



Review

Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies

Jonathan Febrianto^{a,b}, Aline Natasia Kosasih^{a,b}, Jaka Sunarso^b, Yi-Hsu Ju^a,
Nani Indraswati^b, Suryadi Ismadji^{a,*}

^a Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Section 4, Keelung Road, Taipei 10607, Taiwan

^b Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia

ARTICLE INFO

Article history:

Received 7 April 2008

Received in revised form 10 May 2008

Accepted 12 June 2008

Available online 20 June 2008

Keywords:

Heavy metals

Biosorption

Equilibria

Kinetic

ABSTRACT

Distinctive adsorption equilibria and kinetic models are of extensive use in explaining the biosorption of heavy metals, denoting the need to highlight and summarize their essential issues, which is the main purpose of this paper. As a general trend, up until now, most studies on the biosorption of heavy metal ions by miscellaneous biosorbent types have been directed toward the uptake of single metal in preference to multicomponent systems. In particular, Langmuir and Freundlich models are the most common isotherms for correlating biosorption experimental data though other isotherms, which were initially established for gas phase applications, can also be extended onto biosorption system. In kinetic modeling, the pseudo-first and -second order equations are considered as the most celebrated models.

© 2008 Elsevier B.V. All rights reserved.

Contents

1. Introduction	617
2. Equilibrium studies in biosorption of heavy metals using various kinds of biosorbents	618
2.1. Freundlich isotherm	618
2.2. Langmuir isotherm	623
2.3. Other two parameters isotherms	630
2.3.1. Temkin Isotherm	630
2.3.2. Dubinin–Radushkevich equation	631
2.3.3. Flory–Huggins isotherm	631
2.3.4. Halsey isotherm	631
2.3.5. Brunauer–Emmer–Teller (BET) model	631
2.4. Three parameters isotherms	632
2.4.1. Sips isotherm	632
2.4.2. Toth equation	632
2.4.3. Redlich–Paterson isotherm	632
2.4.4. Multicomponent heavy metals biosorption	632
3. Kinetic studies in biosorption of heavy metals using various kinds of biosorbents	634
3.1. The pseudo-first-order kinetic	635
3.2. The pseudo-second-order kinetic	635
3.3. The Weber and Morris sorption kinetic model	642
3.4. First-order reversible reaction model	642
4. Conclusion	643
References	643

* Corresponding author. Tel.: +886 227376642; fax: +886 227376644.
E-mail address: suryadiismadji@yahoo.com (S. Ismadji).

Nomenclature

a	Temkin isotherm constant (L/g) (Eq. (9))
A	specific surface area of biomass (Eq. (30))
b	Temkin constant in relation to heat of sorption (kJ/mol) (Eq. (9))
b_T	Toth parameter (Eq. (16))
B	a constant related to energy of adsorption (Eq. (14))
C	liquid phase concentration of sorbate in the bulk solution at t (Eq. (30))
C_A	concentration of metal in solution at time t (Eq. (32))
C_{A0}	initial concentration of adsorbate (Eq. (32))
C_{Ae}	equilibrium concentration of metal in adsorbate (Eq. (33))
C_B	concentration of metal in sorbent at time t (Eq. (32))
C_{B0}	initial concentration of adsorbent (Eq. (32))
C_{Be}	equilibrium concentrations of metal in adsorbent (Eq. (33))
C_e	equilibrium concentration (Eqs. (1)–(7), (9) and (10), (12)–(21))
C_s	adsorbate solubility at a given temperature (Eq. (10))
C_s^*	saturation concentration of solute (mg/L) (Eq. (14))
C_s^i	concentration of sorbate in the inner pore of sorbent (Eq. (30))
C_0	initial metal ion concentrations (Eqs. (11) and (12))
d_p	mean particle diameter (Eq. (29))
D	intraparticle diffusion coefficient (Eq. (29))
E_a	activation energy of adsorption/heat of adsorption (Eq. (8))
E_0	solid characteristic energy towards a reference compound (Eq. (10))
k_1	rate constant of first order adsorption (Eqs. (22)–(24))
k_2	rate constant for pseudo-second-order model (Eqs. (25)–(27))
k_1^0, k_2^0	first-order rate constants (Eq. (32))
K_c	equilibrium constant (Eq. (33))
K_F	characteristic constant related to the adsorption capacity (Eqs. (1) and (2), (20) and (21))
K_{FH}	equilibrium constant of adsorption (Eqs. (11) and (12))
K_L	sorption equilibrium constant (Eqs. (3)–(7), (18) and (19))
K'_L	liquid–solid mass transfer coefficient (Eq. (30))
K_{WM}	Weber and Morris intraparticle diffusion rate (Eqs. (28) and (29))
K_0	adsorption equilibrium constant (Eq. (8))
K_{RP}, a_{RP}, β	Redlich–Paterson's parameters (Eq. (17))
K_H, n_H	Halsey constants (Eq. (13))
n	characteristic constant related to adsorption intensity or degree of favorability of adsorption (Eqs. (1) and (2), (20) and (21))
n_{FH}	number of metal ions occupying sorption sites (Eqs. (11) and (12))
n_T	specific constant for adsorbate–adsorbent pairs (Eq. (16))
q	amount adsorbed at time t (Eqs. (22)–(27))
q_e	amount adsorbed (Eqs. (1)–(7), (9) and (10), (13)–(21))
q_e	amount of solute adsorbed at equilibrium condition (Eqs. (22)–(27))
q_{max}	saturated monolayer adsorption capacity (Eqs. (3)–(7), (10), (14)–(16), (18)–(21))

R	gas constant (0.0083 kJ/(mol K)) (Eq. (9))
t	time (Eqs. (22)–(28), (30), (32), (34))
T	absolute temperature (K) (Eq. (9))
x_1, y_1, z_1	multi-component Freundlich constants for component 1 (Eqs. (20) and (21))
x_2, y_2, z_2	multi-component Freundlich constants for component 2 (Eqs. (20) and (21))
<i>Greek letters</i>	
β	a constant (proportional to the liquid molar volume) (Eq. (10))
γ	Sips parameter (Eq. (15))
θ	degree of surface coverage (Eqs. (11) and (12))

1. Introduction

Till recent years, the surge of industrial activities has intensified more environmental problems as seen for example in the deterioration of several ecosystems due to the accumulation of dangerous pollutants such as heavy metals [1]. Heavy metals are still being used in various industries due to their technological importance. Yet, imperfect treatment of waste products from these industries will carry other issues to human health and environment [2]. Aside from the environmental damage, human health is likely to be affected as the presence of heavy metals beyond a certain limit brings serious hazards to living organisms. For instance, cadmium(II), copper(II) and nickel(II) ions (in respective order) have been proven to cause kidney damage, liver damage or Wilson disease [3] and dermatitis or chronic asthma [4] (also in respective order).

