Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21256

85 (2017) 339–357
August

On the performance of bioadsorption processes for heavy metal ions removal by low-cost agricultural and natural by-products bioadsorbent: a review

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Received 5 March 2017; Accepted 19 July 2017

ABSTRACT

Nowadays, heavy metal ions produced from industrial and human activities are considered as a major source of environmental contamination that led to deterioration of many ecosystems and social health. This situation represents a big challenge to develop sustainable treatment methods to remove these contaminations. Among the treatment processes that are being applied to remove these hazardous wastes from different types of wastewater, bioadsorption process using low-cost bioadsorbents has been proven as one of the most feasible decontamination method. Unlike other treatment methods, bioadsorption which represents a biotechnological innovation is simple and permits regeneration of toxic metallic sludge. For this reason, this review is devoted to give the reader suitable information about the risk of heavy metal ions and an overview of some potential of biosorbents such as natural or modified agricultural wastes and microorganisms used as bioadsorbents. It was clear that surface modification improves their bioadsorption capacities and performance. In addition, some attention has been given to the role of some functional groups in forming bonds with the ions and the mechanism of the removal process. Since mathematical modelling is one of the important features of engineering processes, this review concentrated on different kinetic, isotherm and diffusion models that have been developed to describe bioadsorption processes. Moreover, the effect of some parameters such as temperature and pH on the bioadsorption process was reviewed and discussed.

Keywords: Bioadsorption; Low-cost bioadsorbents; Modification of bioadsorbents; Adsorption models; Kinetic models; Adsorption isotherms; Diffusion models

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1. Introduction

During the last decades, there has been a significant increase of industrial technologies and human activities that utilize heavy metal ions or compounds [1]. This remarkable industrialization has led to the continuous accumulation of heavy metal ions in ecosystem and caused deterioration of many ecosystems and social health [2–6]. Anthropogenic inputs such as agricultural activities, energy conversion and production, metallurgy and mining, microelectronics, solid and liquid waste disposal have been the major sources of heavy metal ions accumulated in our environment. Both soils and sediment have been found to be major sink for metal contaminants in terrestrial and aquatic system, respectively.

As a result of their natural toxicity and their ability to diffuse into the different water recourses, metal ions pose a serious risk and danger to the different ecosystem. Metal ions are not degradable and most of them have been acknowledged to be persistent in nature, dispersed in water resources [7] and been able to be bioaccumulated [8,9] and bioaugmentated [10]. In addition, most of heavy metal ions and their salts are

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1944-3994/1944-3986

found to be soluble in aqueous solution. Therefore, it is very difficult to separate these ions using traditional separation processes like precipitation [11]. Since these ions cannot also be degraded [12] and converted to harmless products [13–16], it is of paramount to treat and remove these toxic species from all types of wastewater effluents prior its disposal [8,17].

The concept heavy metal ions refer to elements of a specific gravity more than 5.0 such as transition elements. Industrial activities such as mining, electroplating, textile, metallurgy, paints and non-ferrous metals industry are considered as the major sources of these heavy metal ions [7,18]. These heavy metal ions are generally toxic and have adverse effects to human health and to other life forms. Their toxic effects could range from physical discomfort to life-threatening illness including irreversible damage to vital body system.

Table 1 shows the major sources and toxic effects in addition to the maximum contamination limits standards of some heavy metal. It is clear in Table 1 that metals like lead, mercury, chromium(IV) and cadmium, are topping the toxicity list compared with other metals [5].

There are several effective removal processes that have been used to achieve the efficient removal of environmental contaminations such as heavy metal ions [1,27,28]. The processes that have been applied to treat aqueous solutions and industrial wastewater include biological treatment [29], coagulation, membrane filtration, activated carbon [30,31], electrolyte process [32], solvent extraction [33], chemical precipitation [14,15], ion-exchange [34], reverse osmosis [35,36], sedimentation, flotation [7], air stripping, stem stripping, cementation, dialysis/electrodialysis [37], resin chelation, liquid–liquid and solid–liquid extraction [15], electrocoagulation [38,39], flocculation or coagulation, neutralization, adsorption and using lignocelluloses as well [3]. However, some of these physicochemical methods are considered as unfeasible, particularly, if the ions contents in wastewater are in the range of 1–100 mg L^{-1} [10,14,40]. In addition, complete metal removal consumes large amounts of reagents and energy [8,15] and this also leads to new environmental problems related to waste disposal [41]. Moreover, most of the previous treatment methods are not feasible for relatively small scale industries [42]. Table 2 shows a summary of treatment methods applied for heavy metal ions and their advantages and disadvantages [28,43,44]. It is clear from Table 2 that all the present methods have serious technical and economical disadvantages that justify the search for sustainable treatment methods.

During the last decades there have been a tremendous number of publications on using bioadsorption as a promising treatment process for heavy metal ions removal found mainly from industrial wastewater. These publications have studied the use of new bioadsorbents and testing their performance, the development and application of several new or revised kinetic, isotherm and diffusion models as

Table 1
Sources of some heavy metals, their toxic effects and the maximum contamination limits standards (MCLS)

Heavy metal	Main sources	Major toxic effects	MCLS (mg L^{-1})	Reference
Arsenic	Combustion of fossil fuel, mining, pesticides	Bronchitis, bone marrow, skin cancer depression, pigmentation changes, neurological disorders, muscular weakness, dermatitis, hepatomegaly	0.05	[19]
Cadmium	Mining, smelting, plastic, welding, refining pesticide, fertilizer	Kidney damage, emphysema, weight loss, gastrointestinal disorder, Itai–Itai disease, bronchitis, hypertension	0.01	[20]
Chromium	Steel, electroplating, dyes and textile industry	Carcinogenic, severe diarrhoea, skin rashes, respiratory problems, kidney and liver damage, vomiting, weakened immune systems and genetic material	0.05	[21]
Copper	Electroplating, mining, pesticides, batteries, copper cooking pots,	Neurotoxicity, anaemia, hyperactivity, schizophrenia, postpartum psychosis, insomnia, cystic fibrosis. Autism, stuttering, inflammation and dizziness	0.25	[22]
Lead	Batteries, mining, paint, pigments, explosives, electroplating	Anaemia, malaise, brain damage, anorexia, liver, kidney, gastrointestinal damage, mental retardation	0.006	[23]
Mercury	Mining, paper and paint, industries, batteries	Damage to kidney and nervous system, protoplasm poisoning, dermatitis, corrosive to skin, eyes, muscles	0.002	[24]
Nickel	Electroplating, porcelain enamelling, storage batteries, paint	Dermatitis, lung cancer, chronic bronchitis, pulmonary fibrosis, rapid respiration, headache, dizziness	0.20	[25]
Zinc	Mining, refineries, brass manufacturing, plumping	Gastrointestinal distress, metal-fume fever	5.0	[26]

Table 2
Common methods to remove heavy metals from wastewater

Number	Process	Advantages	Disadvantages
1	Adsorption using activated carbon	High efficiency (99%)	Costly, no regeneration, performance depends on adsorbent
2	Adsorption using industrial by-products or mineral substances	Low-cost, high efficiency	Production, reservation and regeneration of the adsorbent still cause much attention
3	Bioadsorption using modified biopolymers	Good adsorption capacity, selectivity	Challenges concerning the proper synthetic methods and optimizing the operating conditions
4	Chemical coagulation	Ease of sludge settling, dewatering	Costly, high consumption of chemicals
5	Chemical precipitation	Ease of operation, cheap	Large quantity of sludge, sludge disposal problems
6	Electrochemical methods	Selectivity for metal ions, no chemical consumption, most of the metals can be removed	High capital and operational cost, current density
7	Electrodialysis	High selectivity	High operation cost due to membrane fouling and energy consumption
8	Ion-exchange	Selective for metal ions, regeneration of materials	Costly, available for less number of metal ions
9	Membrane filtration	Low space requirement, low pressure, high separation selectivity	High operation cost
10	Nanofiltration	Easy operation, reliability, high efficiency	Low anticompacting ability compared with ultrafiltration
11	Photocatalysis	Simultaneous removal of metals and organic pollutant, less harmful by-products	Long-time duration, limited applications

well as some reviews on bioadsorption and bioadsorbents. Accordingly, this paper will be another effort to review the latest publication concerning low-cost natural bioadsorbents as well as modified ones in addition to the most popular kinetic, equilibrium and diffusion models that have been applied. The impact of some parameters such as temperature and pH on the bioadsorption capacity will be discussed.

2. Bioadsorption of heavy metal ions

The technology of bioadsorption of aqueous environmental pollutants has been popular among researchers in the past 20 years [3]. Bioadsorption process uses natural materials of biological origins which have metal-sequestering property to reduce the heavy metals ions concentrations from ppm to ppb level [41,45,46]. Bioadsorption of heavy metals is the physicochemical removal process of heavy ions or their compounds, from wastewater by using bioadsorbents [6]. The term bioadsorption refers to any system which involves interactions between an adsorbate which could be an atom, molecule or a simple or complex ion with a bioadsorbent such as a solid surface of a biological material. This interaction leads the adsorbate accumulation on the adsorbate–bioadsorbent interface. Consequently, the adsorbate concentration in the wastewater decreases until an equilibrium is reached [9]. This technique also allows performing kinetic and equilibrium studies using very sophisticated instruments [47].

Bioadsorption has been recognized as a promising treatment technology due to its high efficiency [48] minimal chemical and/or biological waste sludge [3,37], relatively low-cost and short time [30], the ability to reuse the bioadsorbent [4,14], versatility of bioadsorbents [47], no additional nutrient requirement [49], eco-friendly [35], locally available material [8], the ability to use selective bioadsorbents for specific metals of interest, the ability to remove heavy metal ions regardless of their toxicity, no production of secondary toxic compounds [11], simplicity and availability of the low-cost bioproducts that could be used as bioadsorbents [9].

