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Heavy metal removal from wastewaters by agricultural waste low-cost adsorbents: hindrances of adsorption technology to the large scale industrial application – a review

Alphonse Habineza[a], Jun Zhai[a,*], Theoneste Ntakirutimana[b], Fu Ping Qiu[a], Xiaoting Li[a], Quanfeng Wang[a]

[a]*Faculty of the Built Environment, School of Urban Construction and Environmental Engineering, Department of Environmental Engineering, Key Laboratory of Three Gorges Reservoir Region's Eco-Environment, Chongqing University, Chongqing 400045, China, Tel. (+86) 13637966883; Fax: +86 23 65126313; email: zhaijun@cqu.edu.cn (J. Zhai), Tel. (+86) 15730225754; email: alphonse_habineza@hotmail.com (A. Habineza), Tel. (+86) 17783490217; email: 1054402911@qq.com (F.P. Qiu), Tel. (+86) 15736244421; email: s20111310@163.com (X. Li), Tel. (+86) 18883723715; email: 1804650423@163.com (Q. Wang)*

[b]*College of Medicine and Health Sciences, School of Public Health, Environmental Health Department, University of Rwanda, Republic of Rwanda, Tel. (+250) 789453462; email: tntaki@yahoo.co.uk*

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ABSTRACT

This review paper provides a critical examination on heavy metal removal from wastewaters by the agrowaste low-cost adsorbents, with focus on: (i) water pollution by heavy metals and their adverse effects on flora and fauna, (ii) extent and efficiency of the heavy metal removal from the real industrial effluents by agrowaste adsorbents, (iii) advantages and hindrances of adsorption technology to the large scale industrial application, (iv) heavy metal adsorption mechanisms, (v) biosorbents behavior in a multimetal adsorption system and (vi) biosorbent regeneration and desorptive studies. This was carried out through an extensive examination of relevant published literature on the topic. The review paper found that the agricultural low-cost adsorbents have proven to remove heavy metals from aqueous solutions to some extent and are promising alternatives. However, it is noticeable that the behavior of the low-cost adsorbents with respect to the removal of the heavy metals from the real industrial wastewaters is not well known. In nearly all successful studies, conclusions on these materials potential to treat industrial wastewaters laden with heavy metals are based on the simulations drawn from the treatment of synthetic wastewaters. Furthermore, the prominent agricultural low-cost adsorbents such as *Carica papaya*, maize cob, soybean oil cake, banana peel, walnut shell, sesame leaf and stem, and mango peel, and many others which were proven to have a high adsorption capacity (mg/g): 1,666.67, 495.9, 476.2, 131.56, 151.5, 84.74, and 68.92, respectively, were investigated under the conditions of synthetic wastewaters and not with real industrial effluents. Moreover, the residual metal ion concentrations were higher than the permissible discharge standards. Hence, their applicability to the industrial effluents is still problematic. The main hindrances are: (i) imbalance between laboratory studies and pilot studies at large scale; (ii) low-cost adsorbents have been applied to the solutions which do not reflect the real heavy metals' concentrations found in industrial effluents; (iii) residual concentrations are higher compared with the discharge standard limits and (iv) economic and costs evaluation studies for practical material engineering design and low-cost adsorbents commercialization information are missing. We provide future research directions for efficient removal of heavy metals from the industrial effluents.

Keywords: Adsorption technology; Agricultural waste low-cost adsorbents; Heavy metals; Hindrances; Industrial wastewaters

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* Corresponding author.

1. Introduction

The vital role of water in sustaining life on earth is undeniable. Even though approximately 70% of the earth's surface is covered by water [1], only a very small fraction of freshwater estimated at 0.03% [2] is accessible. Evidence of worldwide scarcity of clean water [2] and growing limitations on fresh surface and groundwater accessibility [3] has been reported as a result of the population exponential growth and economic activities increase [4]. Obviously, this high demand requires a rational management of the limited water resources. Unfortunately the recent urbanization rate, commercial and mining activities coupled with industrial development has largely contributed to the pollution of waters by a variety of pollutants including heavy metals in particular [5]. Contrary to many other contaminants, heavy metals cannot be biodegraded, rather they bioaccumulate and damage aquatic fauna and environment as well [1,6,7].

Research studies [8,9] have proven that at very low concentration beyond the tolerance levels heavy metals cause various noxious effects on ecosystem and human beings. Adverse effects reported in the literature include the reduction of species richness and biomass, changes in the type of biota, energy and nutrient flow [9], destruction of aquatic life and reduction of its reproductive potential [10] and carcinogenicity to the human beings [7,11]. Disruption of the nervous system and liver, enzymatic activity [5], diarrhea, nausea, renal disruption, cancer problems [6,12], autoimmunity and even death of people and animals [12,13] have also been reported. Ordonez et al. [14] reported a significant decrease of taxa richness and percentage of Ephemeroptera, Plecoptera and Trichoptera as a result of high sediment concentrations of metals. Moreover, the reductions in abundance of macroinvertebrates and mayflies were observed in zones highly polluted by heavy metals [14]. Studies [9,15] performed on various crops namely spinach, turnip, millet, wheat, tomato, carrot and rice have proven that significant reduction of their growth and development were attributed to the accumulation and transfer of heavy metals in these plants. The overall consequence was a low yields subsequent to the crops irrigation by untreated industrial effluents (IEs) and/or crop plantation on polluted soils. Substantial killing of the natural wetland vegetation due to the discharge of groundwater contaminated by heavy metals had been previously reported by Lee and Saunders [16]. Recent study by Manzano et al. [17] has observed the genotoxicity effects on mammalian metabolizing cells (hepatoma tissue culture) caused by the waters polluted by Zn. DNA strand breaks and chromosomal aberrations in humans [18] and meristematic root cells of *Allium cepa* (onion) [17] were reported to be caused by Hg and Ni and Cu, respectively. Many other various noxious effects of heavy metals to humans, their symptoms and insights into the toxicity mechanisms have been comprehensively reviewed by Jan et al. [18] and reported in many other literatures.

Conventional methods such as chemical precipitation, chemical oxidoreduction, solvent extraction, ion exchange, cementation, filtration and reverse osmosis, electrochemical and evaporative methods [5,7,19,20] have been employed to remove heavy metals from the polluted waters. However, several research studies have shown that these treatment technologies are expensive in both material and operation, inefficient, time and space consuming, much energy and more chemicals demanding which increase the contaminants load, and consequently the secondary pollution [1,6,20,21]. Moreover, Uddin [7] has recently reported that the aforementioned technologies are not appropriate for the treatment of waters polluted with low concentrations of heavy metals. Hence, their subsequent discharge is more likely to threaten the environment and living organisms. These drawbacks have prompted the need to search for the cost-effective and environmentally friendly technologies for heavy metal removal from the wastewaters.

For many years up to present time, tremendous efforts have been made and invested in the exploitation of agricultural wastes, first, as an alternative method to the conventional treatment technologies, then as a rational waste valorization, and third, as a way of heavy metals recovery and reuse [1,20]. Since then, many low-cost adsorbents have been prepared and investigated for their ability to uptake heavy metals from the polluted waters. Most of all studies concluded that adsorption technology based on low-cost adsorbents, often called biosorption is the least expensive and effective separation method to treat waters laden with heavy metals [22], and therefore, the low-cost adsorbents are promising alternatives, eco-friendly, cost-effective and can be used to treat wastewaters including IEs laden with heavy metals [23]. However, these conclusions are based on experimental studies performed on synthetic wastewaters (SWWs) often with single-metal adsorption system whose composition and metal concentrations are completely different from those of the real IEs. Hence, knowledge about the extent and efficiency of the heavy metal removal from the real IEs by the low-cost adsorbents is limited. Furthermore, little information on the biosorbents behavior in a multi-metal adsorption system and complex wastewater mixture is available. Moreover, the limitations of the low-cost adsorbents are often overlooked in the literature. The present study review seeks to gather and compile knowledge scattered in various literature and provide insights on aforementioned issues for future research studies to bridge gaps and imbalance discovered from the available data.

2. Heavy metals in industrial effluents and treatment issues

Water pollution by the heavy metals mainly generated by the chemical industries has been and is still a big challenge throughout the world. Some researchers [24] perceive it as the most concerned theme of research in the contemporary period. Studies have reported that battery manufacturing industries, electroplating factories, metal surface finishing and metal plating companies, metallurgical, petrochemical process, tannery, plastic, paint, fertilizers, chemical manufacturing, pharmaceutical and mining industries produce enormous wastewaters containing high quantities of heavy metals (Table 2), and therefore, are considered as the big water polluters [2,8,10,20,22,25,26]. Heavy metals such as Pb, Zn, Cu, Cd, Cr, Ni, Mn, Hg and As have been listed by the US EPA and reported to be of a great environmental concern [27,28], and the most common encountered in IEs or urban wastewaters (Table 1) [25,29,30]. While chromium, cadmium, lead and zinc were reported, in some literature, to be the most discharged

Table 1
Heavy metal present in various industrial wastewaters [8,33–36]

Industry	Heavy metals									
	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn	Fe	Co
Pulp and paper mills	NA		X	X	X	X	X	X	NA	NA
Leather tanning	NA	X	X	X	NA	X	X	X	X	X
Organic chemistry	X	X	X	NA	X	X	NA	X	NA	NA
Alkalis, chlorine	X	X	X	NA	X	X	NA	X	NA	NA
Electroplating	NA	X	X	X	NA	X	X	X	X	X
Fertilizers	X	X	X	X	X	X	X	X	NA	NA
Petroleum refining	X	X	X	X	NA	X	X	X	NA	NA
Organic dye production	NA	X	X	X	NA	X	X	X	X	X
Steel works	X	X	X	X	X	X	X	X	NA	NA
Aircraft plating, finishing	NA	X	X	X	X	NA	X	NA	NA	NA
Non-ferrous metallurgy	NA	X	X	X	NA	X	X	X	X	X
Battery industry	NA	NA	X	X	NA	X	NA	X	X	NA
Pharmaceutical industries	NA	X	NA	X	NA	X	NA	X	X	NA

Note: X – presence; NA – no value available in the literature consulted.

into the environment, others indicated that Pb, Ni, Cd and Hg were defined as priority hazardous substances [31]. The latter metal has been shown to be the most toxic [18,32], and its pollution is regarded as of highest environmental and human-threatening concern particularly in the form of methylmercury compound [24]. Chon et al. [31] found that Ni, Pb, Cd and Hg are the mostly discharged into the water bodies while Khayatzadeh and Abbasi [28] indicated that Pb, Cd and Hg were proven to be non-essential elements and recognized to cause, in their bivalent form, severe toxic effects in higher animals upon acute or chronic exposure.

The treatment and removal of heavy metals from IEs to achieve the standards for effluent discharge has been a great challenge due to essentially the high cost in both energy [3] and materials requirements, lack of cheaper treatment technologies, inefficiency and secondary pollution as well as the management issues of the waste generated [37]. Furthermore, it is reported in many literature around the world that strict environmental regulations and stringent discharge standards [2] imposed to the polluting industries, failure of the competent authorities to enforce existing laws and stop the illegal discharge of IE [38] exacerbate and worsen the situation. Consequently, untreated or inappropriately treated domestic and IEs are directly discharged into the receiving environment particularly, water bodies [9,17,34,35,38–42]. Furthermore, most of those authors reported that these untreated IEs contain many other pollutants in addition to the heavy metals. Moreover, they observed that most of the values experimentally found were far beyond the standard discharge limits recommended by various international organizations such as World Health Organization (WHO) and US EPA. Lokhande et al. [39] and Tafesse et al. [41] highlighted the urgent necessity to take and implement appropriate actions (proper treatment of IEs) to cope with the prevailing situation masked by the short-term economic wealth and, therefore, avoid subsequent irreparable ecological long-term harm. In the same line, Singh and Ram [42] have emphasized that higher level of heavy metal concentrations in 10 electroplating IEs (mean values in Table 2) than the recommended standards necessitated a proper preventive mechanism for sludge treatment, recovery and disposal. Furthermore, the study highlighted a positive correlation between these concentrations and their impacts on land, groundwater and surface water bodies. On the other hand, studies by Chon et al. [31] and Salihoglu [38] raised concerns over the works and waste water treatment plants (WWTPs) which were often designed and regulated for suspended solids, biological oxygen demand, chemical oxygen demand and nutrients.