Several methods have been employed to remove heavy metal ions from wastewater, which include precipitation, flotation, ion exchange, membrane-related process, electrochemical technique and biological process [2,5–10]. Low efficiency performance particularly when used on very small concentration of heavy metals, the necessity of using expensive chemicals in some methods as well as accompanying disposal problem are among the drawbacks of these conventional methods [8]. In regards of its simplicity and high-efficiency characteristics even for a minute amount of heavy metals, adsorption is looked upon as a better technology. Activated carbon is a well-known adsorbent and proven to be useful for the removal of heavy metals. Nevertheless, the application of activated carbon for wastewater treatment is not feasible due to its high price and cost associated with the regeneration as a result of high-degree of losses in real process [1].

Removal of heavy metals using agricultural waste and its industrial by-products has been massively investigated due to the abundance of agricultural-related materials in nature and its low cost [11–34]. The use of living and dead microbial cells in biosorption of heavy metals has been demonstrated as well. Several reviews can be referred upon that talk about low-cost adsorbents application for heavy metals removal [4,35–37]. For example, Kurniawan et al. [4] discussed about the removal performance and cost-effectiveness of various low-cost adsorbents derived from agricultural waste, its industrial by-product as well as natural material. The adsorption capacity of these low cost adsorbent are summarized and compared to those using activated carbon for the removal of heavy metals from metal-contaminated wastewater. Later on, a review about biosorption of precious metals was written by Mack et al. [35]. Their summary paper covers 47 studies on recovery of precious metals using biosorption technique. The effects of pH and temperature of solution along with competing

ions on metals recovery are highlighted in their review. Further on, state-of-the-art technique in the field of biosorption in which algae is employed as biomass was looked upon by Romera et al. [36]. These authors carried out statistical evaluation from the available data of maximum sorption uptake and biomass metal affinity for Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) using 37 different algae as biosorbent. Another outline report by Guibal [37] is concerned about sorption of heavy metal in chitosan base. Final addition, Alluri et al. [38] also provide review on the selection and types of biomass in-use for biosorption and desorption of heavy metals.

Even a number of reviews are already available, which deal with elimination of heavy metals using various kinds of biosorbents. However, by acknowledging the complexity of many factors influencing the process, beside its development and remain increasing number of scientific publications within this area, the already available reviews will not adequately cover all the important aspects in the adsorption process. Hence, this work attempts to summarize recent studies in the removal of heavy metals using biosorbents published between 1999 and early 2008. The emphasis will be on the equilibrium and kinetic aspects of heavy metals adsorption. The main content is the various models used in the adsorption studies. A new aspect on both experimental and theoretical studies is also provided.

2. Equilibrium studies in biosorption of heavy metals using various kinds of biosorbents

Biosorption of heavy metal is a passive non-metabolically mediated process of metal binding by biosorbent. Agricultural waste and its industrial by-products, bacteria, yeasts, fungi, and algae can be functioned as biosorbents of heavy metals. Biosorption is considered to be a fast physical/chemical process, and its rate is governed by the type of the process. In another sense, it can also be defined as a collective term for a number of passive accumulation processes which in any particular case may include ion exchange, coordination, complexation, chelation, adsorption and microprecipitation.

Proper analysis and design of adsorption/biosorption separation processes requires relevant adsorption/biosorption equilibria as one of the vital information. In equilibrium, a certain relationship prevails between solute concentration in solution and adsorbed state (i.e., the amount of solute adsorbed per unit mass of adsorbent). Their equilibrium concentrations are a function of temperature. Therefore, the adsorption equilibrium relationship at a given temperature is referred as adsorption isotherm. Several adsorption isotherms originally used for gas phase adsorption are available and readily adopted to correlate adsorption equilibria in heavy metals biosorption. Some well-known ones are Freundlich, Langmuir, Redlich–Paterson and Sips equation. The most widely used among them are Freundlich and Langmuir equations. The application of these isotherms on biosorbent-assisted heavy metals removal from water and wastewater will be discussed in subsequent order.

2.1. Freundlich isotherm

Freundlich isotherm is an empirical equation. This equation is one among the most widely used isotherms for the description of adsorption equilibrium. Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents including biosorbent. This equation has the following form

$$q_e = K_F C_e^{1/n} \quad (1)$$

Eq. (1) can also be expressed in the linearized logarithmic form

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

The plot of $\log q_e$ versus $\log C_e$ has a slope with the value of $1/n$ and an intercept magnitude of $\log K_F$. $\log K_F$ is equivalent to $\log q_e$ when C_e equals unity. However, in other case when $1/n \neq 1$, the K_F value depends on the units upon which q_e and C_e are expressed. On average, a favorable adsorption tends to have Freundlich constant n between 1 and 10. Larger value of n (smaller value of $1/n$) implies stronger interaction between biosorbent and heavy metal while $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites [39].

As a robust equation, Freundlich isotherm has the ability to fit nearly all experimental adsorption–desorption data, and is especially excellent for fitting data from highly heterogeneous sorbent systems as listed in Table 1. Accordingly, this isotherm can adequately represent the biosorption isotherm for most of the systems studied. Still, in some cases, Freundlich isotherm could not fit the experimental data well (as pointed by the low correlation values) or not even suitable for the biosorption equilibria expression. For instance, in the biosorption of Cr(VI) using waste weed, *Salvinia cucullata* [40], this failure is revealed by the value of n which is less than zero.

Apart from the ability to represent well in most cases (as shown by high correlation values), a physical meaning of $1/n$ was not clear in several studied systems. This is demonstrated in the biosorption of B(III) using cotton cellulose at pH 3 [22], Cr(VI) using tamarind fruit shell [30], *Saccharomyces cerevisiae* [41], *Spirulina plantensis* and *Chlorella vulgaris* [42], Ni(II) at 25 °C using tea factory waste [25] as well as Zn(II) at pH 3 using *Caulerpa lentillifera* [43]. A $1/n$ value of higher than unity (n less than one) suggests the presence of a concave/curved upward isotherm, sometimes called as solvent-affinity type isotherm [39]. Within this type of isotherm, the marginal sorption energy increases with increasing surface concentration. In this case, strong adsorption of solvent as a result of strong intermolecular attraction within the adsorbent layers occurs. As evidenced in these examples, the adsorption experimental data has the tendency to be in convex rather than concave form. Yet, in specific system studied using the Freundlich model fitting, the obtained parameter n was less than one (please refer to Table 1). Fig. 1 depicts the biosorption experimental data of Cr(VI) on spent biomass, *Spirulina plantensis* at 25 °C (adapted from reference [42]). Specifically speaking, the experimental data suggesting