Nevertheless, bioadsorption also has several disadvantages such as the early saturation of all bioadsorbents active sites by the adsorbate ions. Therefore, metal ions desorption and bioadsorbent regeneration is required for efficient further use. The mechanisms of the bioadsorption process are rather complex and basically difficult to be understood. However, it may be one or combination of several processes that include complexation, ion-exchange, electrostatic interaction, coordination, chelation, adsorption and microprecipitation. A large variety of bioadsorbents have been used for the metal ions removal. These bioadsorbents have been classified to several categories bacteria, yeast, fungi, algae, agricultural and industrial waste, and others [45]. Bioadsorbent biomass can be subdivided to produce small and stable particles. The particles of biosorbents can be filled in columns to continuously remove heavy metals [36]. Generally, several factors could affect the bioadsorption capacity of any adsorbate such as the presence of electric charge, the types of functional groups, pore size, surface area, pH and temperature of bioadsorption medium [8]. In addition, the selection process of a suitable bioadsorbent for certain adsorbate is difficult since it is influenced by several factors [44]. These factors include easy availability, low-cost high adsorption capacity and selectivity [42,50–52]. A sustainable treatment process should use an adsorbent that meets most of the above requirements especially high adsorption capacity, high selectivity, low-cost, easy desorption and regeneration, negligible leaching into aqueous systems [18,44].

3. Natural and low-cost bioadsorbent

Table 3 shows some examples of these natural bioadsorbents and the values of temperature and pH, and some of the major results concerning the removal efficiency or the bioadsorption capacity.

As shown in Table 3, many cheap bioadsorbents obtained from natural bioadsorbents such as agricultural wastes and some microorganisms have been used for the removal of metal ions. Additional examples of bioadsorbents including oil palm, coconut-based [4], sorghum straw, agave bagasse, oats straw and waste olive cake [8], banana, orange and lemon peels [9], barley straws [24], jack fruit seed [26,33], pine [48], *Uncaria gambir* [55], orange waste [61], juniper [62], nutshell [63], ground coffee [64], *Moringa oleifera* leaves [65] and many others.

These natural and agricultural products are readily available and the principle objective of their use as biosorbents is basically to utilize them in a useful and efficient way and to leave them to cause waste disposal problems if not being managed properly [2,18].

To describe the extent of the bioadsorption process, it is very important to calculate the quantity of metal uptake [49]. For this purpose, the two important parameters that could be used to express metal uptake are the removal percentage, $R\%$ and q, mg g^{-1}, values:

$$R\% = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\% \tag{1}$$

and

$$q = \left(\frac{C_0 - C_e}{m}\right) \times V \tag{2}$$

where C_e and C_0 are the metal ion equilibrium and initial concentrations, mg L^{-1}, m is the dry bioadsorbent mass of the biomass used, g, V is the solution volume, L and q is the adsorbed metal ions mass per 1 g of adsorbent, mg g^{-1}. Eq. (2) has been found to be more appropriate to compare the adsorption capacities of different adsorbents, since $R\%$ value does not give any information concerning the used adsorbent quantity which will be misleading upon the comparison between different types of bioadsorbents [5].

4. Chemical composition of natural by-products for bioadsorbents

The use of agricultural by-products has shown many advantages. The cell walls of the plants is usually rich in polysaccharides especially pectin cellulosic compounds. Alkaline treatment usually ionizes pectin compounds to generate negative charges which can bind to metallic cations. Another advantage of agricultural by-products is the ease of their preparation without the need of any microorganisms such as yeast, since these materials are basically obtained from agricultural by-products and industrial wastes. In addition, undesired microbial growth is also inhibited by the adsorbed heavy metal ions. Moreover, the high potential of metal recovery has also been considered as a further advantage. When the adsorbent becomes saturated, the metal can be separated from the organic materials by incineration and to be reused in other applications [9].

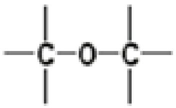
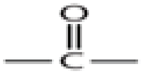
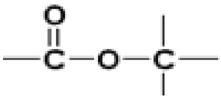
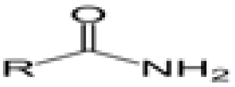
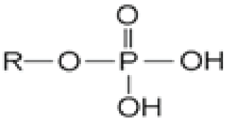
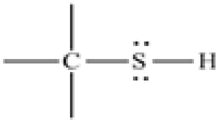
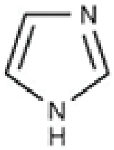
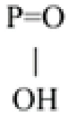
Table 3
Natural bioadsorbents used for heavy metal ions bioadsorption

Bioadsorbent	Metal ion	pH	T (°C)	% Removal or Q_{max}	Reference
Chitosan	Cu(II), Mn(II), Fe(II), Ni(II)	5.3–5.5	30	99.25	[53]
Coconut husk	Cu(II), Fe(II), Pb(II)	5–7	50	90	[54]
Palm fruit fibre	Pb(II), Cu(II)	10	Room temperature	100	[55]
Grape bagasse	Cd(II), Pb(II)	7, 3	25	0.774, 0.428 mg g^{-1}	[56]
Bran	Cd(II)	8.6	20	87	[11]
Durian shell	Cr(VI)	2.5	60	117 mg g^{-1}	[23]
Tea waste	Ni(II)	4	25	15.26 mg g^{-1}	[2]
Cortex fruit wastes	Cd(II), Pb(II), Cu(II)	–	40	50	[9]
Seaweed biomass	Cr(IV)	2	25	113.6 mg g^{-1}	[57]
Algae	Pb(II), Cd(II)	4	25	283 mg g^{-1}	[58]
Fungi	Pb(II)	5	25	45 mg g^{-1}	[59]
Yeast biomass	Cr(IV)	4	30	87 mg g^{-1}	[60]
Ballota undulata	Cd(II)	2–10	20–50	121.1 mg g^{-1}	[17]

Many authors have reported cellulosic materials as good bioadsorbents for heavy metal ions [36]. The main constituents of cellulosic materials are cellulose, hemicellulose and lignin [20,48]. Other constituents include extractives lipid, proteins, sugar and water [5]. It also includes many polar functional groups of lignin such as carboxylic, hydroxyl, lactone [33], alcoholic, ketones, aldehydes, phenolic and etheric groups as shown in Table 4. These functional groups can form coordination bonds with heavy metal ions [61] via an electron pair donation and to from complexes [20]. Some bioadsorbents have shown abundance of carboxylic groups which are considered as good binder with the ions [61]. Table 4 shows the main functional groups found in natural bioadsorbents. The most active functional groups include the hydroxyl, carboxylic, carbonyl and amino groups.

Lignin is an aromatic polyphenolic and highly branched polymer with three-dimensional structure [30] and of an infinite molecular weight [3]. However, lignin molecular weight can be lowered by mechanical cleavage of the long chains. Lignin is a filler in the pores in the cell wall and it

Table 4
The main functional groups found in natural bioadsorbents

Formula of functional group	Name	Ligand atom	Class of compound
R – OH	Hydroxyl	O	Alcohols, carbohydrates, phenols
 $-\overset{\mid}{\underset{\mid}{C}}-O-\overset{\mid}{\underset{\mid}{C}}-$	Etheric	O	Ethers, polysaccharides
 $-\overset{O}{\overset{\|}{C}}-OH$	Carboxylic	O	Fatty acids, proteins, organic acids
 $-\overset{O}{\overset{\|}{C}}-$	Carbonyl group	O	Aldehydes, carbohydrates
 $-\overset{O}{\overset{\|}{C}}-O-\overset{\mid}{\underset{\mid}{C}}-$	Esters	O	Lipids, oils
	Amide	N	Proteins
=NH	Imine	N	Amino acids
 $R-O-\overset{O}{\overset{\|}{\underset{\underset{OH}{\mid}}{P}}}-OH$	Phosphate	O	DNA, RNA, ATP
 $-\overset{\mid}{\underset{\mid}{C}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-H$	Thiols	S	Cysteine, amino acids
	Imidazole	N	Amino acids
 $\underset{\underset{OH}{\mid}}{P}=O$	Phospodiester	P	Teichoic acid

increases the mechanical strength of the cell wall [61]. Lignin is chemically inert material that characterized by relatively high surface area of 180 $m^2 g^{-1}$, and a molecular weight in the range of 2,000–15,000 g mol^{-1}. Accordingly, these good properties present lignin as a promising bioadsorbent for metal ions removal from wastewater [3]. Fig. 1 shows the chemical structure of a lignin unit.

On the other hand, cellulose has been acknowledged to be the primary component of green plants and wood [66]. Cellulose is a straight chain biopolymer, made of D-glucose as a building block. D-Glucose units bind by the stable β-(1,4)-glycosidic linkage [3]. The molecules of cellulose are combined together to form microfibrils [30]. Moreover, cellulose is an insoluble in water and is not affected by acids and enzymatic hydrolysis [3]. Fig. 2 shows the schematic illustration of cellulose structure. It is clear from Fig. 2 that cellulose contains many active functional groups such as hydroxyl, etheric and carbonyl groups. Some of these functional groups participate in the bioadsorption process of heavy metal ions depending on the properties of the ion.