2.1. Industrial effluent and WWTPs pollution contribution to the water bodies

Studies conducted in UK by Chon et al. [31] found that the level of treatment with respect to the values found in 15 WWTPs effluents ranged from 64% to 97.67% for Cd, 80.58% to 92.39% for Pb, 81.48% to 93.33% for Hg and 22.35% to 67.53% for Ni (the mean metal concentrations in these WWTPs influents alongside with removal efficiencies are given in Table 2). It was also found that the WWTPs contributed 37%, 31%, 36% and 60% of the total cadmium, lead, mercury and nickel, respectively, to the pollution of the Aire and Calder rivers. Direct industrial discharge accounted for 1% and 3% for Pb and Ni, respectively. Other fractions were attributed to other sources such as urban surface and agricultural runoffs, natural influence, atmospheric deposition and landfill leachates. While estimating the spatial metal distribution in rivers, it was found that the maximum concentration values of 0.47, 8.54, 0.05 and 10.17 μg/L for Cd, Pb, Hg and Ni, respectively, were caused by the discharge of WWTP effluents. The total metal loads (in ton/year) in these rivers were found to be 0.24, 3.31, 0.04 and 4.55 for Cd, Pb, Hg and Ni, respectively [31]. Similarly, Salihoglu [38] found that the metal concentrations in the two WWTPs effluents (in μg/L) in Turkey were 28 and 44 for As; 5 and 7 for Cd; 22 and 35 for Cr; 13 and 12 for Cu;

Table 2
Industrial effluents and/or WWTPs influents mean heavy metal concentrations (μg/L) and removal efficiency (values in brackets) by conventional methods

Wastewater type/study country		Heavy metals (μg/L)												Ref.
		Cd	Cr	Cu	Ni	Pb	Hg	As	Fe	Zn	Mn	Sb	Sn	
MIWWTPs	France	0.69 (83)	9.42 (73)	65.17 (84)	10.92 (16)	18.56 (96)	–	–	682.4	–	–	–	–	[38]
	Brazil	0.15 (60)	6.87 (17)	17.31 (44)	–	37.42 (40)	–	–	–	79.20 (45)	52.53 (11)	–	–	[38]
	Thailand	2.33 (58)	18.56 (58)	455.05 (62)	32.21 (19)	13.97 (66)	–	–	1,727.1 (84)	310.93 (49)	209.32 (47)	–	–	[38]
	Greece	3.3 (54)	40 (50)	79 (58)	770 (44)	39 (30)	–	–	480 (20)	470 (43)	67 (71)	–	–	[38]
	Italy	1.0 (70)	17.8 (79)	108 (88)	46 (54)	31.1 (88)	–	8.4 (64)	4,650 (79)	356 (62)	91 (58)	–	–	[38]
	Poland	13 (14)	–	100 (52)	–	50 (33)	–	–	–	470 (87)	–	–	–	[38]
	Turkey	18 (61.11)	456 (92.32)	48 (72.91)	77 (42.85)	87 (70.11)		105 (58.09)	1,571 (80.14)	405 (60.24)	114 (57.89)	380 (60.26)	468 (41.02)	[38]
	Turkey	7 (28.57)	147 (85.03)	51 (76.47)	66 (50)	49 (48.97)	–	78 (64.10)	2,478 (86.44)	1,266 (73.77)	154 (58.44)	209 (38.27)	367 (32.15)	[38]
	UK	0.73[a] (80.82)	–	–	16.45[a] (56.96)	25.7[a] (86.49)	0.35[a] (94.85)	–	–	–	–	–	–	[31]
EPIE	Poland	183	125,600	32,950	218,040	1,670	–	–	129,980	250,000	–	–	–	[8]
FRO	Nigeria	55	75	150	103	107	–	–	–	120	–	–	–	[50]
PSD	Nigeria	530	–	2,930	–	730	–	–	7,010	330	–	–	–	[36]
RR	Bangladesh	–	–	–	–	17	–	–	680	45	–	–	–	[51]
SE	–	6,850	110	13,520	740	32,860	60	280	9,210	26,130	–	–	–	[52]
WWTPE	Tunisia	–	167,210	–	–	–	–	–	–	16,000	–	–	–	[43]
EPIE	India	7,900[b]	32,420[b]	14,750[b]	151,516[b]	7,140[b]	–	–	–	238,660[b]				[42]
PIE	Nigeria	40	–	280	–	40	–	–	350	2,620	–	–	–	[35]
BIE	India	–	3.7	6.1 (52.45)	–	32.3 (31.29)	–	–	10	38 (84.21)	–	–	–	[34]
PMIE	India	1,210	48,410	7,360	3,540	1,110	–	–	212,000	50,910	–	–	–	[30]
TTIE	Pakistan	215	800	1,800	–	4,800	–	–	8,350	3,000				[48]
LTE	Poland	56	1,260	49	302	120	–	–	5,100	172	–	–	–	[8]

Note: MIWWTPs – municipal and industrial wastewater treatment plants; EPIE – electroplating industrial effluents; FRO – flood run off; PSD – point source discharge; RR – Rupsha river; SE – smelter effluent; PIE – pharmaceutical industrial effluent; BIE – battery industrial effluent; PMIE – paper mill industry effluent; TTIE – tanneries and textile industrial effluent; LTE – leather tanning effluent; WWTPE – waste water treatment plant effluent.

[a] Data are the mean of 15 WWTPs influents. Consequently, removal efficiency (values in brackets) was calculated based on the mean in effluents.

[b] Data are the mean of 10 industrial effluents.

312 and 336 for Fe; 33 and 44 for Ni; 25 and 26 for Pb; 161 and 332 for Zn, 64 and 48 for Mn, 129 and 151 for Sb, and 249 and 276 for Sn. According to the influent concentrations (Table 2), these effluent concentrations correspond to the treatment efficiency of 64.1% and 58.09% for As, 28.57% and 61.11% for Cd, 85.03% and 92.32% for Cr, 72.91% and 76.47% for Cu, 80.14% and 86.44% for Fe, 50% and 42.85% for Ni, 48.97% and 70.11% for Pb, 60.24% and 73.77% for Zn, 58.44% and 57.89% for Mn, 38.27% and 60.26% for Sb, and 32.15% and 41.02% for Sn. This clearly indicates that the discharged effluents contain heavy metals in various proportions. The same study by Salihoglu [38] also reported high metal concentrations in both influents and effluents of different WWTPs from different literature (data also presented in Table 2).

Belhaj et al. [43] have recently found that the influent in one WWTP in South-Eastern Tunisia contained the mean concentrations of 167.21 and 16 mg/L for Cr and Zn, respectively. Lee and Saunders [16] assessed the levels of groundwater contamination by a lead car-battery recycling plant in Alabama, USA, and found that the maximum contaminant levels for Pb, Cd and Fe were 15, 5 and 300 μg/kg, respectively. It was reported that the contamination level was largely greater than the values recommended by US EPA. Sankpal and Naikwade [10] found that high levels ranging from 0.072 to 2.3 mg/L; 0.647 to 2.34 mg/L and 6.62 to 19.38 mg/L for Cu, Cr and Fe, respectively, in pharmaceutical IE are indiscriminately and openly discharged into the surface waters without prior treatment. Furthermore, Li et al. [44] have recently reported that many rivers in China, in particular Xiawangang River, have been suffering from a long-term and high level metal pollution caused by the discharge of industrial wastewaters and municipal sewage. This study has revealed that the sediments collected from the wastewater drainage outlet at Xiawangang River contained (mg/kg) 174.8 of Cu, 94.4 of Cd, 1,311.3 of Zn and 380.6 of Pb. It has been highlighted that these concentrations, particularly Cd, are highly exceeding the Chinese environmental quality standards. In the same line, Singh and Ram [42] noted that the impacts of the higher levels of IE metal concentrations on the environment, particularly land, groundwater and surface water bodies were correlated. Similarly, Nawab et al. [45] have shown that high concentrations of Cd (0.012 mg/L), Pb (0.016 mg/L), Ni (0.077 mg/L) and Cr (0.061 mg/L) beyond the permissible limits [46,47] were observed in some water samples used for drinking and irrigation purposes. The same study has reported that the water resources were degrading at alarming rate due to the over contamination and improper usage of waters and that the local community was at high health risk. Likewise, Hamid et al. [48] have recently assessed the concentrations of different heavy metals contained in wastewaters from untreated municipal sewage and IEs (tanneries and textile industries) and used for vegetables' irrigation. The study has observed that the mean concentrations (Table 2) of the heavy metals assessed (Cd, Cr, Zn, Cu, Fe and Pb) in all wastewater samples were much higher than the permissible discharge limits [46] and irrigation water standards [49].

From the data reported in Tables 2 and 3, it is apparent that the concentrations of heavy metals in IEs are variable depending on the type of industry, raw materials and additives used, the production processes and the system organization, the source and data collection point. For example, the flood run-off water was reported to receive the effluent discharge from the Benin City which is an industrial park [50]. The point source discharge was described as a source receiving several effluents from various manufacturing industries namely agrochemical, pharmaceutical, paints, dyes, etc. [36]. The sampled site of Rupsha River (Bangladesh) was characterized as being the main IE discharge site [51]. Hence, the determination of the fixed values can be only done based on individual industrial investigation. Furthermore, it can be seen from Table 2 that high concentration levels of heavy metals in IEs are above the toxicity thresholds and recommended limits (Table 3). Previous and recent research studies [8,36,42,44,48,50] have reported the same observations. Those effluents become influents for WWTPs where these treatment facilities are available. However, given the rigorous discharge standards coupled with the high cost and/or inefficiency of the conventional treatment technologies, the hypothesis of effluents dilution before being transferred to the treatment facilities or discharged to the water bodies to achieve the maximum permitted values may not be ignored or excluded. This practice is, however, restricted by the safety guidelines for waste management facilities [54].

Regarding the WWTPs effluents, Fig. 1 represents the residual heavy metal concentrations (values calculated from the data in Table 2, i.e., IEs and/or WWTPs influents values and treatment efficiency) upon treatment using the conventional methods. Furthermore, a comparison with the standard values (Table 3) can be made using Fig. 1. In general, the values in these WWTP effluents are within the permissible international discharge standards (Table 3). However, the residual concentrations for some metals such as As, Ni and Cd are higher than the

Table 3
Recommended discharge limit values (μg/L)

Metal ion									Reference
Cd	Cr	Cu	Ni	Pb	Hg	As	Fe	Zn	
3	50	2,000	70 (20[a])	<50 (10)	6	10 (5[a])	NV	NV	[46]
5	100	3,380	100	50	2	50	NA	2,610	[53]
5	100	300	500	200	2	100	2,000	500	[54]

Note: NA – no value available in the literature consulted; NV – no guideline value is specified because the chemical is not of public health concern in drinking water. Values in parenthesis mean treatment achievability/performance.
[a]The value set is below the achievable quantification level and thus a specific treatment method is recommended and provided.

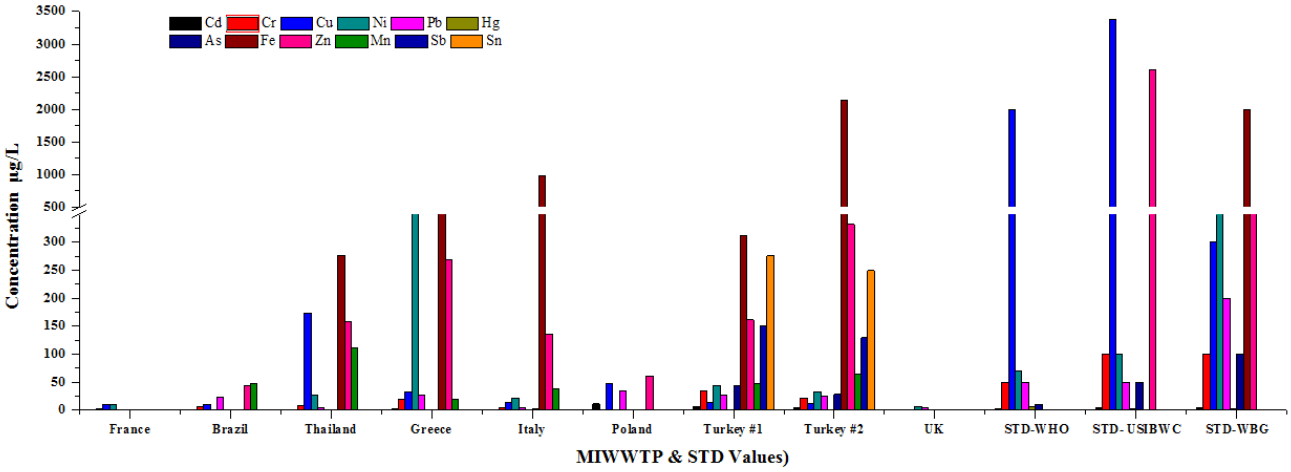

Fig. 1. Residual metal concentrations in WWTPs effluents and international standard discharge limits. MIWWTPs: municipal and industrial wastewater treatment plants; STD: standards; WHO: World Health Organization; WBG: World Bank Group; USIBWC: United States Section, International Boundary and Water Commission.