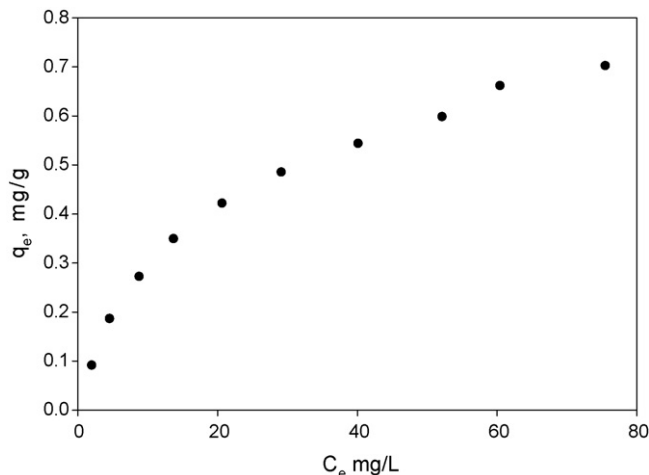


Fig. 1. Adsorption isotherm for Cr(VI) by spent *Spirulina plantensis* at 25 °C (adapted from reference [42]).

Table 1
Freundlich parameters and conditions for adsorption of heavy metals by various kinds of biosorbents

Biosorbent	Solute	Operational condition		Freundlich parameters			Reference	
		pH	Temperature (°C)	K_F (mg/g)	n	R^2		
<i>Aspergillus niger</i>	Cu(II)	–	20	1.77	2.05	0.886	[2]	
			25	1.95	2.09	0.939		
			35	4.46	2.83	0.940		
	Pb(II)	–	20	2.35	2.19	0.904		
			25	3.88	2.62	0.946		
			35	6.69	3.31	0.940		
<i>Cassia fistula</i> (Golden Shower)	Ni(II)	6.0	30	7.44	1.98	0.789	[6]	
				6.78	1.89	0.832		
				29.13	3.19	0.765		
<i>Rhizopus arrhizus</i>	Cr(VI)	1.3	30	8.09	3.55	0.976	[7]	
Crab shell particles	Cu(II)	3.5	–	2.05	1.68	0.979	[9]	
				4.0	2.53	1.72		0.970
				4.5	3.27	1.77		0.963
				5.0	6.29	2.05		0.889
				5.5	8.75	2.16		0.895
				6.0	9.13	2.20		0.897
	Co(II)	3.5	–	0.92	1.37	0.986		
				4.0	1.11	1.37		0.987
				4.5	1.33	1.38		0.980
				5.0	1.40	1.39		0.967
				5.5	1.67	1.40		0.76
				6.0	1.69	1.41		0.979
Dried activated sludge	Cd(II)	6.0	25	2.12	1.17	0.988	[10]	
<i>Tamarindus indica</i> seeds	Cr(VI)	2.0	29	4.99	4.16	0.981	[11]	
				4.0	2.53	2.62		0.993
				6.0	2.09	1.32		0.957
				8.0	3.06	2.26		0.965
Dried activated sludge	Cr(II)	1	25	4.99	1.55	0.994	[12]	
				1.60	1.62	0.991		
	Ni(II)	1	4.5	3.21	1.82	0.992		
				3.80	1.56	0.994		
Palm Tree Leaves	Zn(II)	5.5	25	3.01	3.23	–	[13]	
Tea waste	Cu(II)	5–6	22	0.70	1.35	0.984	[14]	
	Pb(II)			9.65	2.57	0.961		
<i>Carica papaya</i>	Hg(II)	6.5	30 ± 2	0.17	1.26	0.992	[15]	
Tea industry waste	Cu(II)	5.5	25	0.45	1.18	0.992	[16]	
				0.27	1.10	0.982		
	Cd(II)	5.5	25	0.59	11.36	0.983		
				0.32	4.55	0.977		
Wool	Cr(VI)	2	30	2.23	2.29	[17]		
Olive cake				0.49	1.57			
Sawdust				0.88	2.29			
Pine needles				0.27	1.44			
Almond				0.14	1.46			
Coal				0.21	1.68			
Cactus				0.09	1.42			
Palm kernel fiber				Pb(II)	5		36 ± 3	24.40
Coconut copra meal	Cd(II)	6.0	26	1.09	2.76	0.863	[20]	
			38	0.93	2.65	0.857		
			50	0.63	3.28	0.918		
			60	0.56	3.89	0.966		
Rose waste biomass	Pb(II)	5	30	6.75	3.13	0.842	[21]	
	Co(II)	6	19.75	1.58	0.923			
Cotton cellulose	B(III)	6.0	–	0.090	1.46	0.975	[22]	
				0.092	1.29	0.975		
				0.160	1.38	0.987		
				0.053	1.11	0.964		
				0.017	0.95	0.946		

Table 1 (Continued)