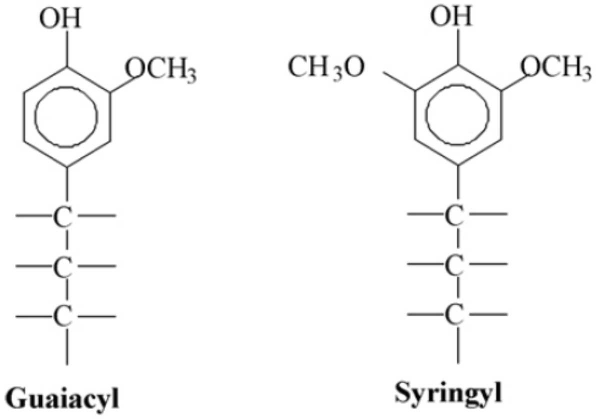


Fig. 1. Building units of lignin (adapted from Malkoc and Nuhoglu [3]); Elsevier license number: 4110800364631.

5. Modification of bioadsorbents

In general, metal ions bind with the bioadsorbents through certain active functional groups of ligands such as carbonyl, carboxyl, phenolic or amino groups. These functional groups are found in some raw bioadsorbents and are reported as the active functional groups towards heavy metal ions that attach them onto bioadsorbents [54]. However, raw bioadsorbents in many cases need surface modification by chemical treatment to improve their sorption capacity [18]. These chemical treatments can be performed using different types of chemical modifying agents. These agents included basic solutions such as sodium hydroxide, acidic solutions like nitric and hydrochloric acid, oxidizing agents like hydrogen peroxide [30], citric acid [65]. Table 5 shows some modified bioadsorbents, the conditions of their application and the removal efficiency or the adsorption capacity.

Among these chemical treatment methods are the hydrolysis process using sodium hydroxide (NaOH), which is able to increase the adsorption capacity of bioadsorbents. The use of NaOH has been reported to remove soluble organic components as well as improving surface properties of the biosorbents [48]. On the other hand, sulphonation treatment of juniper has led to increase its adsorption capacity of cadmium twice as much as the capacity of the unsulphonated juniper. The introduction of phenolic groups to the bioadsorbent also caused the formation of complexes with heavy metals [32]. Pyrolysis treatment which involved heating process to convert lignin to activated carbon with high surface area is another treatment process that improves the adsorption capacity. Other chemical treatment modification methods include esterification, phosphorylation, methylation and hydrolysis of amide and carboxylate groups [3].

Activated carbon has also been reported, which is considered as the most efficient technology to remove adsorbates such as heavy metal ions from wastewater [15]. Activated carbon usually has a relatively large specific surface area with a highly microporous structure. In addition, it has a relatively high mechanical strength that made it suitable adsorbents for heavy metal ions from wastewaters [12,37].

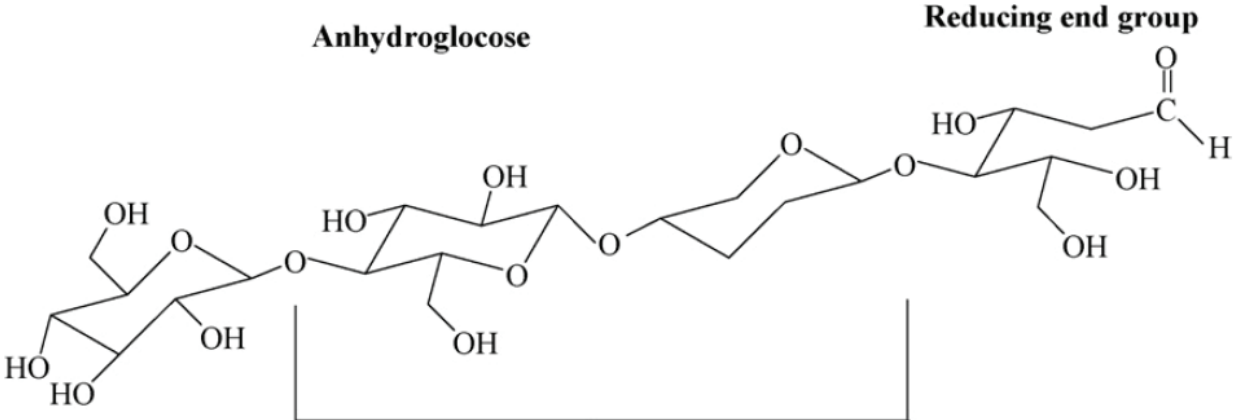


Fig. 2. The structure of cellulose (adapted from Malkoc and Nuhoglu [3]); Elsevier license number: 4110800364631.

The activated carbon surface usually has heteroatoms that play an important role in the adsorption process mechanism. The heteroatoms such as hydrogen, oxygen, nitrogen, sulphur and halogen are bonded to the carbon layers edges. The oxygen-containing functional groups which are also signified as surface oxides have been acknowledged as the common species that exists on the carbons surface. These groups can be formed by chemical, mechanical and electrochemical reactions could significantly influence the adsorption processes. Oxidizing agents have been found to be used to generate three types of oxygen containing groups; basic, acidic and neutral.

Abia and Asuquo [2] used both untreated palm fruit fibre and modified palm fruit fibre (MOPF) treated by 0.5 and 1 M mercaptoacetic acid solution, respectively. They investigated the kinetic models of nickel(II) and lead(II) ions bioadsorption from wastewater. They reported that the ions removal efficiency increased with chemical modifications in the order of 1.0 M MOPF > 0.5 M MOPF > UOPF (unmodified palm fruit fibre). They reported that the specific surface area of the three adsorbents also increased by the chemical modification with methylene blue method. They also found that, nickel(II) ion was adsorbed faster than that of lead(II) ion. It was attributed to the ionic radii of both metals; nickel(II) ion (0.72 Å) and Pb (1.20Å), in which smaller ionic radius diffuse faster through the adsorbents sites compared with the larger ionic radius.

The use of sulphuric acid, H_2SO_4, has also been reported by Martín-Lara et al. [78]. They found that H_2SO_4 could be utilized to improve the bioadsorption of lead from wastewater by sugarcane bagasse. Treatment by H_2SO_4 leads to the formation of negative groups at relatively low or acidic pH range and increases the surface area. In addition, the acid used acts as an oxidizing agent that could oxidize bagasse to acidic groups to carboxylic groups.

Al-Qodah et al. [18] modified green algae by phosphorylation to enhance the bioadsorption of Cu^{2+} ions. They used Fourier transform infrared (FTIR) analysis to determine the functional groups that existed in the raw and phosphorylated algal species *Spirogyra* biomass. Fig. 3 shows the FTIR spectrum of both samples of a raw and a phosphorylated green. It could be seen in Fig. 3 that the FTIR window from 400 to 1,300 cm^{-1} indicates a considerable changes of phosphorylated green algae spectra. It seems that phosphorylation treatment increases the phosphate groups in the algal structure. The shoulders at 504 and 531 cm^{-1} of P–O stretching become sharper in the phosphorylated algae. In addition, C–O–P stretching in phosphate esters at 1,064 cm^{-1} also shows a small shoulder. Finally, sharper peaks present at 1,240 cm^{-1} as a result of P=O asymmetric stretching. This indicated that chemical treatment changes the chemical structure of bioadsorbents and could enhance their bioadsorption capabilities.

6. Adsorption mechanism

It is very necessary to understand how the metal ion binds to the biomass. This will be accomplished by identifying the active functional groups that are able to bind with metal ions. As indicated in section 4, the functional groups are basically found in the cell wall of plants or microorganisms. The hygroscopic and affinity for water characteristic of lignocellulosic material allow water to permeate in the non-crystalline part of the cellulose, hemicellulose and lignin. Consequently, in an adsorption process, solutions can interact with different cell wall constituents [3,79,80].

In most cases, this interaction is referred as chemical adsorption since it produces strong chemical bonds via selective, irreversible and an endothermic reactions. Hui et al. [81] explained the adsorption mechanism of Cu(II)

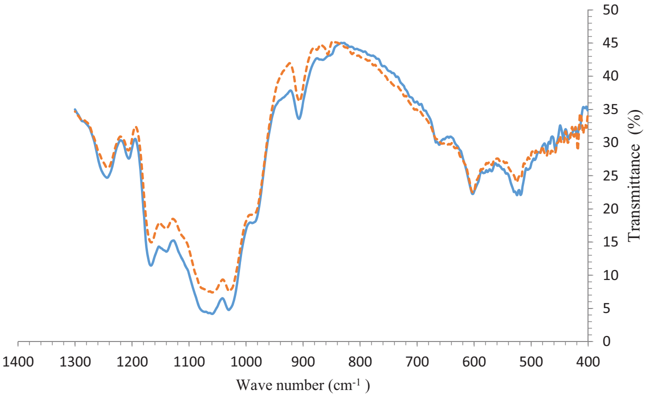


Fig. 3. FTIR analysis for raw green algae and phosphorylated green algae (adapted from Al-Qodah et al. [18]).