allowable effluent discharge values. This is the case, for example, of the WWTPs in Poland, Greece and Turkey. In addition, Chon et al. [31] and Salihoglu [38] had reported that significant concentrations of heavy metals are in sewage sludge (between 9.76% and 8.05% on a dry weight basis) and WWTPs effluents. The values of Ni and Pb concentrations in WWTP effluents are higher than the values established by WHO [46] for treatment achievability/performance. The study by Chon et al. [31] reported that relative high concentrations of Pb and Ni were found in both wastewater influents and effluents for over 600 investigated WWTPs in UK. The same study indicated that the conventional wastewater treatment process could remove a lesser amount of these chemicals. Consequently, metal concentrations in treated effluents were too high and reported to contribute to significant metal loads in the receiving water bodies. Hence, the study by Chon et al. [31] called for a significant decrease of the contribution of the WWTPs effluents for a better and effective mechanism of reducing the overall heavy metal concentrations and pressures exerted by these treatment facilities to the receiving water bodies. In addition to this issue, other challenges such as limited and/or lack of data on WWTPs assessment and their relative contribution to the contamination of the water bodies were highlighted in Chon et al. [31]. This is consistent with other studies' findings. For instance, Vajihabanu et al. [34] have observed that the treatment efficiency for Zn and Cu was estimated at 15.78% and 47.54%, respectively, while Salihoglu [38] had previously reported the splitting of heavy metals into the sewage sludge and the treated effluent during the wastewater treatment process. Hence, these effluent and sludge of the WWTPs were reported to be substantial point sources of heavy metals; in addition to severe impacts these metals may cause to the receiving environment, in particular land and water bodies. On the other hand, Belhaj et al. [43] observed that despite the metal removal efficiency of >93% by the flocculation process, Cr and Ni residual loads were still above the values required by the Tunisian standards for quality criteria. In clear terms, it can be noticed that, from these studies' results, there is a double challenge: first, the treatment efficiency, and then meeting the required standards for effluent discharge.

2.2. Effects of heavy metals on flora and fauna

Water pollution has several adverse effects on all forms of life and affects aquatic and terrestrial animals and plants as well as human beings. Studies by Vinodhini and Narayanan [11] showed that aquatic organisms are vulnerable and frequently exposed to various effects of the heavy metals contained in effluents discharged by industries, sewage treatment plants and drainage from urban and agricultural areas. The situation is worsened by the use of untreated or inappropriately treated wastewater for agricultural practices (irrigation) as this is the prevalent practice in many parts of the world, particularly, the developing countries. Consequently, the safety of the crops irrigated and grown in a soil contaminated with heavy metals is seriously affected. It was reported that these toxic metals can be easily translocated and concentrated into plant tissues from the soil through their absorption from the airborne deposits (especially upper parts of the plants exposed to the air) or via root systems [48,55,56]. Many recent research studies have found that various vegetables (egg plant, green chilli, pumpkin, arvi leaves, spinach and cabbage) [48], cereals and fruits [56] and sugarcane [30] grown in the contaminated soils and/or irrigated with heavy metals were extremely contaminated with heavy metals particularly Cd, Pb, Cr, Ni and Zn. Their concentration values were found to be very far beyond the international alimentarius standards, sometimes the health risk index (HRI) values were >1.0 (safe limit) [48]. It was established that the HRI values >1.0 indicate the toxicity of a particular metal under investigation [45]. It was stressed that the long-term consumption of the contaminated plants may result into severe human health problems. Moreover, Khayatzadeh and Abbasi [28] reported that the heavy metal effects on marine biota and humans were very wide-ranging and that these organisms take up these chemicals directly from water in a dissolved form or indirectly through the food chain network. However, it was proven that these effects, response and survival of aquatic animals, crops and plants as well as human beings depend on various factors including species, physiological state of the intoxicated organism, age, dose and type of the toxicant, time of exposure to the toxicant and developmental stage, physicochemical properties of the soil, growth conditions, presence or absence of other ions, etc. [11,28,30].

Pandey et al. [30] have recently indicated that the effects such as reduced seed germination rate, seedling development, low root growth, depressed biomass and low pigmentation were attributed to Cr toxicity. Other studies by Ghani [56] had previously reported that heavy metals affect negatively the crop biomass production and seed yield. Elevated levels of Cu and Cr were proven to inhibit or reduce the plant enzyme activities, chlorophyll while Ni was reported to be responsible for various toxic effects on plants such as phototoxicity, retardation of germination, inhibition of CO_2 assimilation, leaf necrosis and chlorosis [30,56]. Likewise, individual and combinatorial effects of heavy metals (Mn, Cd, Pb, Co, Cr and Hg) on maize crop (*Zea mays* L.) were extensively studied by Ghani [56]. It was found that the weight of shoots and roots of the maize were significantly reduced: 63.4% and 70.5% for Cd and 17.0% and 13.8% for Cr, respectively. The seed yield was decreased by >40% for Cr and 83.9% for Cd. While the reduction of the nitrogen content in the soil was statistically insignificant, an important decrease of nitrogen in shoots and roots was observed. Similarly, a significant decrease of protein content in seeds was positively correlated with the amount of heavy metal added to the soil. Moreover, individual metal concentration in seeds was observed to be higher for the metal added individually than in a combinatory system. These signs were more noticeable in treatments containing Cd alone while the effects of combinations of two metals were not additive; rather the effects were as severe as the most toxic metal considered individually. The metal antagonistic effects were presumed to explain these observations. The established phytotoxic effect was in the following order: Cr < Pb < Mn < Hg < Co < Cd. Hamid et al. [48] observed that excessive concentrations of lead may hinder the plant cell growth.

Exposure to copper inhibited the fish (*Cyprinus carpio* L.) skeletal ossification [28] while in humans, copper was proven to be responsible for Alzheimer's disease and other conditions [57]. Chromium in its more toxic hexavalent form has been reported to cause severe impacts to the living organisms (in rats and humans), due to its higher solubility and mobility. Furthermore, hexavalent species of chromium were proven to be responsible for DNA impairment in particular genotoxicity and carcinogenicity [11,47]. Moreover, Oss et al. [57] have observed that the fat snook (*Centropomus parallelus*) exposed to various concentrations of copper shown genotoxic effects in their micronuclei as well as negative effects on their growth. Cadmium had been previously reported to cause hyperglycemia by stimulating the glycogenolysis in some marine and freshwater fish species [11]. It was reported that the lethal dose values (LC50) for the fish exposed to cadmium for 96 h ranged from 0.0005 to 21.1 mg/dm^3. Blood cell effects and fish metabolism alteration caused by cadmium and manifested via abnormal behavior, locomotion anomalies or anorexia had been reported [11]. Other studies [28] indicated that cadmium was responsible for the decreased growth in juvenile and adult rainbow trout, *Oncorhynchus mykiss*. A recent study by Nawab et al. [45] has reported that the ingestion of water contaminated with cadmium may cause severe effects such as diarrhea, nausea, vomiting, salvation, renal failure, muscle cramps, sensory disturbance, shock and liver injury convulsions while prolonged health effects include liver, blood, kidney and bone harms. On the other hand, the toxicity of lead on the targeted organs such as skeleton, liver, kidney, heart, male gonads and immune system has been investigated. Furthermore, it was observed that this element inhibits the vital functions of enzymes involved in biosynthesis of heme, in particular porphobilinogen synthase and hence alters the hematological system and may disturb and harm the nervous system [42]. Infants, children and pregnant women are the most vulnerable [11,47,48]. Furthermore, evidence of lead toxic effects to both central and peripheral nervous systems, inducing subencephalopathic neurological and behavioral effects have been reported. At very low concentrations of lead, research studies had evidenced that adverse neurotoxic effects other than cancer in humans were more likely to occur. Recent studies by Nawab et al. [45] have indicated that greater concentration of Pb in human body may lead to several adverse health effects such as headache, abdominal pain, irritability, kidney damage, nerve damage, blood pressure, stomach cancer, lung cancer and gliomas. Moreover, other studies on primates had confirmed significant behavioral and cognitive effects as well as renal tumors [47]. Other studies by Khayatzadeh and Abbasi [28] showed that the fish (*Cyprinus carpio* L.), exposed to lead manifested the symptoms of scoliosis. Nickel was proven to be responsible for chromosomal aberrations [11], carcinogenic to humans and allergic contact dermatitis [47]. Extreme level consumptions of nickel may cause acute and chronic nickel poisoning leading to several health issues including headache, vomiting, chest pain, tightness, cyanosis, skin dermatitis, rapid respiration, pulmonary fibrosis, renal edema and severe damage to the lungs, kidney, nervous system, etc. [58].

The studies on various carps namely *Catla catla*, *Labeo rohita* and *Cirrhinus mrigala* exposed to sublethal concentrations of manganese for 30 d indicated that this metal negatively affected the carps' growth and weight. Moreover, the negative effects on physiological functions, individual growth, reproduction and mortality have been attributed to Mn effects [28]. Arsenic in its trivalent inorganic form was proven to be more reactive and toxic. Through consumption of drinking water, it was shown to cause cancer in humans at various sites principally skin, bladder and lung. However, evidence of carcinogenicity in animals was limited [47]. Extreme intake of Co was proven to be responsible for various pathological problems including unusual thyroid artery, overproduction of red blood cells and right coronary problems [45]. On the other hand, Vinodhini and Narayanan [11] studied the hematological and biochemical changes caused by a combinatory effect of cadmium, chromium, nickel and lead on common carp (*Cyprinus carpio* L.). Respiratory functions of the fish were deteriorated which resulted into massive expulsion of mucus and swelling with necrosis around the gill surface of common carp. In addition, the fragility, permeability of the erythrocytes, significant decrease in red blood cell, cholesterol level increase as well as an important increase in glucose due to hyperglycemia were observed. It was further reported that heavy metals have adverse effects on natural soil microorganisms; as a result of that the vital ecological processes is disrupted. Furthermore, their potential use as bioindicators for the assessment of chemical risk to the ecosystem may be lost or weakened [56]. Vajihabanu et al. [34] observed the inhibition of bacterial growth (*Bacillus subtilis*) by Fe and Zn while Cu, Zn and Mn exerted the same effect on *Staphylococcus aureus*. Furthermore, adverse health impact of the heavy metals on actinomycetes, mineral nitrogen assimilating and oligonitrophilic bacteria were proven [59].

2.2.1. Toxicity mechanism of the heavy metals

Due to the extreme toxicity, long-term persistence (e.g., cadmium toxicity and its biological half-life in humans may range between 10 and 35 years) [47], bioaccumulation and biomagnification of the heavy metals in the environment [45,48], many research studies on the adverse effects of these chemicals on both aquatic and terrestrial flora and fauna have been intensified. Furthermore, their toxicity mechanism on aquatic animals mostly fish and particularly in the most targeted organs such as liver, kidney, stomach, gill, heart, male gonads and immune system has been extensively investigated. It was proven that most of these chemicals exert their toxic effect by producing reactive oxygen species which in turn cause the cell damage and oxidative stress by the formation of free radicals and/or through the processes such as lipid peroxidation and genotoxic effects [11,28,57]. In addition, studies indicated that these toxic metals can replace indispensable metals in pigments or enzymes, and therefore, disrupt their important functions and activities [28,56]. Moreover, other studies shown that heavy metals are strongly bound with sulfhydryl groups of proteins and accumulate in tissues of aquatic organisms. Nevertheless, it was also reported that the reaction of the heavy metals with surface water components may form insoluble salts or complexes which are not harmful to aquatic organisms. However, they become toxic to aquatic biota when their mobilization and release occur as a result of water pH drop [28].

3. Low-cost adsorbents derived from agricultural wastes

As it was mentioned above in this work, water pollution by heavy metals is a worrying challenge worldwide and is seen as the most concerned theme of research in the contemporary period. For many years, adsorption methods using commercial adsorbents such as silica gels, activated alumina, zeolites and activated carbon (A/C) have been used for the treatment of industrial wastewaters. These commercial adsorbents have proven the ability to remove and reduce a wide range of many pollutants from polluted waters [60]. Despite their effectiveness, these commercial adsorbents, particularly the A/C are very expensive [60]. This high cost of commercial A/C has prompted the researchers to find the cost-effective adsorbent materials for heavy metal removal from industrial wastewaters [5,20].