Biosorbent	Solute	Operational condition		Freundlich parameters			Reference		
		pH	Temperature (°C)	K_F (mg/g)	n	R^2			
Waste activated sludge	Cu(II)	5.33	25	3.71	2.37	0.996	[24]		
	Zn(II)			4.67	2.16	0.971			
	Cd(II)			2.67	2.51	0.993			
Tea factory waste	Ni(II)	4	25	0.26	0.93	0.923	[25]		
			45	3.86	3.16	0.968			
			60	5.31	4.00	0.967			
Waste beer yeast by-product (<i>S. cerevisiae</i>)	Pb(II)	–	30	0.51	1.19	0.998	[28]		
Green coconut shell powder	Cd(II)	7.0	27	9.92	1.79	0.966	[29]		
Crude Tamarind Fruit Shells (CFTS)	Cr(VI)	3	–	3.00	0.90	0.980	[30]		
HCl treated shells (H – TS)				3.06	0.70	0.980			
Oxalic acid treated shells (O-TS)				4.87	0.80	0.980			
Leaves of saltbush (<i>Atriplex canescens</i>)	Cu(II)	5.0	24 ± 2	4.02	1.04	0.979	[31]		
	Pb(II)			367.25	0.92	0.958			
	Zn(II)			6.85	0.99	0.996			
Waste weed, <i>Salvinia cucullata</i>	Cr(VI)	4.9	30	843917.50	–0.62	0.920	[40]		
				39.25	3.70	0.980			
<i>Saccharomyces cerevisiae</i>	Cr(VI)	2.0	–	0.37	0.98	0.924	[41]		
<i>Spirulina platensis</i> (fresh)	Cr(VI)	1.5	25	16.95	0.46	0.980	[42]		
<i>Spirulina platensis</i> (spent)				18.55	0.54	0.970			
<i>Chlorella vulgaris</i>				18.90	0.42	0.980			
<i>Caulerpa lentillifera</i>	Cu(II)	5.0	–	10.44	1.27	0.971	[43]		
				4.0	5.45	1.38		0.989	
				3.0	2.18	1.34		0.958	
	Cd(II)	5.0	–	5.54	2.21	0.956			
				4.0	3.00	1.31		0.911	
				3.0	1.74	1.33		0.916	
	Pb(II)	5.0	–	87.68	1.46	0.954			
				4.0	25.67	2.12		0.922	
				3.0	11.90	1.81		0.939	
	Zn(II)	5.0	–	3.13	1.54	0.968			
				4.0	1.79	1.22		0.827	
				3.0	1.21	0.86		0.942	
	Calcium alginate	Ni(II)	5	–	0.93	0.85		0.986	[44]
	Chitosan coated calcium alginate				11.99	2.13		0.973	
	Chitosan coated silica				7.69	1.33		0.976	
Chitosan beads	Cr(III)	5.0	–	5.46	5.48	0.984	[45]		
	Cr(VI)			59.47	4.12	0.986			
<i>Eichhornia crassipes</i>	Cr(VI)	1.0	25	5.39	3.19	–	[46]		
Non-living green algae <i>Cladophora fascicularis</i>	Cu(II)	5.0	25	84.38	2.45	0.998	[47]		
			35	102.94	2.85	0.995			
			45	120.07	2.90	0.993			
	Pb(II)	25	163.47	3.62	0.997				
			35	184.39	3.89	0.995			
			45	208.43	4.18	0.993			
Distillery sludge (untreated)	Pb(II)	5	30	16.25	4.70	0.970	[48]		
Distillery sludge (autoclaved)				16.83	4.46	0.898			
Distillery sludge (HCl treated)				16.08	3.89	0.970			
Distillery sludge (NaOH treated)				24.91	5.40	0.908			
Distillery sludge (HCHO treated)				24.29	5.82	0.891			
Distillery sludge (SDS treated)				19.31	5.11	0.919			
Sour Orange Residue	Cu(II)	4.5	28	9.52	2.90	0.980	[49]		
Sour Orange Residue (NaOH treated)				5.52	3.74	0.980			
Free Biomass <i>Chlorella sorokiniana</i>	Cr(III)	–	25	10.67	2.85	0.877	[50]		
Loofa sponge immobilized biomass of <i>Chlorella sorokiniana</i>				17.93	3.55	0.896			
<i>Rhodococcus opacus</i> (bacteria strain)	Cr(III)	5.2	25	1.71	1.1628	0.923	[51]		
Orange peels	Cd(II)	3	–	1.4×10^{-3}	1.80	0.900	[52]		
				5	1.7×10^{-3}	2.00		0.780	
Grapefruits peels	–	3	–	1.6×10^{-3}	2.50	0.740	–		
				5	2.1×10^{-3}	3.20		0.720	
Lemon peels	–	3	–	1.9×10^{-3}	1.70	0.870	–		
				5	2.1×10^{-3}	1.70		0.940	

Table 1 (Continued)

Biosorbent	Solute	Operational condition		Freundlich parameters			Reference
		pH	Temperature (°C)	K_F (mg/g)	n	R^2	
<i>A. niger</i>	Cr(VI)	2.2	25	17.92	1.18	0.990	[53]
<i>A. sydoni</i>				8.06	1.01	0.950	
<i>P. janthinellum</i>				9.05	1.10	0.910	
Brown seaweed	Cu(II)	5	25	5.70	2.30	0.908	[54]
			40	5.20	2.10	0.953	
			55	5.40	2.00	0.917	
Bengal gram husk	Cr(VI)	2	–	2.82	1.81	–	[55]
Surfactant modified coconut coir pith	Cr(VI)	2	32	0.017	2.8	0.997	[56]
Living ureolytic mixed culture	Ni(II)	6	20	1.55	2.12	0.910	[57]
Non-living ureolytic mixed culture				0.38	1.34	0.910	
Vegetal biomass (olive pits)	Cd(II)	–	21 ± 1	33.60	3.15	0.933	[58]
Litter of poplar forests	Cu(II)	4.5	25	6.14	3.89	0.966	[59]
			45	8.32	3.31	0.875	
			60	14.18	5.57	1.000	
Live <i>spirulina</i>	Cd(II)	6 ± 0.5	35–38		2.30		[60]
Dead <i>spirulina</i>					0.86		
Pristine biomass (baker's yeast)	Pb(II)	4.5	–	11.56	7.67	0.778	[61]
	Cd(II)			2.42	6.16	0.507	
Cystine modified biomass	Pb(II)			35.35	16.00	0.915	
	Cd(II)			7.65	8.64	0.884	
Pretreated <i>Aspergillus niger</i>	Cu(II)	5.5 ± 0.5	–	5.35	2.38	0.890	[62]
Lentil shell	Cu(II)	6	20	0.65	2.77	0.993	[63]
			40	1.20	2.58	0.964	
			60	1.14	2.87	0.901	
Wheat shell			20	0.019	10.91	0.910	
			40	0.034	9.59	0.955	
			60	0.022	13.43	0.945	
Rice shell			20	0.108	2.79	0.996	
			40	0.148	2.82	0.929	
			60	0.130	3.19	0.938	
<i>Cladophora fascicularis</i>	Pb(II)	5	25	37.46	3.62	0.997	[64]
			35	46.72	3.89	0.995	
			45	58.08	4.18	0.993	
Protonated rice bran (using H ₃ PO ₄)	Ni(II)	6	30	2.64	2.31	0.851	[65]
Poly (amic acid) modified biomass of baker's yeast	Pb(II)	4.2	–	199.50	93.50	0.945	[66]
	Cd(II)			182.00	30.30	0.932	
Green algae <i>Spirogyra</i> species	Pb(II)	5	25	8.01	1.87	0.916	[67]
			35	9.12	1.94	0.919	
			45	9.68	1.93	0.933	
Marine brown algae <i>Laminaria japonica</i> (epichlorohydrin crosslinking EC1)	Pb(II)	5.2	–	319.09	6.69	0.789	[68]
Marine brown algae <i>Laminaria japonica</i> (epichlorohydrin crosslinking EC2)				304.58	5.80	0.831	
Marine brown algae <i>Laminaria japonica</i> (modified with potassium permanganate)				246.57	3.15	0.683	
Marine brown algae <i>Laminaria japonica</i> (washed with distilled water)				213.42	4.91	0.916	
Peat	Pb(II)	6.0	10	8.51	2.44	0.970	[69]
			20	8.58	2.45	0.987	
			30	8.57	2.23	0.973	
			40	8.75	2.24	0.993	
Dead <i>Bacillus licheniformis</i>	Cr(VI)	2.5	50	8.61	2.82	0.946	[70]
<i>Lyngbya putealis</i> (HH-15)	Cr(VI)	3.0	25	10.63	1.45	0.870	[71]
Pre-treated arca shell biomass	Pb(II)	–	25 ± 2	4.85	2.83	0.828	[72]
	Cu(II)			3.98	2.76	0.863	
	Ni(II)			3.54	3.95	0.725	
	Cs(I)			1.95	5.75	0.733	
	Co(II)			2.85	3.98	0.921	
Maize husk (unmodified)	Cd(II)	7.5	30	4×10^{-6}	0.38	0.978	[73]
	Pb(II)			6.64×10^{-4}	0.55	0.975	
	Zn(II)			0.49	0.86	0.985	