Table 5
Some modified bioadsorbents

Bioadsorbent	Metal ion	pH	Temperature, °C	% Removal	Reference
Chitosan-coated acid	Cr(IV), Cr(III)	5.0	NS	86	[67]
Modified rice husk with polyaniline	Cd(II)	NS	30	93.08	[68]
Modified cashew nuts	Cd(II),Cu(II), NI(II), Zn(II)	2–7	30–60	90–95	[69]
Modified sugarcane bagasse	Cd(II)	6	30	23 mg g^{-1}	[70]
Modified sugarcane bagasse	Cd(II)	6	30	189 mg g^{-1}	[71]
Chitosan/sisal/banana composite	Cu(II)	5	30	89	[72]
Wood-based adsorbents	Cd(II), Pb(II)	7	50	NaOH (98%), KOH (96%)	[73]
Phosphorylated green algae	Cu(II)	6	30	65 mg g^{-1}	[18]
Acetic acid treated blue green algae	Cr(IV), Ni(II)	5.5	30	84.6, 83.1	[74,75]
$MaNO_3$ modified brown algae	Co(II)	7	45	80.55 mg g^{-1}	[76]
Pretreated *Aspergillus niger* biomass	Cu(II)	6	NS	23.62	[77]

on adsorbent containing amino group (–NH_2) and reported that chemical adsorption or surface complexation Cu(II) in such adsorbents is accompanied by an ion-exchange process. Hui et al. [81] reported that the mechanism of metal ion by fungal bioadsorbents was accompanied by Ca^{2+} and Mg^{2+} release into the medium, which suggests the presence of ion-exchange mechanism. For this reason, Hui et al. [81] considered the adsorption mechanism in this case as a combined ion-exchange–surface complexation [82]. Hui et al. [81] summarized the interaction between Cu(II) and the adsorbents at optimized pH using by the following reaction scheme:

$$-NH_2 + H^+ \Leftrightarrow -NH_3^+ \tag{3}$$

$$-NH_2 + Cu^{+2} \Leftrightarrow -NH_2Cu^{+2} \tag{4}$$

$$-NH_2 + Cu^{+2} + H_2O \Leftrightarrow -NH_2Cu(OH)^+ + H^+ \tag{5}$$

$$-NH_2 + H_2O \Leftrightarrow -NH_2OH^- + H^+ \tag{6}$$

$$\begin{aligned} -NH_2OH^- + Cu^{+2}(CuOH^+) \Leftrightarrow -NH_2OH^- \ldots.\\ Cu^{+2}(-NH_2OH^- \ldots.CuOH^+) \end{aligned} \tag{7}$$

These subsequent pH dependent reactions include protonation/deprotonation reactions of the amino group, Eq. (3), formation of complex from $Cu^{2+}(CuOH^{1+})$ and amino group via coordinate bond shown in Eq. (7). As pH increases an ion-exchange occurs between the amino groups with hydroxyl groups from the solution through hydrogen bond, reacting with $Cu^{2+}(CuOH^{1+})$ through surface complexation and/or electrostatic attraction, Eqs. (6) and (7). In sum, the main contributions are surface complexation which is chemisorption and electrostatic attraction.

Hansda and Kumar [83] reported that the bioadsorption of metal ions by non-living biomass is based on metal bioadsorption due to the high affinities between biomass and metal ions. They simplified the complex nature of the mechanism by Fig. 4.

The main many parameters that affect heavy metal ions bioadsorption process include initial concentration metal, pH, temperature and bioadsorbent dosage [7]. The pH of the bioadsorption solution is a major controlling parameter that could affect the performance of metal ions bioadsorption process [29,63]. The magnitude of the electric charges on the adsorbate ions and on the adsorbent functional groups is usually affected by solution pH value [48]. The pH value usually affects the solubility of the metal ions [40], the charge of the adsorbent functional groups and their availability to bind with metal ions and the competition between metal ions on the bioadsorbent active sites [40,84].

Mukhopadhyay et al. [77] reported a model for the reaction between H^+ ions and the surface functional groups

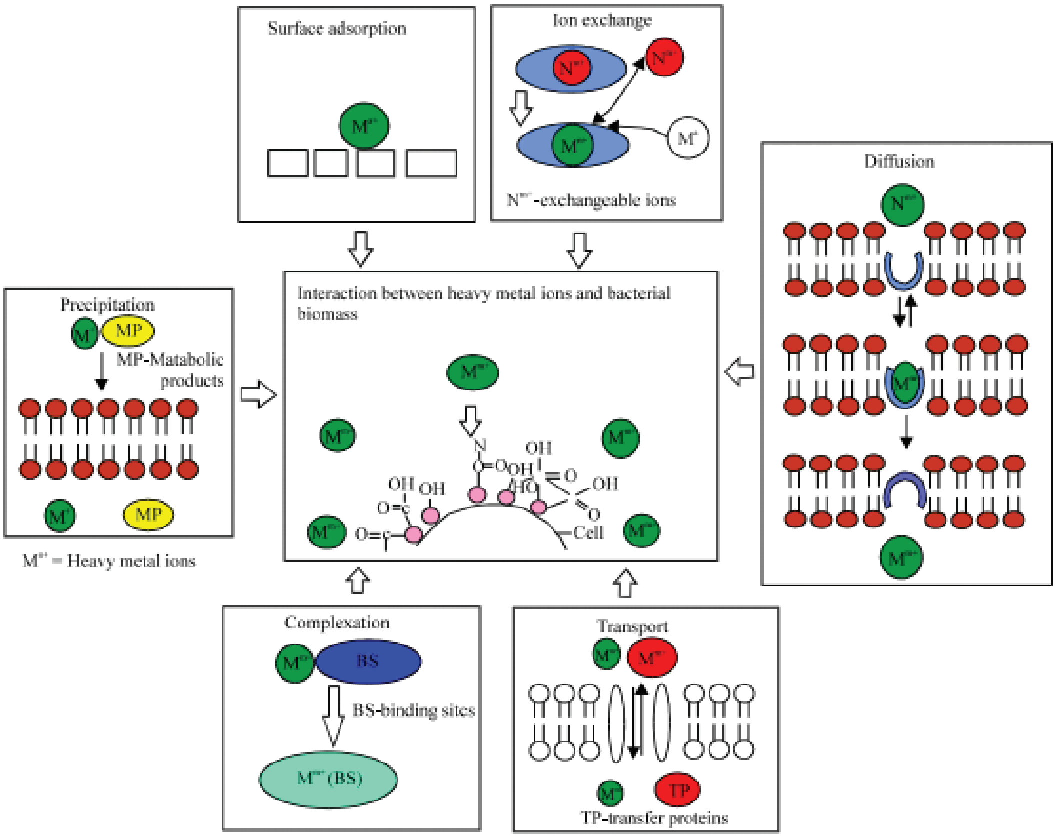


Fig. 4. A simplified diagram for the complex nature of bioadsorption mechanism (adapted from Hansda and Kumar [83] with permission from the publisher).

of algae at different values of pH. The proposed model expressed as:

$$[H_2A^+]\underset{pH\le 2}{\overset{pH\ge 4}{\rightleftharpoons}}[HA]+[H^+]\xrightarrow{pH(4-6.5)}[A^-]+2[H^+] \tag{8}$$

This equation shows that different values of pH lead to the formation of three different functional groups on the cell surface. They are A^-, HA and H_2A^+. The possible reactions between metal ions such as Cu^{2+} and these active sites could be expressed by:

$$2A^- + Cu^{+2} \rightarrow [A[Cu(A)]] \tag{9}$$

$$2HA + Cu^{+2} \rightarrow [A[Cu(A)]] + 2H^+ \tag{10}$$

$$2H_2A^+ + Cu^{+2} \rightarrow [A[Cu(A)]] + 4H^+ \tag{11}$$

Eqs. (7)–(9) depict that there are three possible bioadsorption reactions between Cu^{2+} ions and the three different charged active sites or ligands. However, only one reaction takes place at certain pH value since only one type of ligands is predominant for each value of pH. Actually, each heavy metal ion has an optimum pH value where its bioadsorption is maxima. In the case of Cu^{2+} ions, the optimum pH value falls between 5 and 6. Beyond this range, $Cu(OH)_2$ starts to precipitates [63,77]. Eq. (8) indicates the active sites in this range of pH are in the form A^-. For this reason, the reaction in Eq. (8) should be considered when dealing with kinetics of bivalent Cu^{2+} ions with algae.

Yang et al. [45] reported that the bioadsorption of Fe, Al, Zn and Pb increased as the initial value of pH increased. They found that the metal ions bioadsorption was inhibited at relatively low values of pH where $pH < pK_a$ [48]. This behaviour is attributed to the protonation of lignocellulosic functional groups at low pH values. This will cause repulsion and competition between hydrogen ions and cations approaching the protonated functional groups [21]. When the pH values increase, such that $pH > pK_a$, the bioadsorbent surface will have more negative charges and will become as negatively charged moieties due to the deprotonation of the functional groups [45]. In these conditions, the negatively charged moieties of the bioadsorbent start to attract the positive metal ions. Accordingly, as pH increases from a highly to a slightly acidic region this will convert charge of the biomass from a positive to a negative one [5].

There is an optimum pH for bioadsorption of any metal ion. This pH value corresponds to a state where the amount of negative and positive charges on the bioadsorbents is equal and the net charge on the bioadsorbent functional groups is zero. This pH value is called the pH of zero net charge or pH_{pzc}. Below or above this pH_{pzc} value, the net charge on the bioadsorbent becomes positive or negative, respectively. The functional groups exist at the bioadsorbent may become positive or negative charge depending on the pH value. These functional groups will be protonated and become positive when the pH values of the solution are less than pK_a, and become negative when the pH of the solution is greater than pK_a. Positively charged functional groups could attract the negatively charged ions present in the solution whereas deprotonated or negative functional groups will bind with the positive ions [34]. Consequently, the maximum bioadsorption is expected to take place at pH values greater than pH_{pzc} [65].

7. Adsorption models

The behaviour of a bioadsorption process can be described by using suitable mathematical models. These models are necessary for process scale up and optimization studies. There are several kinetic models that have been used in previous researches to express metal ion bioadsorption processes. The models can be divided into three types: kinetic, equilibrium and diffusion models [41].

7.1. Adsorption kinetic models

There are several adsorption kinetic models that describe the bioadsorption of heavy metal ions. Table 6 shows a list of kinetic models that can describe the bioadsorption processes of heavy metal ions by bioadsorbents. As shown in Table 6, these models include zero-order, first-order, pseudo-first-order, second-order, pseudo-second-order, first-order reversible reaction models and others [85].

