct thermodynamic equilibrium constant (K_e°) is defined as [108, 109]:

$$K_e^{0} = \frac{(1000.Kg.\text{molecular weight of adsorbate. standard concentration of the adsorbate})}{\text{activity coefficient of adsorbate}} \tag{3}$$

where γ is the coefficient of activity (dimensionless), the standard concentration of the adsorbate is 1 mol L^{-1}, and $K°_e$ is the thermodynamic equilibrium constant that is dimensionless [108, 109]. It is calculated by converting the units of K_g (the constant obtained from the best isotherm model fitted, such as K of the Liu equilibrium model, K of the Sips isotherm, or K_L of the *Langmuir* equilibrium isotherm), that is initially given in L mg^{-1}, but its dimension is finally concerted to L mol^{-1} [108]. This conversion is obtained through equation 3, and the dimensionless value of $K°_e$ is acquired by multiplication of the value of K (L mg^{-1}) by 1000, to convert L mg^{-1} into L g^{-1}, and subsequently multiplying the result by the molecular weight of the adsorbate (g mol^{-1}) and the unitary standard concentration of the adsorbate (1 mol L^{-}

^{1}), and finally dividing the result by the activity coefficient (dimensionless) [108]. For this calculation, it is considered that the adsorbate solution is very diluted and, therefore, one can consider the activity coefficient as unitary [108].

Anyway, since thermodynamic studies are of vital value and are indispensable in studying some aspects of adsorption systems, like adsorption mechanisms involved, feasibility extent, spontaneity degree, etc., it is strongly recommended that researcher use true thermodynamic equilibrium constants for estimation of thermodynamic parameters.

Table 5. List of thermodynamic parameters for adsorption of potentially toxic metal(oids) onto various agricultural biosorbents.

Biosorbent	**Heavy metal(oid)s**	**T**	**ΔG^o (kJ/mol)**	**ΔH^o (kJ/mol)**	**ΔS^o (kJ/mol K)**	**References**
Watermelon waste-based biosorbents						
Xanthated water melon rind	As(III)	293	−0.38	86.86	0.30	[16]
		308	−0.25			
		318	−0.17			
Citric acid modified water melon rind	As(III)	293	−0.30	67	0.24	[16]
		308	−0.19			
		318	−0.14			
Xanthated water melon rind	As(V)	293	−0.34	80.28	0.03	[16]
		308	−0.20			
		318	−0.15			
Citric acid modified water melon rind	As(V)	293	−0.32	86.05	0.58	[16]
		308	−0.14			
		318	−0.13			
Raw watermelon rind	Cd(II)	293	−1.23	−19.72	−0.064	[18]
		298	−0.5			
		303	−0.33			

		308	−0.24			
Microwave-radiated watermelon rind in the presence of H_2O_2	Cd(II)	293	−3.15	−19.48	−0.057	[18]
		298	−2.33			
		303	−2.25			
		308	−2.25			
Microwave-radiated watermelon rind in the presence of NaOH	Cd(II)	293	−1.86	−19.92	−0.063	[18]
		298	−0.89			
		303	−0.85			
		308	−0.85			
Microwave-radiated watermelon rind in the presence of deionized water	Cd(II)	293	−3.38	−19.99	−0.057	[18]
		298	−2.59			
		303	−2.49			
		308	−2.47			
Watermelon shell	Cu(II)	303	−4.58	5.49	0.033	[24]
		313	−4.92			
		323	−5.25			
Watermelon seed hulls	Cu(II)	293	−3.1461	17.66	0.072	[23]

		313	−5.1879			
		333	−5.9541			
Watermelon rind treated with 0.1 M HCl	Cu(II)	303	−1.737	−0.117	−0.002	[22]
		313	−1.638			
		323	−1.503			
Watermelon seed hulls	Pb(II)	293	−2.9378	24.47	0.094	[23]
		313	−5.0932			
		333	−6.6648			
Watermelon rind treated with 0.1 M HCl	Pb(II)	303	−8.489	−1.035	−0.009	[22]
		313	−7.104			
		323	−6.418			
Potato and cucumber waste-based biosorbents						
Potato Peels Charcoal (PPC)	Cu(II)	303	−12.39	−37.84	−0.0849	[28]
		313	−10.6			
		323	−10.44			
		333	−9.66			
Carbons derived from Potato Peels (activated with H_3PO_4 and pyrolysis at 600 °C in N_2)	Co(II) 10 mg/L	298	−13.44	52.94	0.226	[47]