Attention and focus have been oriented in agricultural and plant residues. Various parts of the plant materials such as roots, stems, barks, fruit shells, leaves, etc., have been widely studied for heavy metal removal from contaminated wastewaters. Several adsorbent materials from leaves of *Ocimum sanctum* plant [61], macadamia nut shells, rice husks, baobab shells, pigeon pea husks, *Moringa oleifera* husks and marula stones [29], *Adonosia digitata* fruit shells and *Theobroma cacao* pods [62], soybean oil cake [63], pumpkin (*Cucurbita*) [1], seed shells of *Borassus aethiopum* and shells of *Cocos nucifera* (shells) [64], remnants of plantain peel and banana peels [65,66], rice husk and saw dust [67], composted municipal solid waste [20], mango peel [68], potato peels [19], saw dust [69], neem leaves [70], etc., have shown a high potential to remove heavy metals from polluted waters to some extent. Igwe et al. [71] investigated the potential of maize cob and husk to remove Zn^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous solutions. It was observed that these agricultural wastes proven a high adsorption capacity of 495.9 mg/g for Zn^{2+}, 493.7 mg/g for Cd^{2+} and 456.7 mg/g for Pb^{2+} in unmodified form for the initial concentration of 1,000 mg/L of all the three metal ions' solutions. Humelnicu et al. [72] have recently studied the adsorption of Cu^{2+} and Zn^{2+} by soy bran and mustard husk. The two adsorbents have proven a high potential to remove the two heavy metal ions from SWW. Their respective adsorption capacities were found to be (mg/g) 53.76 and 48.78 for Cu^{2+} and 74.07 and 63.69 for Zn^{2+}. Soy bran has shown a high adsorption capacity than the mustard husk. Bamboo charcoal has been studied for Cd^{2+} removal from aqueous solution at pH >8.0. The adsorption capacity was found to be 12.08 mg/g. The maximum monolayer adsorption capacity of unmodified shoots of *Cyperus laevigatus* was found to be 7.49 mg/g at pH = 5.5 in a study of Cd^{2+} removal from aqueous solution. Acheampong et al. [37] studied the removal of Cu^{2+} by coconut shell and found the maximum sorption capacity of this material to be 53.9 mg/g. Alslaibi et al. [23] have investigated the potential of olive stone A/C for adsorption of Zn^{2+}, Ni^{2+} and Cd^{2+} from SWW. Adsorption capacities (mg/g) of this material were found to be 11.14 for Zn^{2+}, 8.42 for Ni^{2+} and 7.80 Cd^{2+}. The study concluded that the pseudo-second-order described better the adsorption kinetics and that the adsorption process was controlled by the chemisorption mechanism. Furthermore, the material was suggested to be potentially suitable for the treatment of wastewaters polluted with heavy metals.

Gutha et al. [58] studied the potentiality of *Lycopersicum esculentum* (tomato) leaf to remove Ni^{2+} from aqueous solution. It was reported that this low-cost agricultural waste has a maximum biosorption capacity of 58.82 mg/g at 323 K and was suggested as an alternative low-cost biosorbent for the detoxification of aqueous solutions polluted by Ni^{2+} ions. Mosca et al. [73] explored the adsorption properties of two adsorbents (sludge and wet pomace) obtained from the olive mill wastes for chromate ions removal from a synthetic aqueous solution. In the range of 2.5 and 250 mg/L of the chromate ion concentration, at pH = 5.5, temperature of 25°C and adsorbent dosage of 10 g/L, over the contact time of 100 h, it was observed a significant decrease of the chromate ion concentration in particular for the low initial concentrations. At 2.5 mg/L of chromate ions, wet pomace and sludge materials removed approximately 94% and 97%, respectively, while the corresponding removal percentages were estimated at 84% and 87.5% for the initial concentration of 250 mg/L. It was concluded that that olive mill wastes may be sourced and reused as an efficient adsorbent material for chromate ions removal. Adie Gilbert et al. [13] studied the adsorption capacity of *Carica papaya* seed to remove Pb^{2+} and Cd^{2+} from aqueous solutions. The biosorbent proven a high adsorption capacity which was evaluated to be, respectively, 1,666.67 and 1,000.00 mg/g. At the initial metal ion concentration of 250 mg/L, the percentage removal range of 96% and 99% for Pb^{2+} and 85% to 98% of Cd^{2+} was observed at the pH range of 3–8, adsorbent dose of 0.5 g, temperature of 298 K, contact time and agitation speed of 2 h and 180 rpm, respectively. More interestingly, it was estimated that under optimum conditions the treatment of 5 m^3 at 100 mg/L of Pb^{2+} and Cd^{2+} would require 43.3 and 49.2 kg of defatted *C. papaya* seeds to remove 95% of the metal ions from aqueous solution. Hence, *C. papaya* was reported to be potentially a good adsorbent in removing heavy metals from wastewaters.

The adsorption capacities of various agrowaste biomaterials which are used to appreciate the capability and strength of the low-cost adsorbent have been investigated by many researchers. The findings have been compiled and published in many original articles [64] and review studies. Bhatnagar and Sillanpää [60] reviewed the low-cost adsorbents and their adsorption capacities for water treatment. Malik et al. [22] have recently published an article on cellulosic low-cost adsorbents used for metal detoxification in water and wastewaters. Srivastava et al. [74] have written a review paper on progress on heavy metal removal using various adsorbents. Fu and Wang [75] reviewed the current methods employed for heavy metal wastewater treatment while Barakat [12] published a review article on new adsorbents for metal-contaminated wastewater treatment. It was concluded that these low-cost adsorbents are promising alternatives, eco-friendly, cost-effective and can be used to treat industrial wastewaters laden with heavy metals.

3.1. Use of low-cost adsorbents for treatment of waters laden with heavy metals

The treatment of polluted waters is one of the most studied fields that has attracted the attention and focus of many researchers for obvious reasons. First, because water is a basic need to sustain life, and then the water pollution can spread easily and lead to disasters faster that could lead to death. Moreover, the increase demand of clean water for domestic purposes, industrial use and agricultural irrigation requires a wise management of water resources. Heavy metal removal from polluted waters using a cheaper adsorbents prepared from agricultural residues has been widely studied. As it was mentioned above in this work, a big number of original articles [64] and review papers [12,22,60,74,75] on heavy metals adsorption by the low-cost adsorbents have been published. High abundance of agricultural wastes, their low-cost, chemical composition together with their disposal issues have made those materials to be valued and explored for heavy metal removal from polluted waters. Table 4 provides a general overview of the extent at which the low-cost adsorbents from agrowastes and plant residues have removed heavy metals from SWWs and IE. The maximum adsorption capacities of various biosorbents, initial heavy metal concentrations and the percentage of the removal efficiency are also reported.

As it can be seen from Table 4 and other data reported in this work, various adsorbent derived from agrowastes have proven their potential to reduce significantly heavy metal concentrations in wastewaters to some extent. Looking at the studied concentrations, it is apparent that either the concentrations are lower or higher compared with the heavy metal concentrations found in various real IEs. Furthermore, there is a huge discrepancy between studies performed on SWWs and real IEs. Given the complexity of IEs in terms of constituents and their concentrations, an adsorbent may prove its high efficiency for heavy metal removal from SWW but when applied to the IEs its sorption capacity may be reduced. This is, for example, the case of the rice straw which exhibited a significant decrease of its adsorption capacity from 8.63 to 2.261 mg/g when applied to the removal of Zn^{2+} from the SWW and IE, respectively (Table 4). Rocha et al. [98] reported that high adsorption capacities resulting from the studies performed on higher metal concentrations beyond the real effluent's concentrations discharged into the environment are not representative of the real problems and cannot be translated into the real world.

Moreover, the residual metal concentrations (Fig. 2) calculated from some prominent agrowaste adsorbents (data picked from Table 4) are higher compared with the discharge standard limits (Table 3). Study findings by Memon et al. [66], Memon et al. [84], Yao et al. [89], Zabihi et al. [32] and others are typical illustrative examples of these higher residual concentrations despite high adsorption capacity of the investigated materials. Many other studies reported higher metal concentration values upon treatment despite high efficient metal removal by the low-cost adsorbents. For instance, the residual heavy metal concentration values found by Zhao et al. [99] for Pb, Cr, Cd, As and Hg were 0.22, 0.09, 1.66, 0.26 and 0.03 mg/L, respectively. Acheampong et al. [37] have reported the residual concentrations of Cu^{2+} equivalent to 9.85 mg/L despite high sorption capacity (53.9 mg/g) of the coconut shell adsorbent. On the other hand, some research studies by Chamanchi et al. [94] and Dhabab and Hussien [100] reported that the adsorbents have been applied to the effluents of very low initial concentrations while other studies by Rocha et al. [98] reported that most of the studies for Hg removal were performed on higher concentrations than the real values discharged into the environment and that the residual concentrations were higher than the allowed values for effluent discharge. It was concluded that the skills on the potential of the biosorbents to remove heavy metals under realistic conditions were missing [98].

It is apparent from Table 4 and Fig. 2 that there is still a huge imbalance and gaps between studies performed on SWW and real industrial wastewaters. The review studies by Varma et al. [5] also observed the same discrepancies and recommended the test of the adsorbents behavior and analysis of the adsorption capacities with real IEs containing various heavy metals. However, some few studies such as those by Memon et al. [66], Iqbal et al. [68] attempted the applicability of the adsorbents derived from the agrowaste for the removal of the metal ions from the real IEs. It can be seen from these studies that the samples had very low metal concentration (2.2 μg/mL) [66] or have been conducted in batch adsorption experiments, and therefore, much more information needs to be acquired for the practical and engineering design

Table 4
Heavy metal removal from wastewaters by agricultural low-cost adsorbents

Metal ion	Adsorbent material	Initial concentration (mg/L)	% Removal	Adsorption capacity (mg/g)	Type of wastewater treated	Reference
Pb^{2+}	Soybean oil cake	300	40.81	476.2	SWW	[63]
	Chestnut shell	100	–	8.5	SWW	[76]
	Hazelnut shell	207.2	90	28.18	SWW	[77]
	Almond shell	207.2	68	8.08	SWW	[77]
	Eragrostis tef	0.12	68.9	17.5	IE	[78]
	Borassus aethiopum (seed shell)	20	99.75	12.19	SWW	[64]
	Mango peel	50	90	99.05	SWW	[79]
	Carica papaya seed	250	97.5	1,666.67	SWW	[13]
Cd^{2+}	Banana peel	50	95	35.52	SWW	[66]
		2.2	100	35.52	IE	[66]
	Eragrostis tef	1.23	82.9	27.2	IE	[78]
	Borassus aethiopum (seed shell)	20	99.92	10.20	SWW	[64]
	Cocos nucifera (shells)	20	99.85	25.797	SWW	[64]
	Rice straw	112.4[a]	–	14.95[a]	SWW	[80]
		4.50	100	4.50	IE	[80]
	Mango peel	50	87	68.92	SWW	[79]
	Sesame leaf and stem	20	92.95	84.74	SWW	[81]
	Barley hull	30	95.8	–	SWW	[82]
	Barley hull ash	30	99.2	–	SWW	[82]
	Cyperus laevigatus	5	70	0.70	SWW	[83]
		50	47.3	4.73	SWW	[83]
	Olive stone	20	94.88	7.80	SWW	[23]
	Carica papaya seed	250	96	1,000	SWW	[13]
Cr^{6+}	Banana peel	0.5–8	80–99	131.56	SWW	[84]
		10–100	60–79	131.56	SWW	[84]
		12.40	98.9	–	IE	[84]
	Bael fruit shell	50–125	>90	17.27	SWW	[85]
	Neem leaf powder	25–125	–	7.43	SWW	[86]
	Tamarind hull	25–75	–	85.91	SWW	[87]
	Eleocharis tuberosa corn peels	10	56.1	1.19	SWW	[88]
	Wet pomace (olive)	2.5–250	94–84	–	SWW	[73]
	Sludge (olive)	2.5–250	97–87.5	–	SWW	[73]
Cr^{3+}	*Eragrostis tef*	0.98	74.5	21.3	IE	[78]
	Eleocharis tuberosa corn peels	10	59.61	2.01	SWW	[88]
Cu^{2+}	Chestnut shell	100	–	5.5	SWW	[76]
		50	92.4	12.56	SWW	[89]
	Coconut shell	10	95	53.9	SWW	[37]
	Eragrostis tef	2.54	81.5	34	IE	[78]

(*Continued*)

Table 4 (*Continued*)