The most used kinetic models in the case of heavy metal ions are second-order, pseudo-second-order and Elovich models.

Currently, the linear regression is being often used to investigate the most suitable kinetic model. The so-called linear least squares method has also been practiced with the linearization of the kinetic rate equation to fit the experimental results by using coefficients of determination. In this method, as the determination coefficient, R^2, value approaches unity this indicates a good fit. In addition, this method is also used to estimate model parameters. However, some researchers have also utilized a non-linear optimization modelling because the linearization of the model equations could affect the error variance and normality assumptions of the standard least squares [94].

Generally, adsorption kinetic experiments are basically performed to investigate the effect of various parameters on the reaction rates to calculate the time required to achieve equilibrium during the bioadsorption process [47]. In addition, chemical kinetic models can explain the reaction pathways to describe the efficiency of the adsorbents [18]. Moreover, bioadsorption kinetics usually depends on the physicochemical properties of the bioadsorbent used in a particular study [41].

Some of the most popular models that have been applied in metal ion bioadsorption will be discussed below. One of the most common models is the pseudo-first-order model which has been developed by Lagergren [95]. This model has been used in adsorption processes to describe the uptake of an adsorbate such as metal ions from aqueous solutions by an adsorbent [7]. It is based on the solid adsorption capacity [63]. The pseudo-first-order model can be described as:

$$-\frac{dq_t}{dt} = k_{s1}(q_e - q_t) \tag{12}$$

where q_e and q_t are the equilibrium adsorption capacities of an adsorbent and that capacity at any time t, respectively, k_{s1} (min^{-1}) is the first-order rate constant of this adsorption model [6,41,88].

Table 6
A list of rate kinetics equations for the bioadsorption of heavy metal ions by bioadsorbents

Kinetics	Rate equation	Integral equation		Reference
Zero-order	$-\frac{d[A]}{dt} = k$	$[A] = [A_o] - kt$	$[A]$ vs. t	[23]
First-order	$-\frac{d[A]}{dt} = k[A]$	$\ln[A] = \ln[A_o] - kt$	$\ln[A]$ vs. t	[86]
Second-order	$-\frac{d[A]}{dt} = k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A_o]} + kt$	$1/[A]$ vs. t	[86]
nth-order	$-\frac{d[A]}{dt} = k[A]^n$	$\frac{1}{[A]^{n-1}} - \frac{1}{[A_o]^{n-1}} = (n-1)kt$	$1/[A]^{n-1}$ vs. t	[86]
Pseudo-first-order	$-\frac{dq_t}{dt} = k_{s1}(q_e - q_t)$	$\log(q_e - q_t) = \log q_e - \frac{k_{s1}}{2.303}t$	$\log(q_e - q_t)$ vs. t	[87]
Reversible first-order model	$\frac{dC}{dt} = k_1 C - k_{-1}X$	$-\ln\left[\frac{(C - C_e)}{(C_o - C_e)}\right] = kt$	$\ln\left[\frac{(C - C_e)}{(C_o - C_e)}\right]$ vs. t	[88]
Pseudo-second-order	$-\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t$	$\frac{1}{(q_e - q_t)}$ vs. t	[87]
Elovich model	$\frac{dq}{dt} = ae^{-\alpha q}$	$q = \frac{1}{\alpha}\ln\left(t + \frac{1}{\alpha a}\right) - \frac{1}{\alpha}\ln\frac{1}{\alpha a}$	q vs. $\ln\left(t + \frac{1}{\alpha a}\right)$	[89]
Ritchie's model	$\frac{d\theta}{dt} = \alpha(1-\theta)^n$	$\frac{1}{(1-\theta)^{n-1}} = (n-1)\alpha t + 1$	$\frac{q_\infty}{q_\infty - q}$ vs. t	[90]
Sobkowsk and Czerwiński	$\frac{d\theta}{dt} = k(1-\theta)^n$	$\frac{\theta}{1-\theta} = k_2 t$, when $n = 2$	$\frac{\theta}{1-\theta}$ vs. t	[91]
Blanchard et al.	$-\frac{dn}{dt} = k[n_o - n]^2$	$\frac{1}{n_o - n} - \alpha = kt$	$\frac{1}{n_o - n}$ vs. t	[92]
Ho	$-\frac{dq_t}{dt} = k(q_e - q_t)^2$	$\frac{1}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$	$\frac{1}{q_t}$ vs. t	[93]

Eq. (12) can be integrated with the boundary conditions for and $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ to give:

$$\frac{q_e}{q_e - q_t} = e^{k_{s1}t} \tag{13}$$

The linear form of Eq. (13) is expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_{s1}t \tag{14}$$

If a plot of $\ln(q_e - q_t)$ vs. t gives a straight line, this will confirm the applicability of this empirical model. The values of q_e and k_{s1} can be obtained from the values of the intercept and that of the slope of the straight line, respectively [6].

The pseudo-second-order kinetic model assumes the presence of chemisorption that involves electrons exchange between the –OH or the ligand groups and the metal ions [63] as described by Eqs. (7)–(9). The differential form of this model can be described as [48]:

$$-\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{15}$$

where k_2 (g mg^{-1} s^{-1}) is the model rate constant. By integrating Eq. (15) after separating the variables with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ to give Eq. (16) or Eq. (17):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{16}$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{17}$$

For Eq. (16), a plot of $1/(q_e - q_t)$ vs. t could give a straight line of a slope of $1/q_e$ and intercept of k_2. On the other hand, for Eq. (17), a plot of $1/q_t$ against t will give a straight line with $1/k_2q_e^2$ as an intercept and a slope of $1/q_e$. In both cases q_e can be estimated and compared with the experiment data.

Elovich's model was formulated based on the adsorption capacity in a chemisorption process. Zeldowitsch [89] reported that the adsorption rate decreased exponentially as the amount of adsorbed gas increased, q. This model known as the Elovich's model can be expressed as:

$$\frac{dq}{dt} = ae^{-\alpha q} \tag{18}$$

where a is the desorption constant and α is the initial adsorption rate. Integration of Eq. (18) will give:

$$q = \frac{1}{\alpha}\ln(t + \frac{1}{\alpha a}) - \frac{1}{\alpha}\ln\frac{1}{\alpha a} \tag{19}$$

Eq. (19) was simplified by Chien and Clayton [96] who assumed that $a\alpha t \gg 1$ and applied the boundary conditions of $q = 0$ at $t = 0$ and $q = q$ at $t = t$ to give:

$$q = \alpha\ln(a\alpha) + \alpha\ln t \tag{20}$$

Therefore, a and α can be calculated from the intercept and the slope of the linear plots of q against $\ln(t)$.

The second-order model of Ritchie [90] was developed to express the adsorption process of gaseous systems. In this model, θ was assumed as the fraction of occupied surface sites by an adsorbed gas, n is the number of occupied surface sites by the adsorbent and α is a rate constant. The adsorption process was assumed to completely depend on the unoccupied fraction of sites at time t, then the differential form of the model can be described by Eq. (18) [56]:

$$\frac{d\theta}{dt} = \alpha(1-\theta)^n \tag{21}$$

Integrating Eq. (21) will give Eq. (22) or Eq. (23):

$$\frac{1}{(1-\theta)^{n-1}} = (n-1)\alpha t + 1 \text{ for } n \neq 1 \text{ and} \tag{22}$$

$$\theta = 1 - e^{-\alpha t} \quad \text{for } n = 1 \tag{23}$$

Usually, $\theta = 0$ at $t = 0$. If q, or the adsorption capacity is introduced instead of θ.

Eqs. (22) and (23) will become as Eqs. (24) and (25), respectively:

$$\frac{q_\infty}{(q_\infty - q)} = (n-1)\alpha t + 1 \tag{24}$$

$$q = q_\infty(1 - e^{-\alpha t}) \tag{25}$$

where q_∞ is the amount adsorbate adsorbed after infinite time. For Eq. (24), a plot of $q_\infty/(q_\infty - q)$ vs. t will generate a straight line with $(n - 1)\alpha$ as the slope. On the other hand, for Eq. (25), a plot of $\ln(q/q_\infty)$ vs. t will give a straight line with α as a slope and an intercept of zero.

7.2. Adsorption isotherm models

Adsorption isotherm models are being applied to predict the capacity of adsorbents [3,80]. In addition, these isotherm models are being used to further explore the adsorption mechanism [73]. These isotherm models describe an adsorbent capacity and the equilibrium between the adsorbate loaded on the adsorbent and the adsorbate still in the solution at certain temperature [5]. For this reason, isotherm models are important to optimize the quantity of the used adsorbent [15]. Many isotherm models are being used to investigate the adsorbate distribution between the solution and the adsorbent. These models include Freundlich, Langmuir, Temkin, Redlich–Peterson, Dubinin–Radushkevich (D–R) [5], BET, Koble–Corrigan, Toth isotherm models and others as shown in Table 7 [41]. Among these models, Freundlich and Langmuir isotherms are the most popular models [10,79].

The first model Freundlich model which usually used to describe the bioadsorption of an adsorbate ions onto solid bioadsorbent. In this model, it is assumed that the solid surface is heterogeneous and non-equivalent binding sites. The general Freundlich model can be defined by:

$$q_e = K_F C_e^{1/n} \tag{26}$$

where C_e is the metal ion concentration at equilibrium (mg L^{-1}), K_F is Freundlich constants relating to the bioadsorption capacity and n is a measure of the bioadsorption intensity and how favourable is the adsorption process. In addition, n which varies with the heterogeneity of the adsorbent [52]. Freundlich isotherm also states that the adsorption energy is exponentially decreased on completion of the adsorption sites of the adsorbent used [30]. The non-linear form of Freundlich model is:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{27}$$

A plot of $\ln q_e$ against $\ln C_e$ gives a straight line with $1/n$ as the slope and $\ln K_F$ as the intercept, respectively [10,97] (Fig. 5). The value of K_F determines the degree or strength of adsorption. Large K_F values indicate maximal adsorption and vice versa as shown in Fig. 5. On the other hand, $1/n$ is a heterogeneity factor which could indicate the adsorption intensity. If the values of $n > 1$, this indicates favourable adsorption conditions.