Table 1 (Continued)

Biosorbent	Solute	Operational condition		Freundlich parameters			Reference
		pH	Temperature (°C)	K_F (mg/g)	n	R^2	
Maize husk (EDTA modified)	Cd(II)			114.10	3.42	0.974	
	Pb(II)			117.19	3.99	0.961	
	Zn(II)			614.11	40.82	0.628	
Brown seaweed <i>Sargassum filipendula</i> Immobilized <i>Saccharomyces cerevisiae</i>	Pb(II)	4	30 ± 1	4.71 ± 0.02	2.66 ± 0.01	0.981	[74]
	Pb(II)	5	20	1.37	2.70	0.965	[75]
Atlantic Cod fish scale	As(III)		–	0.685	1.64	0.964	[76]
	As(V)			0.396	1.54	0.984	
<i>Myriophyllum spicatum</i> L.	Co(II)	–	20	0.62	2.90	0.760	[77]
	Cu(II)			1.60	1.20	0.950	
	Ni(II)			0.63	2.50	0.850	
	Zn(II)			1.60	2.50	0.740	
<i>Bacillus thuringiensis</i> (vegetative cell)	Ni(II)	6	30	5.70	2.87	0.990	[78]
<i>Bacillus thuringiensis</i> (spore-crystal mixture)				12.26	4.42	0.990	
Magnetically modified brewer's yeast	Hg(II)	5	4	11.30	2.79	0.793	[79]
			15	19.20	2.96	0.778	
			25	25.40	3.14	0.865	
			35	30.40	2.84	0.923	
<i>Bacillus jeotgali</i>	Cd(II)	7	25	0.03	1.67	0.708	[80]
			30	1.91	1.49	0.886	
			35	2.18	1.37	0.823	
	Zn(II)		25	3.39	1.11	0.949	
			30	15.04	1.54	0.917	
Baker's yeast	Ni(II)	6.75	27	3.73	5.88	0.980	[82]
			40	2.74	4.62	0.970	
			50	1.84	3.61	0.964	
			60	1.22	2.92	0.955	
Cedar sawdust	Cu(II)	5–6	25	0.59	1.02	0.938	[83]
			35	1.04	1.13	0.969	
			45	1.19	1.25	0.986	
Crushed brick			25	0.75	1.19	0.957	
			35	1.04	1.23	0.968	
			45	1.54	1.49	0.964	
<i>Sargassum wightii</i>	Ni(II)		3.0	2.85	2.24	0.921	[86]
			3.5	3.52	2.23	0.940	
			4.0	3.97	2.22	0.936	
			4.5	3.74	2.24	0.942	
<i>Lyngbya putealis</i> exopolysaccharides	Cr(VI)	2	45	45.03	2.98	0.717	[87]
<i>Chlorella vulgaris</i>	Cd(II)	4.0	25	2.92	2.13	1.000	[90]
	Ni(II)			3.68	1.81	0.999	
PVA- <i>Sargassum</i>	Cu(II)	5	22 ± 1	0.19	7.143	0.83	[95]
Freely suspended <i>Sargassum</i>				0.56	3.226	0.95	
<i>Rhizopus oryzae</i> (viable)	Cu(II)	4–6	21	8.65	6.67	0.921	[96]
<i>Rhizopus oryzae</i> (NaOH treated)				11.07	11.07	0.836	
Nopal (<i>Opuntia streptacantha</i>)	Pb(II)		–	115.07	1.46	0.995	[101]
			3	50.00	1.61	0.986	
			4	74.69	1.79	0.989	
			5	92.47	1.77	0.990	
			6	73.01	1.54	0.984	
<i>Azadirachta indica</i> bark	Zn(II)	6	30 ± 1	2.58	0.64	0.981	[103]
Water lily	Cr(III)	5 ± 0.5	30	0.33	1.34	0.972	[104]
	Cr(VI)			0.25	1.55	0.999	
Water hyacinth	Cr(III)			1.44	2.38	0.918	
	Cr(VI)			0.15	6.21	0.995	
Green taro	Cr(III)			0.21	1.14	0.994	
	Cr(VI)			0.12	2.00	0.999	
Mangrove leaves	Cr(III)			0.52	1.64	0.990	
	Cr(VI)			0.19	1.25	0.992	
Reed mat	Cr(III)			1.85	4.05	0.990	
	Cr(VI)			0.13	1.94	1.000	

Table 1 (Continued)

Biosorbent	Solute	Operational condition		Freundlich parameters			Reference
		pH	Temperature (°C)	K_F (mg/g)	n	R^2	
Agaricus bisporus	Cr(VI)	1	20	1.79	3.13	0.970	[105]
			30	2.18	3.03	0.980	
			40	4.37	3.57	0.730	
Sugar beet pulp	Pb(II)	5.0–5.5	25 ± 1	5.60	1.00	0.990	[106]
	Cd(II)			7.16	0.98	0.990	

a convex isotherm ($1/n < 1$), but Freundlich model gave $1/n > 1$. A concave type of isotherm experimental data of the biosorption of Ni(II) on calcium alginate along with Freundlich model is given in Fig. 2 [44]. As-depicted irregular pattern of experimental data and isotherm curve represented by Freundlich equation are likely to be caused by the complex nature of the sorbent material and its varied multiple active sites as well as the complex solution chemistry of some metallic compounds.

As a trend, strong interaction takes place between most biosorbent and heavy metals as evidenced in Table 1. Sorption of solute on any sorbent can occur either by physical bonding, ion exchange, complexation, chelation or through a combination of these interactions. In the first case of physical bonding, as the solute is loosely bound, it can easily be desorbed using distilled water. Given the fact that miscellaneous functional groups such as hydroxyl, carbonyl, carboxyl, sulfhydryl, thioether, sulfonate, amine, imine, amide, imidazole, phosphonate, and phosphodiester groups, can present within the structure of biosorbent, the mechanism of adsorption will not be restricted to physical bonding [2,6,10,11,13–16,22,24,25,28–30,40,42–68]. Different mechanisms as mentioned can be involved as the interaction between sorbent and solute molecules is expected to be strong. The parameter n of Freundlich equation in Table 1 expresses these phenomena.