Metal ion	Adsorbent material	Initial concentration (mg/L)	% Removal	Adsorption capacity (mg/g)	Type of wastewater treated	Reference
		63.55[a]	–	8.134[a]	SWW	[80]
	Rice straw	2.54	100	2.54	IE	[80]
	Rice husk	5	87.1	17.03	SWW	[90]
	Mango peel	25	89.02	46.09	SWW	[68]
		10.91	85.97	46.09	IE	[68]
	Banana peel	5–25	–	4.75	SWW	[91]
	Orange residue	300	33.3	21.70	SWW	[92]
	Carrot residue	500	–	32.74	–	[68]
	Soy bran	100	–	53.76	SWW	[72]
	Mustard husk		–	48.78	SWW	[72]
	Olive waste	40	≈85	3.6	SWW	[93]
	Eleocharis tuberosa corn peels	10	78.29	3.29	SWW	[88]
Zn^{2+}	Chestnut shell	100	–	2.4	SWW	[76]
	Walnut shell	10	90.0	–	SWW	[94]
	Grain rice	10	95.0	–	SWW	[94]
		65.38[a]	–	8.630[a]	SWW	[80]
	Rice straw	2.62	99.6	2.61	IE	[80]
		25	67.27	28.21	SWW	[68]
	Mango peel	11.34	78.30	28.21	IE	[68]
	Carrot residue	500	–	29.61	–	[68]
	Banana peel	5–25	–	5.80	SWW	[91]
	Soy bran	100	–	74.02	SWW	[72]
	Mustard husk	100	–	63.69	SWW	[72]
	Olive stone	20	99.03	11.14	SWW	[23]
Ni^{2+}	*Lansium domesticum* peel	58.7[a]	90	10.1	SWW	[95]
	Eragrostis tef	3.53	88	41.2	IE	[78]
	Bael tree leaf powder	10	60.21	1.527	SWW	[96]
	Walnut shell	10	98	–	SWW	[94]
	Grain rice	10	96	–	SWW	[94]
		25	76.40	39.75	SWW	[68]
	Mango peel	16.96	79.42	39.75	IE	[68]
	Banana peel	5–25	–	6.88	SWW	[91]
	Orange peel	5–25	–	6.01	SWW	[91]
	Olive waste	40	≈60	1.7	SWW	[93]
	Olive stone	20	97.34	8.42	SWW	[23]
Hg^{2+}	Rice straw	200.59[a]	–	22.06[a]	SWW	[80]
		8.02	100	8.02	IE	
	Walnut shell	107	≈98	151.5	SWW	[32]
	Rice straw	300	–	119	SWW	[97]
		0.05	82	0.16	SWW	[98]
	Rice husk	0.50	92	24.1	SWW	[98]

Note: SWW: synthetic wastewater; IE: industrial effluent; –: data not available.
[a] Converted from original unit.

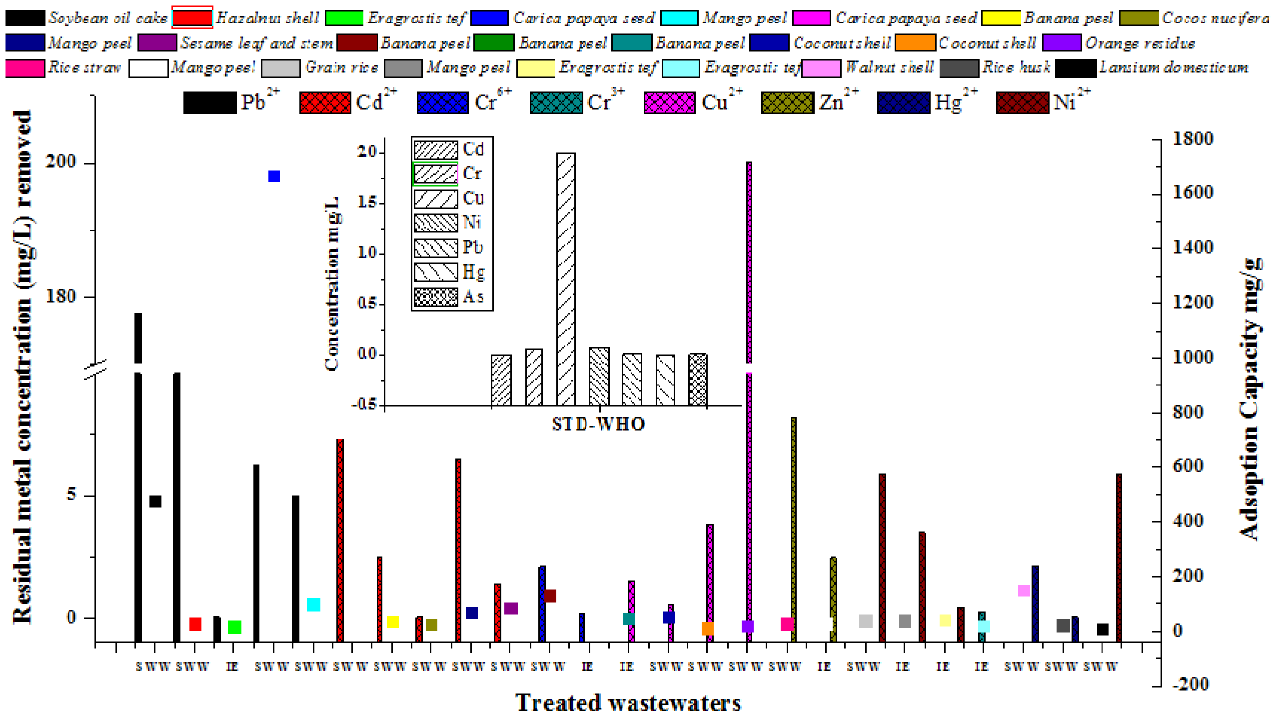

Fig. 2. Residual metal concentrations upon adsorption by some prominent adsorbent and type of treated wastewaters. SWW: synthetic wastewater; IE: industrial effluents; STD: standards; WHO: World Health Organization.

application. Hence, it can be suggested that further studies address these issues to provide knowledge on the biosorbent behavior with real IEs and bring new insights on adsorption competition, selectivity and extent at which other contaminants can be removed. Furthermore, it can also be suggested that the ultimate goal of treatment should be to meet the required environmental standards and regulations as well as the permissible discharge limits.

4. Variant forms of low-cost adsorbents and characteristics of good adsorbents

Research studies have shown the use of the low-cost adsorbents prepared from the biomaterials in both natural form, i.e., unmodified material form [1,72,98,100,101] and modified material form [12,60] for heavy metal removal. In unmodified form, slight and simple pretreatment are required. The material is washed with deionized water, dried and ground. In the second case the physicochemical treatment is applied to the material to produce an A/C which is the most widely and frequently studied form [27,63,75]. Activating the biomass material aims at enhancing its adsorption capacity [1,22,100] by increasing the surface of the active sites (ASs) [23,97]. Furthermore, it was reported that the activation process enhances the pyrolytic effect which leads to the significant decrease of the volatile matter content and increase of the fixed high pure carbon [23]. The end result is, therefore, the improvement of the adsorbent effectiveness in removing heavy metals from wastewaters. Other studies by Uddin [7] have recently reported that the degree of the physicochemical treatment, alteration and activation have a significant influence on these adsorption capacities and efficiency of the adsorbent materials. This is consistent with the study findings by Alslaibi et al. [23] on comparison of the adsorption capacity of different low-cost adsorbents. These authors noted that the observed variation in adsorption capacities was due to the different precursors used as well as the activation methods and/or conditions used for the preparation of the A/C.

Other research studies had previously indicated that this preparation of an A/C involves mainly three processes namely the raw material dehydration, carbonization and activation [60]. A number of chemicals such as steam, CO_2, $ZnCl_2$, H_2SO_4 and H_3PO_4, KOH, K_2CO_3 and NaOH are used as activating agents [6,63]. Recently, Song et al. [97] have reported the improvement of the biosorption capacity of the adsorbents by modifying their properties through the functionalization methods with sulfur bearing groups such as thiols, dithiocarbamate and xanthates. The adsorption capacity of the rice straw and rice husk biosorbent was increased using carbon disulfide (CS_2) which improved significantly the adsorption of Hg^{2+} from aqueous solutions. The amount of adsorbed Hg^{2+} per unit of biosorbent was approximately 120 mg/g compared with about 70 mg/g for the modified and unmodified biosorbents, respectively. Rocha et al. [98] reported that the sorption capacity of the rice husk chemically treated with H_2SO_4 was 10 times higher than that of unmodified rice husk, i.e., 250 and 24.1 mg/g, respectively. Zhang et al. [90] observed that adsorption capacity of unmodified rice husk was 1.6173 mg/g. However, the same material treated with H_3PO_4 increased its adsorption capacity by more than 10 times.

Research studies proven that for an adsorbent (A/C) to be effective in purification of the solutions, it must be endowed with a large mesopore and micropore volume [27,75], offering a high porous structure, and a large surface area compared with its mass, generally ranging from 600 to 2,000 m^2/g [23,60], high ability to exchange cations and anions [7] and reusability for several times during the adsorption–desorption process [24]. These excellent properties of the A/C coupled with high affinity for organic compounds probably made the adsorption method to be appreciated and recommended by the WHO and US EPA for polluted water treatment [46,93]. Previous research findings had shown that the material with a high fixed carbon, adsorption capacity, surface area and K_f (Freundlich's constant) is a better adsorbent, and hence, exhibits a high percentage removal [102]. Carbonization yield, ash content and fixed carbon proportion are important factors for selecting a good adsorbent [102]. High organic carbon and low inorganic contents have been proven to be good quality of an adsorbent [60]. These inorganic constituents have been reported to interfere with heavy metal adsorption. Recent research studies have further proven that the low solubility of adsorbents in water, in common usual organics or acidic solutions [64,99] not only protect the adsorbents from leaching [99] but also make them to be stable in neutral and acidic media [64]. Other studies confirmed that high percentage of volatile solids indicates that the adsorbent regeneration and metal recovery are possible through the material destruction [64]. Therefore, volatile solids proportion can be a qualitative aspect of an adsorbent.

5. Adsorption mechanisms by low-cost adsorbents

Known since the ancient times and widely used in the mid-second half of eighteenth century [60], adsorption is defined as the accumulation or a mass transfer of a liquid solute on the surface of a solid substance often known as adsorbent [102]. Adsorption technology based on A/C has been widely used all over the world. The A/C became the most popular in the field of wastewater treatment because of its application to the removal of a variety of pollutants including heavy metals [60].

Research studies have demonstrated that the adhesion of toxic heavy metals to the bioadsorbent's surface is attributable to the special chemical structures such as cellulose, hemicellulose, lignin and extractives [1,22,63] and functional groups such as carboxylic acid, phenols, alcoholic groups, –CN, C–O (ether group), C=O (ketone), C–H (aliphatic group), amide and RNH_2 (primary amine) [1,13,76,79,84,103] of the non-living biomass materials. These functional groups have a high affinity with heavy metal ions in solutions [97]. Naushad et al. [24] have indicated that the chemical functional groups such as carbonyl, hydroxyl and free oxygen groups are nucleophiles, and hence, tend to donate electrons to the metal cations, resulting into electrostatic attractions between the metal ion and the adsorbent ASs. This is consistent with the previous study findings by Adie Gilbert [13] who observed that the presence of the functional groups (Lewis acid) on the ASs of *C. papaya* seed biosorbent may have been involved in the adsorption of the Pb^{2+} and Cd^{2+} ions from aqueous solution. However, the authors excluded the possibility of the ion exchange to be the strict mechanism by which the metal ions were adsorbed onto the surface of the biosorbent. Other research works proven that the adsorbate is bound on the surface by physical and/or chemical interactions [12,63] and that the contaminant sorption is achieved into three main steps [12] namely its transportation from aqueous solution to the adsorbent surface [63], its adsorption on the particle surface and finally its transportation within the adsorbent particle. Other literature [13] characterized this mechanism as external mass transfer of solute onto the adsorbent's surface followed possibly by intraparticle diffusion.

Physicochemical interactions [71] such as electrostatic attractions, cationic metallic complexation with adsorbent negatively charged sites, chelation [12,13,24,29,61,99,104,105], van der Waals interactions as well as ion exchange [61,79] have been proven to be the main mechanism pathways involved in heavy metal adsorption. At the adsorbent surface, the adsorption may be characterized as physical adsorption (physisorption) or chemisorption. In the first case, the adsorption is due to the weak van der Waals forces while the chemisorption involves chemical bonding between adsorbate and adsorbent [60,85,96]. Physisorption is unselective, low energy of adsorption generally 8–20 kJ/mol [37,78], with values between 20 and 40 kJ/mol allocated to pore diffusion [93]. However, the chemisorption is selective, strongly dependent on both solute and solid surface and the enthalpy of adsorption (40–800 kJ/mol) is higher than that of physisorption [37,78]. The chemisorption and physisorption processes can also be distinguished using the Freundlich adsorption intensity constant (n). In case of physical process, n is greater than one unit while this constant is less than one unit when the chemical process is involved [78].