In contrast to Freundlich model, the Langmuir model assumes that the adsorption active sites are evenly distributed on the adsorbent surface. This finite distribution leads to a monolayer formation of the adsorbate ions on the adsorbent surface. The general Langmuir model can be defined as:

$$q_e \frac{q_m K_a C_e}{(1 + K_a C_e)} \tag{28}$$

where $q_{\max}$ is the maximum adsorption capacity at certain conditions, mg g^{-1}, K_a is the Langmuir model constant, L mg^{-1} [52]. In addition, K_a is also equal to the ratio of adsorption/desorption rates [41]. Linearization of Eq. (28) gives:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{C_e}{q_m} \tag{29}$$

Table 7
List of bioadsorption isotherms, equations, linearized form and constants significance

Isotherm model	Equation	Linearized form	Constants	Reference
Two parameters isotherm models				
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + 1/n \log C_e$	K_F and n: constants that determine the isotherm curvature and steepness	[100]
Langmuir	$q_e \frac{q_m K_a C_e}{(1+K_a C_e)}$	$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m}$	K_a and q_m (mg g^{-1}) are Langmuir constant and adsorption capacity	[101]
Langmuir constant	$K_a = \frac{1}{(1+K_a C_o)}$		K_a indicates the adsorption type: $K_a = 0$, irreversible, $K_a = 1$, linear $0 < K_a < 1$, favourable $K_a > 1$, unfavourable	[102]
Dubinin–Radushkevich	$q_e = q_{\max} \exp\left(-\beta\left[\mathrm{RT}\ \ln\left(1+\frac{1}{C_e}\right)\right]^2\right)$	$\ln q_e = \ln q_{\max} - \beta\left[RT \ln\left(1+\frac{1}{C_e}\right)\right]^2$	q_D isotherm constant β is related to free energy of adsorption	[103]
BET model	$q_e = \frac{q_{\max} B C_e}{(C_e - C_e)\left[1+(B-1)\frac{C_e}{C_s}\right]}$	$\frac{C_e}{(C_s - C_e) q_e} = \frac{1}{B q_{\max}} + \frac{(B-1) C_e}{B q_{\max} C_s}$	C_s is the adsorbate saturation concentration, B is a constant related to the interaction energy	[41]
Flory–Huggins	$\frac{\Theta}{C_o} = K_{\mathrm{FH}}(1-\Theta)^n$	$\log \frac{\Theta}{C_o} = \log K_{\mathrm{FH}} + n \log(1-\Theta)$	Θ degree of surface coverage, n number ions occupying sorption site, K_{FH} equilibrium constant	[104]
Temkin	$q_e = K_T C_e^b$	$\ln q_e = \ln K_T + b \ln C_e$	K_T adsorption equilibrium constant, b relates to the heat of adsorption	[105]
Frumkin	$\beta X = \frac{\theta}{1-\theta} \exp(-2a\theta)$	$\log\left(\frac{\theta}{1-\theta}\right) C = \log\left(\frac{\beta}{55.55}\right) + \frac{2a\theta}{2.303}$	$\Theta = M/M_{\mathrm{ad}}$, $\beta = \exp[\Delta G_{\mathrm{ad}}/RT)$	[106]
Three parameters isotherm models				
Redlich–Peterson	$q_e = \frac{A C_e}{1 + B C_e^g}$	$\ln A \frac{C_e}{q_e} - 1 = g \ln C_e + \ln B$	A, B and g are constants	[107]
Langmuir–Freundlich (Sips)	$q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}}$	$\frac{1}{q_e} = \frac{C_e^n}{b q_m} + \frac{1}{q_m}$	b constant	[108]
Radke–Prausnitz	$q_e = \frac{K_{\mathrm{RP}} C_e}{1 + (K_{\mathrm{RP}} / F_{\mathrm{RP}}) C^{1-N_{\mathrm{RP}}}} K$	Solved by a non-linear statistical method	K_{RP}, F_{RP} and N_{RP} are the model parameters	[109]
Khan	$q_e = \frac{q_k b_k C_e}{(1 + b_k C_e)^{a_k}}$	Non-linear optimization method	q_k, b_k (L mg^{-1}) and a_k represent the model parameters	[110]
Toth	$q_e = \frac{q_t b_t C_e}{(1 + b_t C_e^t)^{1/t}}$	Non-linear optimization method	q_t, b_t (L mg^{-1}) and t represent the model parameters	[110]

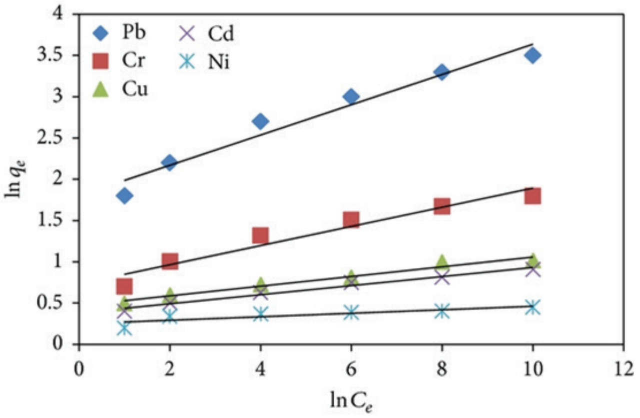


Fig. 5. Linearized Freundlich isotherm model representing the variation of ln(q_e) vs. ln(C_e) for adsorption of metal ions onto Activated Teff Straw (adapted from Desta [97] with permission from the publisher).

A plot of C_e/q_e against C_e gives a straight line with $1/q_{max}$ and $1/K_a q_{max}$ values are the slope and an intercept, respectively [35,97] (Fig. 6). If the q_{max} values increase as the temperature increases this indicates that the adsorption process is favourable and endothermic in nature. An opposite behaviour indicates that the adsorption process is exothermic [15].

The applicability of both Freundlich and Langmuir and isotherms models have been found to be limited to batch adsorption processes. Batch processes permits sufficient contact time to achieve equilibrium between the adsorbate and the adsorbent [3]. As mentioned above, Langmuir isotherm model, as the most popular model of all non-linear isotherms, assumes that the adsorbent is structurally homogenous and the available adsorption sites are energetically identical or equivalent. Accordingly, the adsorption capacity of the adsorbent is finite from an adsorbate at certain conditions [33]. The entire process involves the same mechanism, in which it has the same structure of the complete sorbent complex, the same affinity for sorbent sites and there is no interaction or competition between the adsorbed solutes and the process occurs is reversible [98].

Freundlich isotherm model is commonly regarded as an empirical model [98]. It assumed that the adsorbents have heterogeneous surface in which the heat of adsorption involves a non-uniform distribution. The total amount of the adsorbed material equals the sum of all adsorbed particles in all sites. The model also can represent the reversible adsorption processes and not restricted to the case of monolayer formation [33]. The Langmuir isotherm model is more successfully used in comparison with Freundlich isotherm model, indicating that most metal ions are adsorbed in monolayer fashion [5].

Both Langmuir and Freundlich equations can be combined altogether to form [41]:

$$q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}} \tag{30}$$

This form of the model assumes a homogenous surface of the adsorbent and the adsorption process is a cooperative process due to the interaction between the adsorbate constituents.

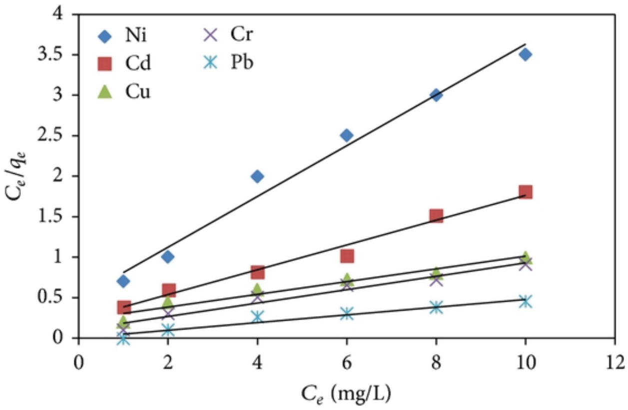


Fig. 6. Linearized Langmuir isotherm model representing the variation of C_e/q_e vs. the equilibrium concentration, C_e, for adsorption of metal ions onto activated Teff Straw (adapted from Desta [97] with permission from the publisher).

In addition, there is an essential feature of Langmuir model that it could be expressed in terms of dimensionless equilibrium or separation factor, R_L, as expressed [99]:

$$R_L = \frac{1}{1 + (1 + bC_o)} \tag{31}$$

where b and C_0 are the Langmuir constant and the initial concentration of the metal ion (mg L^{-1}), respectively. The R_L value could give an idea about the shape and the isotherm type and feasibility as well. The possible values of R_L are: $R_L > 1$, $R_L = 1$, $R_L = 0$ and $0 > R_L > 1$ which corresponds to unfavourable, linear, irreversible and favourable adsorption, respectively. A plot of R_L vs. C_0 could show the isotherm type [5,34,49]. The R_L values also could indicate the order of selectivity or the preference order for bioadsorption process of several metal ions by a bioadsorbent. This information is very useful to design the experimental procedure for multimetal ion systems.