Adsorption capacity is the most important characteristic of an adsorbent. It is defined as the amount of adsorbate taken up by the adsorbent per unit mass of adsorbent. This variable is governed by a series of properties, such as pore and particle size distribution, specific surface area, cation exchange capacity, pH, surface functional groups, and also temperature. Most of the adsorption capacity for biosorbents (obtained from Freundlich K_F parameter) summarized in this paper is quite low in comparison to the commercially available activated carbons. Apart from this fact, different types of biosorbents are still attractive due to its biosorption advantages and cost-effectiveness for metal biosorption.

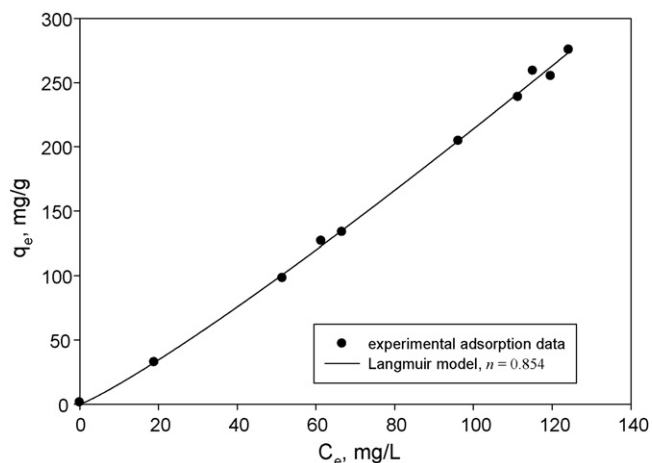


Fig. 2. Adsorption isotherm for Ni(II) on calcium alginate (adapted from reference [44]).

As a precaution note, Freundlich equation is unable to predict adsorption equilibria data at extreme concentration. Furthermore, this equation is not reduced to linear adsorption expression at very low concentration. Moreover, it does not have limit expression at very high concentration. However, researchers rarely face this problem, as moderate concentration is frequently used in most biosorption studies,

2.2. Langmuir isotherm

Another widespread-used model for describing heavy metals sorption to biosorbent is the Langmuir model. Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. Table 2 abridges a number of studies that draw upon Langmuir isotherm to interpret biosorption equilibrium data. This isotherm based on three assumptions, namely adsorption is limited to monolayer coverage, all surface sites are alike and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy. By applying these assumptions, and a kinetic principle (rate of adsorption and desorption from the surface is equal), the Langmuir equation can be written in the following form

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (3)$$

This equation is often written in different linear forms [20,69]

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}} \quad (4)$$

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\max}} \right) \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (5)$$

$$q_e = q_{\max} - \left(\frac{1}{K_L} \right) \frac{q_e}{C_e} \quad (6)$$

$$\frac{q_e}{C_e} = K_L q_{\max} - K_L q_e \quad (7)$$

Ho [69] contrasted the linear least-square method (for Eqs. (4)–(7)) and a non-linear method (for Eq. (3)) of three well-known isotherms (Langmuir was among them) using Pb(II) adsorption equilibria data at different temperatures. Langmuir isotherm parameters obtained from the four Langmuir linear equations using the linear method differ among each other but they were identical when the non-linear method is applied. Hence, he claimed that the non-linear method is a better way to obtain the isotherm parameters. Even though non-linear method provides a better result, the linear least-square method is still often preferred in favor of its simplicity and convenience [6,9,11,14,17,21,22,25,28,31,40,41,44,45,49,51–57,60,61,63,65,70–79]. Only narrow understanding of the data fitting process is required and the calculation can be done in spreadsheets such as Microsoft Excel.

Within the Langmuir model, the saturation capacity q_{\max} is supposed to coincide with saturation of a fixed number of identical

Table 2
Langmuir parameters and conditions for adsorption of heavy metals by various kinds of biosorbents

Biosorbent	Solute	Operational condition		Langmuir parameters			Ref.
		pH	Temperature (°C)	K_L (L/mg)	q_{max} (mg/g)	R^2	
<i>Aspergillus niger</i>	Cu(II)	–	20	0.0120	33.11	0.944	[2]
			25	0.0150	33.23	0.941	
			35	0.0260	33.54	0.939	
	Pb(II)	–	20	0.0210	34.69	0.987	
			25	0.0220	34.92	0.966	
			35	0.0390	34.92	0.961	
Green alga <i>Cladophora fascicularis</i>	Cu(II)	5.0	15	0.1406	47.019	[5]	
			25	0.1607	70.53		
			35	0.1649	92.77		
			45	0.1882	110.56		
<i>Cassia fistula</i> (Golden Shower)	Leaves Stem bark Pods bark	6.0	30	0.0126	163.93	0.971	[6]
				0.0020	172.41	0.959	
				0.0345	196.07	0.981	
<i>Rhizopus arrhizus</i>	Cr(VI)	1.3	30	0.3310	23.92	0.965	[7]
Crab shell particles	Cu(II)	3.5 4.0 4.5 5.0 5.5 6.0	–	0.0022	163.90	0.980	[9]
				0.0023	188.70	0.986	
				0.0026	204.10	0.988	
				0.0039	208.30	0.977	
				0.0054	222.20	0.979	
				0.0055	243.90	0.985	
	Co(II)	3.5 4.0 4.5 5.0 5.5 6.0	–	0.0015	212.80	0.975	
				0.0016	235.50	0.977	
				0.0017	270.30	0.973	
				0.0018	285.70	0.964	
Dried activated sludge	Cd(II) Pb(II)	6.0 4.0	25	0.0210	84.30	0.988	[10]
				0.0320	131.60	0.977	
<i>Tamarindus indica</i> seeds	Cr(VI)	2.0 4.0 6.0 8.0	29	16023.07	0.098	0.938	[11]
				3191.93	0.055	0.907	
				72.43	0.08	0.954	
				1.3600	0.023	0.958	
Dried activates sludge	Cr(II)	1 4.5	25	0.0063	294.10	0.986	[12]
				0.0055	95.20	0.992	
	Ni(II)	1 4.5	25	0.0079	106.40	0.991	
				0.0048	238.10	0.987	
Palm Tree Leaves	Zn(II)	5.5	25	0.0560	14.60	–	[13]
Tea waste	Cu(II) Pb(II)	5–6	22	0.0076	48.00	0.994	[14]
				0.0494	65.00	0.957	
<i>Carica papaya</i>	Hg(II)	6.5	30 ± 2	0.0040	155.63	0.995	[15]
Wool	Cr(VI)	2	30	7.15×10^{-3}	41.15	[17]	
Olive cake				4.70×10^{-3}	33.44		
Sawdust				9.15×10^{-3}	15.28		
Pine needles				5.44×10^{-3}	21.50		
Almond				5.46×10^{-3}	10.62		
Coal				11.50×10^{-3}	6.78		
Cactus				6.13×10^{-3}	7.08		
Coconut copra meal	Cd(II)	6.0	26	0.1760	4.92	1.000	[20]
			38	0.1410	4.68	0.998	
			50	0.1190	2.66	0.999	
			60	0.0990	2.01	1.000	
Rose waste biomass	Pb(II) Co(II)	5 6	30	0.0280	151.51	0.985	[21]
				0.0372	27.62	0.982	
Cotton cellulose	B(III)	6.0 6.5 7.0 7.5 8.0	–	0.3040	6.88	0.981	[22]
				0.7370	13.06	0.947	
				1.3580	15.41	0.979	
				0.8460	17.79	0.793	
				0.8660	41.49	0.047	
Spent grain	Cu(II)	4.2	–	0.0800	10.47	0.995	[23]