Adsorption mechanism of heavy metals by adsorbent's functional groups has been documented in many literatures. It has been shown that the adsorbent material AS containing phenol or carboxylic group loses protons in the first step [80]. However, the extent of this dissociation is adsorbent specific and the pH values at which it takes place depend upon the acidic dissociation constants [80]. Second, the metal ion loses the hydration waters and finally the non-solvated ion is adsorbed by the fibrous material [80]. The H^+ ions from AS-C_6H_5–OH and AS –COOH functional groups of the adsorbent reactive centers are then exchanged with metallic ions in the solution [72].

$$\text{AS-}C_6H_5\text{–OH} \rightarrow \text{AS-}C_6H_5\text{–O– + }H^+$$

$$\text{AS-}C_6H_5\text{–O– + }M^{n+} \rightarrow \text{AS-}C_6H_5\text{–(O)}_n\text{M + }nH^+$$

and similarly:

$$\text{AS –COOH} \rightarrow \text{AS –COO– + }H^+$$

$$\text{AS –COO– + }M^{n+} \rightarrow \text{AS –CO(O)}_n\text{M + }nH^+$$

where AS is the adsorbent active site, M is the metal and n is the number of charges.

Research studies attempted to explain the adsorption mechanism where the adsorbent amine groups and probably amide functional groups are involved. Studies by Memon et al. [84] on chromium adsorption shown that the adsorbent active centers presenting protein amino groups are protonated in acidic medium, and therefore, the electrostatic forces occur as a result of positive and negative charge interactions.

$$\text{AS-NH}_2 + \text{H}^+ \rightarrow \text{AS-NH}_3^+$$

$$\text{AS-NH}_3^+ + \text{HCrO}_4^- \rightarrow \text{AS-NH}_2\text{H}^+{}_4^-\text{OCrH}$$

A better understanding of the metal binding mechanism to the adsorbent necessitates a deep comprehension of the adsorption parameters. Heavy metal adsorption studies have demonstrated that the adsorption process is largely influenced by the solution pH, agitation time, initial metal concentration, adsorbent mass, adsorbent particle size and temperature which are the most widely studied variables.

5.1. Effect of solution pH and adsorbent point of zero charge (pH_{pzc})

Research studies demonstrated that pH is the most important parameter driving the metal adsorption by the adsorbent [66] while others have shown that both the solution pH and adsorbent point of zero charge (pH_{pzc}) are very critical to understand the mechanism of the metal binding to the adsorbent [37]. Mahapatra et al. [27] have recently reported that at low pH of the solution the adsorbent binding sites are protonated by the hydronium ions and consequently, there is a repulsion between the metallic ions and adsorbent. The increase in pH results in a diminution of H^+ ions and an increase of available free surface sites and when the adsorbent surface becomes negatively charged then the metal binding to various functional groups of the adsorbent takes place [27,29,104]. On the other hand, it was proven that the metal ion uptake increases as the adsorbent surface changes from positive to negative charges via a point of zero charges (pH_{zpc}). Under this point (pH value at which the net charge of the adsorbent surface is zero) the active sorption sites are positively charged [68] and attached with protons [95]. Consequently, a competition between the protons (H^+) and positive metal ions occurs [29,94]. The presence of H^+ ions reduces the adsorbent free surface sites, and therefore, decreases the rate of the mass transfer [94]. While, much of the positive metal species adsorption occurs at pH greater than pH_{zpc}, the negative species adsorption takes place at pH less than the pH_{zpc} [37,63].

It can be summarized from the literature that in general the metal removal efficiency increases with pH rise until the optimum value is reached. Song et al. [97] have recently observed the Hg^{2+} removal increase as the solution pH was increased. These observations were explained from two perspectives namely the pH_{pzc} and surface complexation theory. At the pH below pH_{pzc} the adsorption decreases while at the pH above pH_{pzc} the biosorption increases, which correspond to the positive and negative charge of the biosorbent surface, respectively. Basing on the theory of complexation, it was reported that the increase in heavy metal adsorption with pH increase was due to the diminution of competition for the surface ASs between the H^+ ions and metal species. However, at higher pH generally above five, studies have indicated that the biosorption decrease because many heavy metal ions are susceptible to be hydrolyzed and may form hydroxide precipitates or oxides [80,97]. Vazquez et al. [76] and Meena et al. [106] previously observed that the increase of the hydroxide ions resulted into metal soluble hydroxyl complexes. Consequently, the metal uptake by the adsorbents decreased. This may lead to the double metal removal by both adsorption and precipitation processes and consequently to the overestimation of the adsorption process. A typical example to explain this double metal removal is the recent study by Lam et al. [95] for nickel removal by *Lansium domesticum* peel biosorbent. In this study, it was observed that above the pH value of 8, both adsorption and precipitation mechanism occurred and significantly contributed to the decrease in concentration of Ni^{2+} from the solution. In most studies, it can be seen that the metal hydroxide precipitation pH is not often taken into consideration and the extent of its contribution is not evaluated. In this case, it is more likely that the adsorption can be overestimated. It can be suggested that in addition to the knowledge of the metal pH precipitation, the use of blank experimental tests without adsorbent [37] may be one way of assessing the contribution of the precipitation reaction in heavy metal removal from the contaminated waters.

Chromium ions seem, however, to follow a reverse trend. For instance, studies on Cr^{6+} adsorption by bael fruit shells [85] proven that much of chromium ions was adsorbed at low pH = 2.0 when the adsorbent surface is protonated. Lin et al. [88] observed a high adsorption of Cr^{6+} at pH < 1.0. It was postulated that at low pH there is an electrostatic attraction between the H^+ ions and the dominant ion forms of Cr^{6+} namely $HCrO_4^-$, $Cr_2O_7^{2-}$, $Cr_4O_{13}^{2-}$ and $Cr_3O_{10}^{2-}$ [85,88]. As the pH increased up to pH = 8 where CrO_4^{2-} predominates, the maximum adsorption decreased progressively due to the repulsion between the hydroxide ions and CrO_4^{2-} [70,85]. Similar observations at pH range of 1.0–6.0 were reported in the literature [84,88]. It was proven that the adsorption was accompanied by a reduction of Cr^{6+} to Cr^{3+} caused by the presence of reducing substances such as polysaccharides, glycoproteins, glucolipids and nucleic acids [84]. Lin et al. [88] reported an increase in adsorption efficiency of Cr^{3+} in the pH values ranging from 1.0 to 6.0 while Cr^{6+} adsorption decreased significantly in the same pH range.

5.2. Effect of agitation time and stirring rate on metal uptake

It was experimentally observed that heavy metal removal efficiency and amount of metal adsorbed increase with contact time increase [13,62,63,76,77,84,85,95]. Studies have shown that during the adsorption process, the metal is taken up very quickly in the first minutes and slows down gradually as the time goes on until the equilibrium time is attained. Study by Chouchene et al. [93] found that the fast removal of Cu and Ni by the olive waste at the beginning was due to the abundance of more ASs and their gradual occupancy decreased the biosorption efficiency. Similar observations were reported by Rocha et al. [98] who explained that the rapid uptake of Hg^{2+} ions by the rice husk during the first hours of contact followed by a slow adsorption was due to the driving forces in the commencement of the adsorption process. Lin et al. [88] also observed a rapid uptake of Cu^{2+} in the first minutes which decreased after 20 min of contact time. Chamanchi et al. [94] reported that increasing the contact time and the mixing rate of the metal solution-adsorbent reduces significantly the fluid phase resistance.

Consequently, the rate of metal mass transfer from the solution to the adsorbent surface increases until equilibrium is reached. This equilibrium time is, however, dependent on many factors including the nature and structure of the adsorbent, stirring rate and solution concentration. Similarly, Mosca et al. [73] indicated that the rapid initial uptake of chromate ions, and then the slow uptake at 100 h of contact time depended on the initial chromate concentration. The acute jump in the initial phase of adsorption process was explained as being caused by the fast initial external mass transfer and chemical ion-adsorbent surface interaction. Furthermore, Zhao et al. [99] have recently observed that more adsorbent's functional groups shorten the adsorption equilibrium time. Humelnicu et al. [72] observed that the mobility of metal ions is high in the dilute solutions, and therefore, the interaction of adsorbent–adsorbate is also high. The study recommended a dilution of waters polluted with heavy metals before adsorption process for effective metal uptake during the adsorption.

5.3. Effect of initial metal concentration and adsorbent dose

Initial heavy metal concentration and adsorbent dose are also the variables widely studied by many researchers to understand the adsorption phenomenon. Most studies on heavy metal adsorption by the low-cost adsorbents have found that the percentage removal decreases with increase in initial metal ion concentration but increases as the adsorbent mass is raised [13,62,64,78,83–85,96,100]. For instance, a recent study by Ammari et al. [83] has shown that Cd percentage removal by *C. laevigatus* decreased from 70% to 47.3% when its concentration was raised from 5 to 50 mg/L, respectively. According to these studies, it was explained that the active binding sites of the sorbent gradually become more and more saturated, and then the decrease in adsorption of heavy metals starts at the maximum initial metal concentration. When the adsorbent binding sites are saturated at higher concentration, then the metal ions remain unadsorbed in the solution [72,97]. This is in perfect agreement with other study findings by Mosca et al. [73] on chromate ions removal by the adsorbents derived from the olive mill wastes. These authors noted that for each biomass there was a critical initial chromate concentration beyond which the adsorption process was not dependent on the initial concentration of the chromate ions. It was found that at 16 mg/L of initial chromate concentration; the biomass was saturated, meaning that the rate was independent of the initial concentration. From this value, the initial concentration range of 16 ± 3 mg/L was established as a value for the affinity between biomass and chromate ions. On the other hand, Naushad et al. [24] have observed a decrease of Hg^{2+} adsorption percentage removal from 99.5% to 72.5% when the initial concentration was increased from 10 to 150 mg/L. It was reported that this was due to the decrease of available adsorption sites at the surface of the starch/SnO_2 nanocomposite for the higher metal ion concentration. Contrary to this general pattern, Rocha et al. [98] observed that a highest percentage of Hg^{2+} removal (92%) was observed for the highest initial concentration (0.5 mg/L) compared with 82% when the concentration was 0.05 mg/L. This fact was explained as being due to the sufficient driving force provided by a high concentration to overcome the adsorbate mass transfer process between the aqueous phase and adsorbent phase.

Heavy metal initial concentration not only affects the percentage removal but has an impact on metal adsorbed amount. Many studies [72,97,107] have indicated that the amount of metal ion taken up per a weight unit of adsorbent was dependent on the initial heavy metal concentration and increased consistently with the metal concentration increase. Rocha et al. [98] found that the amount of Hg^{2+} adsorbed per unit weight of the rice husk increased with increase in initial concentration. Song et al. [97] observed that the amount of mercury ions adsorbed increased gradually with increase in initial metal concentration until it reaches the maximum before decreasing. Humelnicu et al. [72] have found that Cu^{2+} and Zn^{2+} uptake increased with initial metal concentration up to 100 mg/L. Iqbal et al. [68] observed that the adsorption capacity increased proportionally with metal ion concentration increase up to 500 mg/L. It was reported that the increase of the metal amount was due to the increased mass transfer rates subsequent to the concentration rise [72,97].

On the other hand, the influence of the adsorbent mass on heavy metal uptake has been largely investigated. For example, Rocha et al. [98] observed that an increase of adsorbent mass from 0.005 to 1.0 g/L resulted in increase of Hg^{2+} percentage removal from 24% to 94%, respectively. Lin et al. [88] also reported a gradual increase of efficiency for Cu^{2+}, Cr^{3+} and Cr^{6+} ions removal as the adsorbent increased from 10 to 70 mg. According to many literature including studies by Rocha et al. [98], Lin et al. [88] and Humelnicu et al. [72] as the biosorbent mass increases, the free active sorption sites increase in number, and therefore, the surface area also augments. However, the decrease in metal adsorption after an optimal amount of sorbent was explained in the literature as a direct consequence of ASs overlapping. Moreover, Rocha et al. [98] observed that beyond an optimal amount of adsorbent (0.25 g/L), adsorption efficiency was no longer dependent on free ASs and no significant enhancement in metal uptake has taken place.