The chemical or physical nature of bioadsorption process can be investigated by calculating the mean value of the bioadsorption free energy, E, shown as:

$$E = \frac{1}{(2\beta)^{1/2}} \tag{32}$$

where β is a coefficient related to the mean value of the adsorption free energy (mol^2 J^{-1}) and can be estimated using Dubinin–Radushkevich (D–R) model, as:

$$q_e = q_{max} \exp(-\beta\varepsilon^2) \tag{33}$$

where ε is called as Polanyi potential (J mol^{-1}) which can be expressed as:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{34}$$

The linearized form of D–R model is shown as:

$$\ln q_e = \ln q_{max} - \beta\left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2 \tag{35}$$

The slope of the plot of $\ln q_e$ vs. ε^2 will give the β value.

Therefore, the nature of adsorption could be determined using the value of E. A physical adsorption process occurs when $E < 8$ kJ mol^{-1}. Chemical adsorption or chemisorption occurs for $8 < E < 16$ kJ mol^{-1}. Therefore, it is very useful to comprehend the bioadsorption mechanism [11,35].

The Brunauer, Emmett and Teller model or BET equation has also been used. This model is an extension of Langmuir isotherm model to represent a multilayer adsorption isotherm at the surface of the adsorbent. The BET model states that the Langmuir equation is applicable for each layer and a next layer can be formed before the completion of the previous one. The model can be described as [41]:

$$q_e = \frac{q_{\max} B C_e}{(C_e - C_e)\left[1 + (B-1)\dfrac{C_e}{C_s}\right]} \quad (36)$$

where C_s is the adsorbate saturation concentration and B is a constant related to the interaction energy between the adsorbate and the surface. The other symbols have been previously described. The linearized form of the BET equation is expressed by:

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{Bq_{\max}} + \frac{(B-1)C_e}{Bq_{\max}C_s} \quad (37)$$

A plot of $C_e/[(C_s - C_e)q_e]$ vs. C_e will yield a straight line with $(B-1)/[Bq_{\max}C_s]$ as a slope and $1/[Bq_{\max}]$ as an intercept.

Table 7 shows some more isotherm models such as Redlich–Peterson model can be applied in both systems of homogenous and heterogenous due to its high versatility, Radke–Prausnitz, Khan, Temkin and Toth models. These models are not common and used for special applications.

7.3. Adsorption diffusion models

In liquid–solid systems, diffusion usually occurs before the adsorption step. The diffusion process involves two subsequent steps including liquid phase mass transfer, film diffusion, intraparticle diffusion [111]. Xu et al. [112] used a macroscopic schematic illustration for these diffusion models as shown in Fig. 7. Accordingly, in the case of good mixing, the bioadsorption process could be classified as either film diffusion or particle diffusion controlled process. The slower step becomes the rate-determining step of the adsorption process. The adsorption intraparticle diffusion models that have been used to describe different adsorption or bioadsorption processes as listed in Table 8.

Weber and Morris [113] found that the adsorbate removal from aqueous solution by an adsorbent usually proportional to square route of the adsorption time, $t^{0.5}$ as expressed by [114]:

$$q_t = K_{\text{id}}(t)^{0.5} \quad (38)$$

where q_t is the quantity of metal ion adsorbed, t is the process time and k_{id} is the intraparticle diffusion coefficient. The linear form of Eq. (38) is:

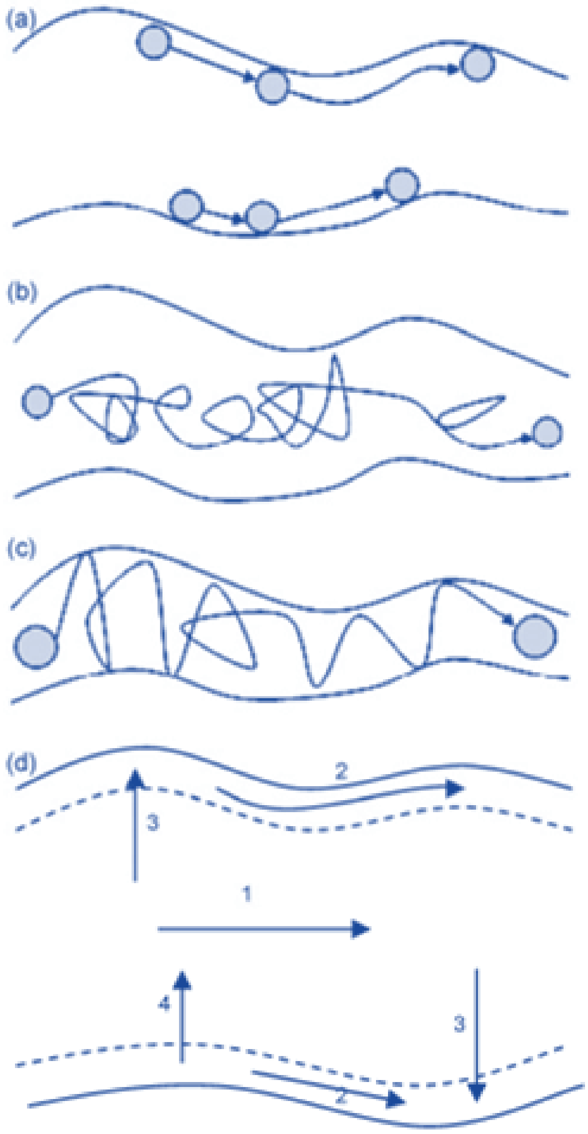


Fig. 7. Macroscopic schematic illustration of basic diffusion and adsorption steps inside the pore. (a) Surface diffusion. (b) Pore diffusion. (c) Pore diffusion with significant Knudsen diffusion. (d) Combination of intrapellet diffusion and adsorption: 1, pore diffusion; 2, surface diffusion; 3, adsorption; and 4, desorption (adapted from Xu et al. [112] with permission from the publisher).

$$\log q_t = \log K_{\text{id}} + 0.5 \log t \quad (39)$$

A plot of $\log(q_t)$ vs. $0.5\log(t)$ could produce a straight line that goes through the origin if the intraparticle diffusion step is the sole rate-determining step. The positive intercept equals the log of intraparticle diffusion coefficient, k_{id}. The value of k_{id} is proportional to the rate of adsorption, which means the higher the k_{id} value indicates the higher is the bioadsorption rate.

Another intraparticle diffusion model was developed by McKay and Poots [115]. They applied this model to describe the mechanism of an adsorption process when they observed that the fraction of adsorbate adsorbed was

Table 8
List of rate kinetics equations for the biosorption of heavy metal ions by bioasdsorbents

Name	Rate equation	Integral equation		Reference
Weber and Morris	$R = K_{\mathrm{id}}(t)^a$	$\log R = \log K_{\mathrm{id}} + a \log t$	$\log R$ vs. $\log t$	[113]
Mckay and Poots	$q_t = X_i + K^1 t^{1/2}$	$q_t = X_i + K^1 t^{1/2}$	q_t vs. $t^{1/2}$	[115]
Dumwald–Wagner model	$\log(1-F^2) = -\frac{K}{2.303} t$	$\log(1-F^2) = -\frac{K}{2.303} t$	$\log(1-F^2)$ vs. t	[45]
Elovich	$\frac{dq_t}{dt} = \alpha(-\beta q_t t)$	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	q_t vs. $\ln t$	[3]

related to the square root of time, $t^{0.5}$. Accordingly, McKay and Poots equation can be given as:

$$q_t = X_i + K^1(t)^{0.5} \tag{40}$$

where X_i is the diffusion effects of the boundary layer and K^1 is the intraparticle diffusion rate constant, mg g^{-1} min$^{-0.5}$.

If the data fit McKay and Poots equation shown from Eq. (40), a plot of q_t, the amount adsorbed at any time t, vs. $t^{0.5}$ will give a straight line. This will confirm the intraparticle diffusion adsorption. The slope of the linear part of the plot gives K^1, mg g^{-1} min$^{-0.5}$, and the intercept is X_i which is proportional to the thickness of the boundary layer. The initial curved part of the plot is referred to external film resistance.

Dumwald–Wagner proposed another intraparticle diffusion model as [116]:

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2}\sum \frac{1}{n^2}\exp(-n^2 K t) \tag{41}$$

where K, min^{-1}, is the rate constant of adsorption. Eq. (41) can be simplified as:

$$\log(1-F^2) = -\frac{K}{2.303} t \tag{42}$$

A plot of $\log(1 - F^2)$ vs. t will give a straight line and the rate constant K can be obtained from the slope. It was shown that Dumwald–Wagner model is satisfactory to model different adsorption processes such as the adsorption of *p*-toluidine from aqueous solutions using hyper crosslinked polymeric adsorbents.

8. Effect of some parameters on the kinetics of the bioadsorption process

8.1. Effect of pH

As mentioned above and shown in Eq. (8), pH of the adsorption medium affects the adsorbent surface charge and the degree of ionization of the functional groups. Accordingly, pH affects the mechanism, kinetics and equilibrium conditions of the adsorption process. The effect of the pH on the equilibrium state of the adsorption process can be expressed by the following simplified equation [117]:

$$\mathrm{pH} = pk_a - \log\frac{[\mathrm{AH}^+]}{[\mathrm{A}^-]} \tag{43}$$

where k_a is the acid hydrolysis constant.