Table 2 (Continued)

Biosorbent	Solute	Operational condition		Langmuir parameters			Ref.	
		pH	Temperature (°C)	K_L (L/mg)	q_{max} (mg/g)	R^2		
Tea factory waste	Ni(II)	4	25	0.0880	15.26	0.992	[25]	
			45	0.0930	17.73	0.999		
			60	0.0980	18.42	0.999		
Waste beer yeast by-product (<i>S. cerevisiae</i>)	Pb(II)	–	30	0.0883	55.71	0.998	[28]	
Green coconut shell powder	Cd(II)	7.0	27	0.0190	285.70	0.986	[29]	
Crude tamarind fruit shells (CTFS)	Cr(VI)	3	–	0.0500	74.62	0.990	[30]	
HCl treated shells (H-TS)				0.0700	140.84	0.990		
Oxalic acid treated shells (O-TS)				0.0350	151.51	0.990		
Leaves of saltbush (<i>Atriplex canescens</i>)	Cu(II)	5.0	24 ± 2	9.0900	590.92	0.0001	[31]	
	Pb(II)			–3491.2000	–85.78	0.138		
	Zn(II)			–24.8400	–255.71	0.0088		
Rice bran	Zn(II)	5.0	30	0.0110	14.17	0.981	[33]	
			40	0.0150	14.84	0.981		
			50	0.0190	18.31	0.981		
Waste weed, <i>Salvinia cucullata</i>	Cr(VI)	4.9	–	–0.0100	23.98	0.860	[40]	
			30	0.0130	232.60	0.990		
<i>Saccharomyces cerevisiae</i>	Cr(VI)	2.0	–	0.1259	384.61	0.938	[41]	
<i>Spirulina platensis</i> (fresh)	Cr(VI)	1.5	25	0.0270	188.68	0.960	[42]	
<i>Spirulina platensis</i> (spent)				0.0500	212.76	0.990		
<i>Chlorella vulgaris</i>				0.0360	163.93	0.960		
<i>Caulerpa lentillifera</i>	Cu(II)	5.0	–	0.0760	5.57	0.968	[43]	
			4.0	0.0618	42.37	0.995		
			3.0	0.0290	2.64	0.995		
	Cd(II)	5.0	–	0.0742	4.69	0.995		
			4.0	0.0229	4.34	0.952		
			3.0	0.0106	2.95	0.914		
	Pb(II)	5.0	–	0.0711	28.99	0.984		
			4.0	0.0324	24.19	0.996		
			3.0	0.0144	15.94	0.998		
	Zn(II)	5.0	–	0.0671	2.66	0.999		
			4.0	0.0500	1.65	0.995		
			3.0	0.0201	1.37	0.971		
	Calcium alginate	Ni(II)	5	–	0.0036	310.40	0.990	[44]
	Chitosan coated calcium alginate			0.0240	222.20	0.990		
	Chitosan coated silica			0.0026	254.30	0.994		
Chitosan beads	Cr(III)	5.0	–	1.320×10^{-4}	30.03	0.998	[45]	
	Cr(VI)		3.421×10^{-3}	76.92	0.998			
Non-living green algae <i>Cladophora fascicularis</i>	Cu(II)	5.0	25	0.0652	102.55	0.997	[47]	
			35	0.1241	106.81	0.998		
			45	0.1750	112.97	1.000		
	Pb(II)	5.0	25	0.0396	200.42	0.998		
			35	0.0431	217.99	0.999		
			45	0.0759	229.92	0.998		
Distillery sludge (untreated)	Pb(II)	5	30	0.0188	71.43	0.983	[48]	
Distillery sludge (autoclaved)			0.0170	81.30	0.980			
Distillery sludge (HCl treated)			0.0235	85.47	0.995			
Distillery sludge (NaOH treated)			0.0219	91.74	0.984			
Distillery sludge (HCHO treated)			0.0189	85.47	0.980			
Distillery sludge (SDS treated)			0.0228	74.63	0.993			
Sour orange residue	Cu(II)	4.5	28	0.0660	52.08	0.990	[49]	
Sour orange residue (NaOH treated)			0.0540	23.47	0.980			
Free biomass <i>Chlorella sorokiniana</i>	Cr(III)	–	25	0.1100	56.56	0.991	[50]	
Loofa sponge immobilized biomass of <i>Chlorella sorokiniana</i>			0.3870	68.51	0.996			
<i>Rhodococcus opacus</i> (bacteria strain)	Cr(III)	5.2	25	0.0015	714.29	0.037	[51]	
Orange peels	Cd(II)	3	–	1.779×10^{-3}	123.65	0.880	[52]	
			5	1.379×10^{-3}	150.63	0.350		
Grapefruit peels		3	–	5.649×10^{-3}	76.44	0.990		
			5	5.382×10^{-3}	110.16	0.930		

Table 2 (Continued)