		318	−15.65			
		338	−17.98			
Carbons derived from Potato Peels (activated with H_3PO_4 and pyrolysis at 600 °C in N_2)	Co(II) 700 mg/L	298	−0.48	15.92	0.056	[47]
		318	−1.09			
		338	−1.60			
Cucumis sativus (cucumber) peels	Cd(II)	298	−8.24	−2.125	0.0087	[50]
		308	−6.60			
		318	−6.09			
Cucumis sativus (cucumber) peels	Pb(II)	298	−0.77	−1.225	0.0045	[51]
		308	−1.23			
		318	−1.43			
Cucumis sativus (cucumber) peels HCl modified	Cd(II)	298	−2.06	+15.8	0.0055	[52]
		308	−2.95			
		318	−5.01			
Cucumis sativus (cucumber) peels	Pb(II)	293	−1.57	17.94	0.06644	[53]
		313	−2.82			
		333	−4.24			

Cucumis sativus (cucumber) peels	Cu(II)	293	−6.21	42.15	0.16662	[53]
		313	−11.21			
		333	−12.72			
Peanuts and almond waste-based biosorbents						
Peanut shells	Cu(II)	303	−21.56	−31.04	−0.074	[59]
		308	−21.42			
		313	−21.09			
		318	−21.36			
		323	−20.63			
		328	−20.82			
		333	−21.05			
Citric acid modified peanut shells	Cu(II)	303	−24.30	−61.70	0.167	[59]
		308	−23.79			
		313	−22.36			
		318	−20.83			
		323	−20.77			
		328	−20.64			

		333	−20.50			
Bleached almond shells	Cu(II)	303	−6.603	25.879	0.107	[66]
		318	−8.226			
		333	−9.818			
Lyophilized-bleached almond shells	Cu(II)	303	−4.797	−23.411	−0.061	[66]
		318	−3.723			
		333	−2.961			
Pistachio and tea waste-based biosorbents						
Pistachio Shell Carbon	Pb(II)			5.47	0.047	[76]
		303	−9.01			
		313	−9.52			
		323	−10.1			
Alkali treated tea residue	Cu(II)	277	−19.04	2.89	0.079	[90]
		289	−19.99	2.89	0.079	
		299	−20.71	2.89	0.079	
		311	−21.72	2.89	0.079	
Magnetite-decorated tea waste	Cr(VI)	298	−2.5817	11.964	0.048	[93]
		308	−3.0214			

		318	−3.5593			
Sulfonated tea waste	Cr(VI)	298	−2.19	16.85	0.058	[94]

4. Conclusions and future work

This article reviewed publications reported in the literature so far based on the use of agricultural biomass, as raw and modified forms (e.g. chemically modification, pre-tretaments, biochar, hybrid materials), to remove toxic metal(oid)s from wastewaters. Good removal efficiencies were reached in the majority of studies. Regarding maximum adsorption capacities, values from 0.38 to 820 mg/g were obtained, which is highly affected by the biosorbent nature and the system metal-biosorbent. Moreover, most of these studies are focused on kinetic, equilibrium and thermodynamic aspects of biosorption, showing *Langmuir* and pseudo-second order models as dominant isotherm and kinetic models, respectively.

Based on the present review following future perspectives and challenges can be commented:

I) Agricultural biomass involves a wide group of biosorbents that are widespread and easy to obtain, suggesting that several non-previously studied biosorbents can be assayed for the removal of toxic metal(oid)s.

II) The majority of studies refer to the use of agricultural biomass for the removal of a a single toxic metal in “ideal” aqueous solution. The use of real samples is mandatory in order to apply the biosorption process considering competition reactions and possible matrix effects that can be associated with the complex chemical composition of real samples.

III) Some studies are offering the use of a magnetic field as an attractive alternative technique for phase separation compared to conventional practices (e.g. filtration, centrifugation). Additional studies and alternatives for the separation procedure are welcome.

IV) Some studies use agricultural biosorbent in combination with other material (e.g. nanoparticles). It is desirable to continue working in this way, creating new hybrid materials with superlative properties for the removal of pollutants.

V) Most studies are performed at lab-scale and as batch-type experiments. Hence, it is necessary to continue with including continuous systems and scaling-up the biosorption process.

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Graphical Abstract

Highlights

- Review on the use of agricultural biomasses as adsorbents for toxic metal removal
- Comprehensive compilation of factors affecting the adsorption
- Presentation and summary of best isotherm, kinetic models and maximum adsorption capacities
- Extensive discussion of the thermodynamic aspects associated with the adsorption process