However, this equation does not show the direct effect of pH on the adsorption capacity, q_e. For this reason, Esposito and Reverberi [118] proposed the following several semi-empirical equations which were used to fit bioadsorption experimental data for copper into four different bioadsorbents:

$$q = (\alpha.\mathrm{pH} + \alpha_2).\frac{C_e}{\alpha_3 + C_e} \tag{44}$$

$$q = (\alpha.\mathrm{pH}^{\alpha_2}).\frac{C_e}{\alpha_3 + C_e} \tag{45}$$

$$q = (\alpha.e^{-\alpha \mathrm{pH}}).\frac{C_e}{\alpha_3 + C_e} \tag{46}$$

$$q = \frac{\alpha_1.\mathrm{pH} + \alpha_2}{\alpha_3 + \mathrm{pH}}.\frac{C_e}{(\alpha_4.\mathrm{pH} + \alpha_5) + C_e} \tag{47}$$

where α_1, α_2, α_3, α_4 and α_5 are constants.

It is clear that the above four equations are built based on considering Langmuir isotherm model as a reference isotherm and the effect of pH appeared in the two Langmuir isotherm parameters, the maximum adsorption capacity, $q_{\max}$ and K_s. Actually, if the pH value is kept constant, the above semi-empirical models reduce to the simple Langmuir isotherm.

Vilar et al. [84] used what they called the discrete model to describe the effect of pH on the bioadsorption of copper by algal biomass. They assumed two assumptions: the basic mechanism of the bioadsorption process includes two steps which are complexation and ion-exchange and in the range of pH values used there will be only one predominant active sites. Accordingly, they assumed the following reversible reactions:

$$L_s + H^+_{\mathrm{aq}} \Leftrightarrow LH_s \quad K_H = \frac{q_H}{(Q_{\max} - q_H - q_M)C_H} \tag{48}$$

$$L_s + M_{\mathrm{aq}} \Leftrightarrow LM_s \quad K_M = \frac{q_M}{(Q_{\max} - q_H - q_M)C_M} \tag{49}$$

where L stands for an active functional group, K_H, L mmol^{-1} and K_M, L mmol^{-1} are the hydrogen ion and the metal equilibrium constants, respectively. If Eq. (49) is solved for q_H and substituted into Eq. (48), an equation relating the adsorption capacity, q_M and the equilibrium hydrogen ion C_H and the equilibrium metal C_M as expressed by:

$$q_M = \frac{Q_{\max} K_M C_M}{1 + K_H C_H + K_M C_M} \tag{50}$$

It is clear from Eq. (50) that hydrogen ion concentration appears in the model equation for the adsorption capacity of the metal by a bioadsorbent.

Recently, Al-Shannag et al. [17] studied the effect of pH on Cd(II) adsorption onto *Ballota undulata* bioadsorbent at various aqueous solutions with different initial concentrations. With solution volume of $V = 200$ mL, adsorbent dose of $m = 100$ mg, adsorbent particle size of $D_p = 297$ µm and contact time of $t = 2$ h, it is found that that the optimum pH value was 6 at which the corresponding mean removal efficiencies were 33.3%, 20.8% and 14.9% for initial Cd(II) concentration of 150, 250 and 350 ppm, respectively (Fig. 8).

8.2. Effect of temperature

Temperature is an important parameter in the bioadsorption process of metal ions. The medium temperature affects the process thermodynamics via its effect on the kinetic energy of the adsorbate ions. Consequently, a change in the adsorption medium temperature will change the adsorbed quantity of the adsorbate by the biomass. Usually, any change in temperature will cause changes in some thermodynamic parameters such as Gibbs free energy of activation, $\Delta G°$, enthalpy of activation, $\Delta H°$, and entropy of activation, $\Delta S°$, which are important in elucidating the adsorption process [48]. For example, $\Delta G°$ explains the possibility and feasibility of the adsorption process. If $\Delta G°$ of a process has a negative value this indicates that the process is spontaneous and feasible. If $\Delta G°$ decreases as the temperature increases this indicates that the adsorption capacity will increase. The route of the energy is shown by $\Delta H°$ in which the positive and the negative values indicate the process is endothermic and exothermic, respectively. On the other hand, negative $\Delta S°$ means that the metal ions were stable when they adsorbed on the active sites.

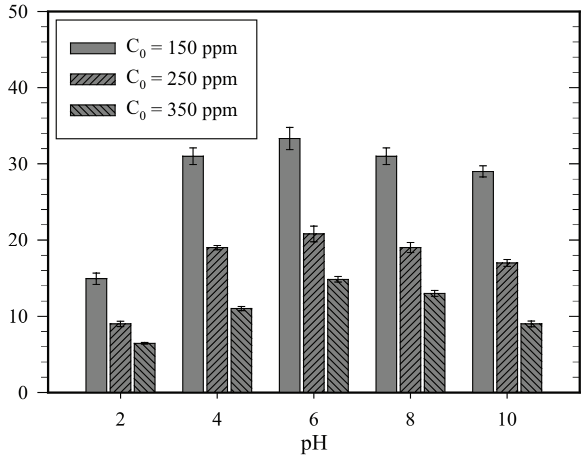


Fig. 8. Effect of pH on the removal of Cd(II) heavy metal ions onto *Ballota undulata* from aqueous solutions by batch adsorption at different initial concentrations. $V = 200$ mL, $m = 100$ mg, $D_p = 297$ µm and $t = 2$ h (adapted from Al-Shannag et al. [17]).

The thermodynamic parameters for the bioadsorption process can be expressed by the following equations [119]:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{51}$$

where R is the gas constant, T is the absolute medium temperature, K_d is the distribution coefficient given by:

$$K_d = \frac{C_{Ae}}{C_e} \tag{52}$$

where C_{Ae}, mg L^{-1}, is the amount of Cu^{2+} ions adsorbed on algae at equilibrium and C_e, mg L^{-1}, is Cu^{2+} ions equilibrium concentration. A plot of $\ln K_d$ vs. $1/T$ will give a straight line of a slope equal $-\Delta H°/R$, and an intercept of $\Delta S°/R$. On the other hand, $\Delta G°$ can be estimated using:

$$\Delta G° = -RT \ln K_d \tag{53}$$

On the other hand, Al-Shannag et al. [17] performed adsorption isotherm experiments for the removal of cadmium ions, Cd(II), from aqueous solutions using *B. undulata* at different operating temperatures (20°C, 30°C, 40°C and 50°C). Fig. 9 shows their results under the following operating condition: solution volume, $V = 200$ mL, adsorbent dose, $m = 100$ mg, adsorbent particle size, $D_p = 297$ µm, contact time of $t = 2$ h and pH = 6. It is found that the optimum values of all temperature were considered. They found that the loading capacity, q_e, increases significantly at relatively low equilibrium concentration, C_e, followed by a slight increase at C_e level to reach asymptotic value (Fig. 9). At the same equilibrium concentrations, Fig. 9 shows that the loading capacity of *B. undulata* slightly increases with increasing temperature. For example, as the temperature increases from 20°C to 50°C, q_e, increases by about 20%.

9. Conclusions

In this article, models and some parameters affecting the biosorption process of heavy metal ions from wastewater is reviewed. It is clear that this treatment technology has been developed to be one of the promising treatment methods for heavy metals ions. This development was in the application of many new effective bioadsorbents, investigating new modification procedures of the bioadsorbents to enhance their adsorption capacity and in the reduction of the bioadsorption costs and feasibility. In addition, a remarkable progress has been achieved in understanding the mechanism of the bioadsorption process and in developing suitable mathematic models to fit their equilibrium, kinetic and diffusion experimental data. However, there should be more research to clarify the mechanisms in different operational conditions and different surface functional groups.

This review indicates that the researches on bioadsorption and the use of low-cost by adsorbents are still in the laboratory

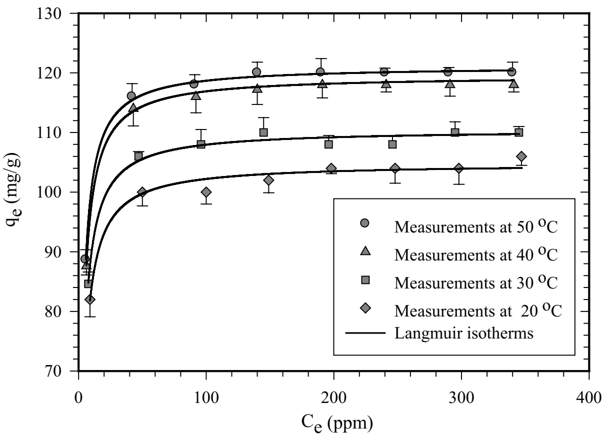


Fig. 9. Variation of equilibrium adsorption capacity with equilibrium concentration for Cd(II) adsorption onto *Ballota undulata* at different temperatures. *V* = 200 mL, *m* = 100 mg, D_p = 297 µm, pH = 6 and *t* = 2 h (adapted from Al-Shannag et al. [17]).

scale. Scaling up of this technology to a pilot plant or industrial scale levels is a vital step to examine the applicability of this technology from one side and to test its sustainability from the other side. It is very crucial to develop sustainable technologies with very limited and recyclable wastes. In other words, any treatment method for heavy metal ions should consider an easy and feasible method for the metal regeneration. Otherwise, scaling up of processes that do not fulfil this criterion will be impossible. Moreover, most bioadsorption researches consider a single ion or multicomponent ions in synthetic wastewater and not a real wastewater. It should be pointed out that real wastewater unlike laboratory synthetic wastewater contain many pollutants other than heavy metal ions. For this reason, most of the results will be limited unless it is verified by results obtained by using real wastewater. This will encourage the search to develop some low-cost bioadsorbents characterized by the presence of powerful but non-selective function groups that are able to remove all pollutants existing in the wastewater. Otherwise, multistage adsorption process could be applied to remove different pollutants using several adsorbents in subsequent steps.

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