5.4. Adsorbent particle size

Adsorbent particle size affects the adsorbent efficiency, and therefore, plays an important role in heavy metal adsorption. Cheraghi et al. [81] have recently observed that Cd^{2+} percentage removal decreased from about 75% to 50% when the adsorbent size increased from 0.5 to 2 mm. Acheampong et al. [37] observed a decrease in percentage removal of Cu^{2+} from 93.60% to 86.20% when coconut shell adsorbent particle size was increased from 0.25–0.5 to 1.4–1.6 mm, respectively. Dhanakumar et al. [103] and Mosca et al. [73] observed that the smaller is the adsorbent particle size the more surface area to volume ratio is available. Consequently, the absorption properties of the material are favored, and therefore, the heavy metal percentage removal becomes higher. Chouchene et al. [93] have reported that the differences in adsorption capacity for Ni^{2+} removal from aqueous solutions were due to the particle size. The adsorption capacities were found to be 1.5 and 10.6 mg/g when the diameter of the particle size was between 1 and 1.6 mm and 0.15 and 0.25 mm, respectively. Smaller is the particle diameter bigger is the Brunauer–Emmett–Teller

(BET) surface area. The BET surface area of the olive waste adsorbent with a diameter between 0.15 and 0.25 mm was five time higher than (1.24 m^2/g) the one with a diameter between 1.0 and 1.6 mm (0.252 m^2/g) [93].

5.5. Temperature effect

Even though the effect of temperature is not widely reported in many literatures, some studies on Ni, Cd, Cu, Cr and Pb removal by *Eragrostis tef* [78], Hg^{2+} adsorption [32], Cu^{2+} and Zn^{2+} uptake [72] have shown that the metal removal efficiency increases with temperature rise. It was explained that the temperature rise decreases the adsorbent layer resistance to the mass transfer which results into a diminution of the thickness of the boundary layer, and therefore, increase more available binding sites. Moreover, it was observed in other studies that the diffusion speed of the solute molecules increases as the temperature was increased [72]. Song et al. [97] observed that a high biosorption of Hg^{2+} consistently with the rise of temperature was due to the high diffusion rates of the solute molecules (Hg^{2+} ions) subsequent to the low solution viscosity. Furthermore, these studies shown that high temperature increases the adsorbate mobility and reduces the retardant forces acting on the adsorbate diffusion. Nevertheless, the study by Chouchene et al. [93] found that the adsorption capacity of olive waste adsorbent for Cu and Ni removal decreased with increase of temperature from 2.7 to 2.23 mg/g for Cu^{2+} and from 1.7 to 1.46 mg/g for Ni^{2+}, corresponding to 15°C and 75°C, respectively. It was explained that this trend was due to the exothermic character of the adsorption process.

From what has been discussed above, it is important to note that the heavy metal adsorption process is largely affected by the aforementioned parameters. Dhabab and Hussien [100] have reported that the optimization of adsorption process for a maximum heavy metal removal necessitates to find their optimum conditions. More often, these optimum experimental conditions are achieved at the equilibrium state from which the studies' results such as the adsorption capacity of the adsorbents [108] and effects of the variables discussed above are reported. While studying the effect of adsorption parameters (pH, initial concentration, contact time, temperature and adsorbent mass variation), one parameter is varied and others are kept constant [23,66,72]. However, it can be seen in some studies that the distinction between preliminary and conclusive experiments is not apparent because of either some variables' values under optimum conditions are not kept constant for further experiments or lack of a systematic and coherent approach. In addition, the experimental conditions are not often indicated while presenting the study results on diagrams. This may lead to the difficulty of experiment reproducibility, misunderstanding and results' misinterpretation.

Moreover, some questions related to the extent at which the operating conditions have been optimized may arise and this may lead to the overestimation or underestimation of the adsorbent capacity. On the other hand, more other issues related to the low-cost adsorbent-based adsorption have been pointed out by some authors. Simonin [108] has recently published an excellent article in which the author re-examined the comparison issues related to the pseudo-first-order rate (K_1) and pseudo-second-order rate (K_2) laws. It is proven that the method used by many researchers for the comparison suffers from a methodological bias which unfairly favors pseudo-second-order rate laws. A number of published articles which concluded that the pseudo-second-order rate law described better the experimental kinetic data were randomly selected for re-examination. Simonin [108] has demonstrated that in some of those selected literature K_1 described the adsorption process better than K_2 while in others neither K_1 nor K_2 fit the experimental data. The conclusion on whether K_2 supersedes K_1 or vice versa (which can be calculated from the plots of t/q vs. t for K_2 and $\log(q_e - q_t)$ vs. t for K_1) [24,63,89,108] is based on the comparison of the corresponding correlation coefficient (r^2) values [108], which can also be determined from the aforementioned plots [23]. However, Simonin [108] has lately proven that it was irrelevant to compare r^2 values for the two different functions namely $y^{(1)} = \ln(q_e - q)$ for K_1 and $y^{(2)} = t/q$ for K_2 (q_e being the amount adsorbed metal per unit of adsorbent and t time). Hence, this author suggested a more carefulness in the comparison and kinetic data analysis and proposed a different method for experimental data analysis. It was recommended that a determination of the coefficient r^2 be based on the same function $y = q$ in both cases K_1 and K_2.

In addition to the gap filling and contribution brought by the study by Simonin [108], there are some other recent works [23,72] that have shown a good methodological and systematic approach for the optimization of the media performance and operating experimental conditions. Furthermore, it can be seen from the study [23] that cautions are taken to avoid, for example, the double metal removal by both adsorption and precipitation processes whereby the pH precipitation of the hydroxide metal ions under investigation was considered. Moreover, other literature [73] provided useful information such as the critical initial metal concentration beyond which the adsorption process was not dependent on the initial concentration as well as the concentration values in which there is affinity between biomass and metal ions to be removed.

6. Multi-metal system adsorption and selectivity

Though the single-metal removal is the widely studied, some research studies have studied the simultaneous removal of some metal ions from the SWWs. Studies by Maximous et al. [101] on the removal of Cr^{3+}, Cd^{2+} and Pb^{2+} indicated that maize leaves and rice husk adsorbents have a high affinity to Pb^{2+} with respect to other ions because of relatively high bond stability and high concentration of Pb-sorbent in wastewater compared with that of Cd-sorbents or Cr-sorbents. It was established an adsorbent's selectivity order Pb > Cd ≈ Cr. Vazquez et al. [76] and Mahapatra et al. [27] observed the selectivity and affinity order to be $Pb^{2+} > Cu^{2+} > Zn^{2+}$ and Pb > Cu > Cd, respectively. Large ionic size of Pb^{2+} which results into less hydration in aqueous solution [13], electronegativity and covalent index [76] have been postulated to justify this affinity and preference of Pb^{2+} with respect to other ions. According to these studies, higher electronegativity value implies better sorption. Similarly, the greater the covalent index, the more likely formation of covalent bonds between the metal ions with adsorbent ligands. Previous research studies [68,109] had reported that the difference in affinity was dependent on the metal ionic size, the characteristics and structure of adsorbent ASs and the types of the interactions involved. Furthermore, it was observed that the biosorption increased consistently with increase of atomic weight and ionic radius [68,109]. In a study for the removal of Cr^{3+} and Pb^{2+} ions from the wastewater by a dehydrated pumpkin (*Cucurbita*), Lauren [1] reported that the efficacy of removal followed the pattern of ion molecular mass: greater was the molecular mass and greater was the removal efficiency. Misihairabgwi et al. [29] have found the following order of competitive metal binding and affinity by the pigeon pea husks and baobab shells: Fe > Pb > Hg > Cu > Zn > Cr > As > Ni > Mn > Cd. Parab et al. [107] had previously found that the adsorption preference in the order Cr > Ni > Co while studying the concomitant multi-metal removal from the SWW.

It was observed that the multi-metal removal system has a negative effect on adsorbent sorption capacity found in a single-metal removal system. For example, Adie Gilbert et al. [13] observed that the adsorption capacity of *C. papaya* seeds which was found to be 1,666.67 and 1,000 mg/g for Pb^{2+} and Cd^{2+}, respectively, in a single-metal removal reduced by a factor of 0.833 and 0.908 for the two metal ions, respectively, when their ratio in a mixture was one unit. Even though the adsorption capacity of each metal decreased in a binary metal system, Adie Gilbert et al. [13] and Unuabonah [110] observed that the lighter ions (Cd^{2+}) were mostly affected. Contrary to these observations, the study by Bhatnagar and Sillanpää [60] reported a significant decrease of the tea waste adsorption capacity for Cd^{2+} from 11.29 mg/g in a single-metal system to 2.59 mg/g for binary metal system (Cu^{2+} and Cd^{2+}). It was concluded that the heavier ions Cd^{2+} were most affected than the lighter Cu^{2+} ions. Similar results of the leveling effect of the adsorption capacity of the maize cob and husk due to the mixture of ions had been earlier observed by Igwe et al. [71]. It was explained that this decrease of the adsorption capacity was due to the metal ion competition for the ASs of the adsorbent. Furthermore, it was reported that the accessibility to these sites depends on a number of factors such as diffusion of the solute, the external and intraparticle mass transfer resistance as well as the ionic radii of the metals. Moreover, this study [71] pointed out the negative effect caused by the introduction of the carboxymethyl group ($–COCH_3$) and the presence of other chemicals in particular isopropanol on the adsorbent capacity. It was indicated that the carboxymethyl group and isopropanol exerted a stearic hindrance to the adsorption process and diffusion process, blocking some micropores of the adsorbent, and therefore, limiting the access by the metal ions. Similarly, Memon et al. [84] have indicated that the presence of other ions or complexing agents decreases the metal sorption due to precipitation and complexation reactions or competition for adsorbing sites. Furthermore, the study by Memon et al. [84] showed that the presence of Fe^{2+} suppressed the sorption of Cr^{6+} to some extent. In the light of this literature, it seems that the behavior of the adsorbent in the presence of other ions depends largely on its inherent characteristics and/or possibly on the presence of other chemical species in the solution. Hence, it can be suggested that further scientific explanations are needed to elucidate the driving forces of this selectivity and affinity toward the metal uptake.

7. Adsorbent reusability and desorption studies

One of the advantages of adsorption process based on low-cost adsorbents is their regeneration for reutilization and heavy metal recovery for subsequent reuse at industrial level. Heavy metals recovery and reuse is seen by some researchers as the sole way of avoiding their release into the environment and subsequent adverse health effects [72]. Some research studies have attempted to reutilize the biosorbent upon adsorption process and heavy metals recovery. Ye and Yu [104] attempted to desorb Pb^{2+} adsorbed on rice bran, but the yield was unsatisfactory with the maximum range of 15%–20% due to strong bonding between the adsorbent and adsorbate. Hazelnut and almond shells could be used up to three times and Pb^{2+} recovered was in the range of 20%–30% [77]. Dhanakumar et al. [103] recovered 82.28% of the total Cr adsorbed. Desorption studies by Memon et al. [66] fully recovered all Cd^{2+} sorbed amount (0.1 g). Study by Iqbal et al. [68] recovered 87%, 84% and 99% of the total amount adsorbed of Cu^{2+}, Ni^{2+} and Zn^{2+}, respectively. Previously, Iqbal et al. [79] had recovered 98.23% and 99.07% of the adsorbed Cd^{2+} and Pb^{2+}, respectively. The adsorbent could be reused up to five cycles without decreasing the adsorption capacity. Unexpectedly, the adsorption capacity increased to some extent for the second cycle because of more release of alkaline and earth alkaline metal ions by the adsorbent. Rocha et al. [80] proven that the adsorption capacity was maintained constant up to 15 cycles. Desorption studies by Humelnicu et al. [72] have recovered 89.12% and 90.25% of Cu^{2+} and Zn^{2+}, respectively. Chouchene et al. [93] have reported a recovered amount (96%) of Cu^{2+} and Ni^{2+} closer to the fraction initially adsorbed. Very recently, *L. domesticum* peel could be regenerated for subsequent reutilization up to four cycles, and Ni^{2+} recovery was successful up to 85% [95]. Mango peel was proven to be reused repeatedly up to five cycles and the metal ions were completely recovered [79]. The low-cost adsorbent prepared from sesame [81] was recently utilized up to four cycles in the study for Cd^{2+} adsorption. From the first to fourth cycle, it was observed a gradual increase of Cd^{2+} equilibrium concentration as a result of adsorption capacity decrease which in turn reduced the desorption percentage from 93.81% to 72.41% corresponding to the first and fourth cycle, respectively. Similar trends were also reported for the removal of As^{3+} by the tea waste [103]. The reusability percentages decreased from 99.0 to 49.0 for the first and fifth cycle, respectively [81]. Song et al. [97] have regenerated the biosorbent (rice husk and rice straw) up to four cycles. However, they observed a gradual decrease of their adsorption capacities up to 50% corresponding to the decrease of an average of 40–45 to 20–25 mg/g). This decrease was due to the equilibrium established between the Hg^{2+} concentration in the solution and ASs on the surface of the biosorbents and the decomposition of the activating agent used in acidic medium. Naushad et al. [24] reported a slight reduction of 2.5% from 97% in the adsorption percentage after four cycles, showing an excellent regeneration possibility of the starch/SnO_2 nanocomposite used as adsorbent material.

From the above literature, it is evident that the biosorbent regeneration and metal recovery studies have been successful to some extent. It was observed that almost complete metal recovery is possible if the ion exchange is the main mechanism involved in adsorption process [66]. It was also indicated that other mechanisms such as complexation lead to a small amount of the recovered metal compared with the total adsorbed metal [68]. In addition to the type of adsorption mechanism, other studies have indicated that high desorption rates also depend on the regenerating agent used. For instance, strong acids such as HCl [95,97], H_2SO_4 [84], HNO_3 or alkaline solution [72] were proven to be the most effective eluents especially in adsorption processes where the ion-exchange mechanism (chemisorption) is mainly involved. This is because under acid conditions, the protons H^+ compete and displace the adsorbed cationic ions causing the metal desorption [95]. Humelnicu et al. [72] have observed that the distilled water can also be used for desorbing the adsorbed ions if the weak bonds are involved in adsorbate–sorbent binding.

8. Advantages and limitations of low-cost adsorbent-based adsorption

Like other technologies, adsorption technology presents both advantages and limitations. In recent years, heavy metal adsorption-based technique has become popular and considered to be better among other technologies used for water treatment due to its noteworthy environmental and economic advantages [7,60]. Easy operation, convenience, low-cost, simple design, adsorbent reuse for the practical application and heavy metal recovery and large applicability to the removal of various pollutants from the polluted water [22,24,60] are among the benefits of this technology. In addition, it was reported in some literature that the low-cost adsorbent-based adsorption has proven to be higher effective than the conventional technologies. For instance, the A/C prepared from macadamia nut shells, baobab shells, pigeon pea husks, rice husks, *M. oleifera*, marula stones [29], grain rice [94], soybean oil cake [63], maize leaves and rice husk [101] and plantain peel charcoal [65] has proven to be more efficient than the commercial A/C in adsorbing some metal ions from the aqueous solutions. In some instances, their adsorption capacity was found to be >20 times higher than that of the commercial A/C [29]. Research studies reported that less energy is required for converting the adsorbent into charcoal [65], and the resulting A/C has a great surface area, microporous structure and porosity properties and can be used in both batch and column operation system [22,27]. Furthermore, the adsorption process is very quick, adsorbent materials are cheaper, abundant and affordable [75]. For instance, it was estimated that 1 kg of biomass from the pumpkin would cost about 865 times less expensive than 1 kg of activated charcoal [1]. Moreover, the adsorbent reclamation at low cost is possible; the quality of treatment, selectivity and adsorption capacity are often high [22,64,75,94].

Although heavy metal adsorption by the low-cost materials has many advantages over the conventional technologies, some hindrances and inherent limitations of this technology to the large scale application have been reported in the literature. Naushad et al. [24] have recently reported that one of the greatest restrictions of the biopolymeric materials (adsorbent extracted from natural plant) is that their organic ion exchangers lack the thermal stability. On the other hand, Kyzas and Kostoglou [111] observed that the main disadvantages of the adsorption technique were related to the studies which were still at the laboratory stage. In addition to this, it can be seen from the published papers that most of the adsorption studies are based on batch experiments. In the same line, a recent research study by Uddin [7] has concluded that almost all 10 years studies on heavy metal adsorption experiments were based on the batch technique to report and confirm the applicability and selectivity of the adsorbent maximum adsorption capacities toward the targeted metal contaminants. Moreover, uneven distribution between batch adsorption experiments and continuous flow modes had been reported by Varma et al. [5]. This study had suggested a trial of different modes of operation including continuous flow for the maximum adsorption capacity exploration.

It was reported in the literature [81] that the batch experiment studies provide fundamental information regarding the biosorbents performance, but continuous mode experiments were needed for more detailed information and practical application. Laboratory column experiments and subsequent pilot scale studies had been also previously recommended as prerequisite for the biosorbents application at industrial scale [37]. Other studies by Rocha et al. [98] have reported concerns over the possibility of overestimation and/or underestimation of the low-cost adsorbents removal capacity due to the limited studies performed under realistic conditions of real IEs concentrations in heavy metals. For instance, Rocha et al. [98] have reported that some studies on Hg^{2+} removal by rice husk adsorbent used higher initial concentrations between 8 and 2,000 mg/L. Consequently, the residual concentrations were still higher (10 times) than the guideline limits despite high removal efficiency achieved. High residual concentrations of 0.05 and 41.25 mg/L of the Hg^{2+} ion were observed in a study by Naushad et al. [24] despite the high adsorption capacity of 333 mg/g of the composite materials (starch/SnO_2 nanocomposite), and their respective removal efficiency rate of 99.5% and 72.5%.

Other studies have reported that the suitability of the biosorbents is limited to the treatment of heavy metal at low concentrations in wastewater [22,27,75,95]. It was shown in many experimental studies [62,84,85,96] that an increase in metal concentration resulted into decrease of the percentage metal removal efficiency. A wide range of low-cost adsorbents are adsorbate specific [60]. This suggests that their effectiveness is also adsorbate specific. Kyzas and Kostoglou [111] have reported that the complex mixture of various pollutants such as dyes, phenols, metals, pesticides and pharmaceuticals in IEs, and their simultaneous existence constitute a major hindrance. Other research studies have indicated that most of the low-cost adsorbents have proven poor adsorption capacity and low efficiency [29,104]. Desorption studies for metal recovery may not yield satisfactory results [103], sometimes give poor results [104,112]. On the other hand, some researchers have raised issues and concerns over the costs and marketable products derived from the biomaterials. Rocha et al. [98] have reported that the use of low-cost adsorbents is time consuming and increases the cost of the material. This is probably due to the physicochemical pretreatment of the biomaterial, use of chemicals as solvents (e.g., *n*-hexane and ethanol) and/or desorption agents as it can be observed in the literature [73]. For instance, Lauren

[1] reported that the NaOH precipitate price was estimated at around $106/kg. Kyzas and Kostoglou [111] have recently reported that the modification process of the green material to produce A/C increases drastically the costs due to the use of the chemical agents and regeneration costs which limits its use in large-scale application. Similarly, other research studies have reported that to increase the efficiency of heavy metal removal from the contaminated water requires additional substances such as additives of alginate, magnesium, tannic acid and surfactants [75], suggesting additional costs. Likewise, the study by Kyzas and Kostoglou [111] underlined that the detailed information on economic and market analyses of the biosorbents was still limited. Therefore, the production of marketable products for commercialization and use for industrial wastewater treatment is still problematic. In the same direction, Zhang et al. [90] have recommended a detailed study of operational and economic costs for reference of practical engineering applications.

9. Conclusions and further research directions

The present work has reviewed the low-cost adsorbents derived from agricultural wastes, and the hindrances to the removal of heavy metals from IEs. The most heavy metals encountered in IEs, their relative contribution to the contamination of the water bodies, and their adverse effects on ecosystem have been discussed. More importantly, the use of the low-cost adsorbents for the treatment of waters laden with heavy metals, the advantages and limitations of these adsorbent materials and their adsorption mechanisms, the multi-metal adsorption system, adsorbents regeneration and heavy metal recovery have been the focus of this review paper. We have tried to give a general overview of the actual situation and trends of the treatment of waters laden with heavy metals which can be schematically represented in Fig. 3.

It is evident that the research studies on heavy metal adsorption from the wastewaters by the agricultural low-cost adsorbents have achieved significant and satisfactory results. However, their applicability to the IEs is still problematic for several reasons outlined below and future research may try to solve these issues.

- Studies focusing on heavy metal removal from real IEs are still scarce, and therefore, the agro-based biosorbents behavior with respect to the complex mixture of the contaminants is not well known. Further studies should focus on pilot studies with industrial wastewaters in order to evaluate the real adsorption potential of the adsorbents under their typical metal concentrations and the presence of the complex mixture of various pollutants. This will help to determine the extent at which the adsorbents can remove heavy metals as well as other contaminants, and therefore, improve water pollution control. Hence, the ultimate goal should be meeting the effluent discharge standards.
- Batch biosorption studies have provided fundamental skills and information on performance of agricultural waste materials. Adsorption studies on continuous mode experiments are still scarce for practical application at industrial scale. Hence, much still needs to be done and improved notably qualitative and quantitative data on how much (both contaminants and adsorbent), what type of pollutants can be removed and at what extent the treatment can be efficient.

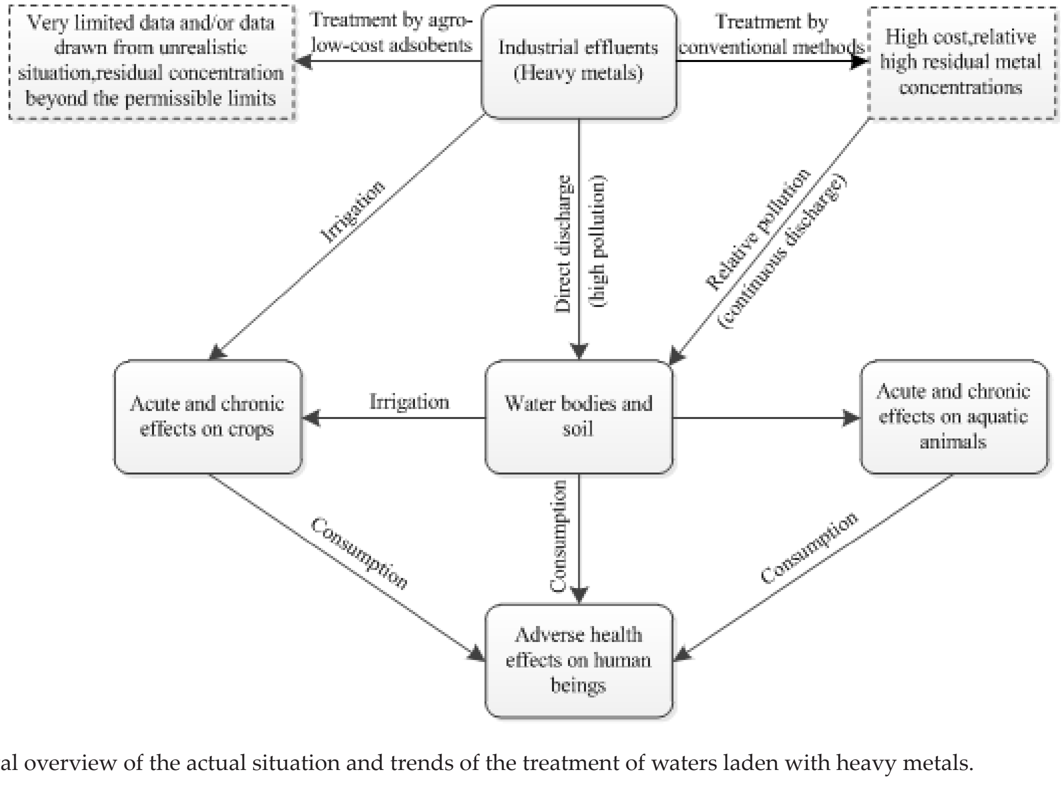

Fig. 3. General overview of the actual situation and trends of the treatment of waters laden with heavy metals.

- Detailed economic and costs evaluation for material engineering design and the low-cost adsorbents commercialization (marketable product) should be the target of future research.
- Adsorption capacities of the adsorbents vary depending on experimental conditions, treatment and preparation conditions of the adsorbent raw material, their form and nature among others. More studies aiming at exploring and optimizing the adsorbents qualities for maximum heavy metal adsorption capacity are suggested. In this regard, a detailed procedure and methodological approach is of great importance.
- For the purposes of practical application, experiments reproducibility and comparison, it is recommended that while evaluating the efficacy of the adsorption process in optima conditions, data be explicitly expressed in terms of percentage removal, amount of metal adsorbed per unit weight of the adsorbent, initial and residual metal concentrations. Furthermore, the experimental conditions should be highlighted when the study findings are being reported on graphical representations.
- It was recently reported [24] that the latest research studies on wastewater treatment have proven that some of the low-cost adsorbents limitations may be overwhelmed by the application of the synthesized composites. It was shown that the combination of suitable organic materials including, resins, and agricultural residues, synthetic and natural polymers with inorganic precursors (such as SnO_2) not only offers an excellent physicochemical properties to the resulting composite material but also increases its adsorption capacity, and therefore, enhances adsorption efficiency. Moreover, the new composite material was reported to be suitable for column adsorption studies which are needed for large industrial scale application.

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