Biosorbent	Solute	Operational condition		Langmuir parameters			Ref.
		pH	Temperature (°C)	K_L (L/mg)	q_{max} (mg/g)	R^2	
Lemon peels		3		2.046×10^{-3}	159.62	0.970	
		5		1.557×10^{-3}	209.08	0.880	
<i>A. niger</i>	Cr(VI)	2.2	25	0.0026	17.61	0.980	[53]
<i>A. sydoni</i>				0.0022	9.07	0.970	
<i>P. janthinellum</i>				0.0042	9.35	0.950	
Brown seaweed	Cu(II)	5	25	0.0260	82.60	0.998	[54]
			40	0.0240	88.00	0.997	
			55	0.0254	93.90	0.996	
Bengal gram husk	Cr(VI)	2	–	0.0090	91.64	0.995	[55]
Surfactant modified coconut coir pith	Cr(VI)	2	32	0.1240	76.30	0.979	[56]
Living ureolytic mixed culture	Ni(II)	6	20	8×10^{-5}	12.58	0.880	[57]
Non-living ureolytic mixed culture				5.9×10^{-5}	7.41	0.690	
Vegetal biomass (olive pits)	Cd(II)	–	21 ± 1	0.0440	9.39	0.999	[58]
Litter of poplar forests	Cu(II)	4.5	25	1.66×10^{-4}	19.53	0.991	[59]
			45	1.86×10^{-4}	29.76	0.995	
			60	3.574×10^{-4}	29.33	0.972	
Live <i>spirulina</i>	Cd(II)	6 ± 0.5	35–38	0.0004	625.00		[60]
Dead <i>spirulina</i>				0.0013	355.00		
Pristine biomass (baker's yeast)	Pb(II)	4.5	–	1.0600	19.01	0.999	[61]
	Cd(II)			1.3200	3.90	0.999	
Cystine modified biomass	Pb(II)			1.2500	45.87	0.998	
	Cd(II)			1.5200	11.03	0.996	
Pretreated <i>Aspergillus niger</i>	Cu(II)	5.5 ± 0.5	–	0.1888	2.61	0.990	[62]
Lentil shell	Cu(II)	6	20	0.0190	8.98	0.980	[63]
			40	0.0220	9.51	0.981	
			60	0.0410	9.59	0.999	
Wheat shell			20	0.0020	7.39	0.925	
			40	0.0040	16.08	0.791	
			60	0.0050	17.42	0.883	
Rice shell			20	0.0110	1.85	0.991	
			40	0.0160	2.31	0.982	
			60	0.0180	2.95	0.987	
<i>Cladophora fascicularis</i>	Pb(II)	5	25	0.0359	198.50	0.998	[64]
			35	0.0435	215.80	0.999	
			45	0.0766	227.70	0.998	
Protonated rice bran (using H_3PO_4)	Ni(II)	6	30	9.43×10^{-6}	46.51	0.941	[65]
Poly (amic acid) modified biomass of baker's yeast	Pb(II)	4.2		6.6000	210.50	0.999	[66]
	Cd(II)			4.0000	95.20	0.999	
Green algae <i>Spirogyra</i> species	Pb(II)	5	25	0.0210	140.84	0.990	[67]
			35	0.0230	144.93	0.991	
			45	0.0240	151.57	0.997	
Marine brown algae <i>Laminaria japonica</i> (epichlorohydrin crosslinking EC1)	Pb(II)	5.2	–	0.1568	352.24	0.965	[68]
Marine brown algae <i>Laminaria japonica</i> (epichlorohydrin crosslinking EC2)				0.0815	343.95	0.994	
Marine brown algae <i>Laminaria japonica</i> (modified with potassium permanganate)				0.0109	391.61	0.835	
Marine brown algae <i>Laminaria japonica</i> (washed with distilled water)				0.0299	273.50	0.916	
Peat	Pb(II)	6	10	0.4370	27.80	0.995	[69]
			20	0.4160	28.30	0.992	
			30	0.4150	29.50	0.996	
			40	0.3820	30.80	0.984	
Dead <i>Bacillus licheniformis</i>	Cr(VI)	2.5	50	0.0300	69.35	0.997	[70]
<i>Lyngbya putealis</i> (HH-15)	Cr(VI)	3.0	25	0.1040	105.30	0.900	[71]
Pre-treated arca shell biomass	Pb(II)	–	25 ± 2	0.0690	30.39	0.985	[72]
	Cu(II)			0.0590	26.88	0.979	
	Ni(II)			0.2810	11.75	0.992	
	Cs(I)			0.2280	4.76	0.997	
	Co(II)			0.2250	11.53	0.984	

Table 2 (Continued)

Biosorbent	Solute	Operational condition		Langmuir parameters			Ref.
		pH	Temperature (°C)	K_L (L/mg)	q_{max} (mg/g)	R^2	
Maize husk	Cd(II)	7.5	30	-6.88×10^{-4}	-151.51	0.962	[73]
	Pb(II)			-4.58×10^{-4}	-217.39	0.850	
	Zn(II)			-3.26×10^{-4}	-3330.00	0.627	
Maize husk (EDTA modified)	Cd(II)			8.93×10^{-3}	833.33	0.979	
	Pb(II)			7.36×10^{-3}	714.29	0.974	
	Zn(II)			0.0400	769.23	0.997	
Brown seaweed <i>Sargassum filipendula</i> Immobilized <i>Saccharomyces cerevisiae</i>	Pb(II)	4	30 ± 1	4.9600 ± 1.44	1.80 ± 0.02	0.999	[74]
	Pb(II)	5	20	0.0140	30.04	0.995	[75]
Atlantic Cod fish scale	As(III)	-	-	5.2000	0.0248	0.985	[76]
	As(V)			8.8000	0.0267	0.988	
<i>Myriophyllum spicatum</i> L.	Co(II)	-	20	0.3200	2.30	1.000	[77]
	Cu(II)			0.0120	113.00	0.110	
	Ni(II)			0.2500	3.00	1.000	
	Zn(II)			0.8800	6.80	0.990	
<i>Bacillus thuringiensis</i> (vegetative cell) <i>Bacillus thuringiensis</i> (spore- crystal mixture)	Ni(II)	6	35	0.0160	35.46	0.990	[78]
				0.0360	45.87	0.990	
Magnetically modified brewer's yeast	Hg(II)	5	4	0.1470	48.30	0.991	[79]
			15	0.1720	74.10	0.989	
			25	0.1580	93.40	0.992	
			35	0.1190	133.30	0.995	
<i>Bacillus jeotgali</i>	Cd(II)	7	25	0.2000	37.30	0.991	[80]
			30	0.0700	47.50	0.986	
			35	0.0700	57.90	0.996	
	Zn(II)		25	0.0600	105.20	0.528	
	30		0.0800	222.20	0.834		
<i>Gelidium</i>	Cu(II)	5.3	20	$1.5 \pm 0.2 \times 10^{-2}$	33 ± 2	0.986	[81]
			35	$1.3 \pm 0.3 \times 10^{-2}$	45 ± 4	0.940	
Algal waste			20	$2.8 \pm 0.5 \times 10^{-2}$	16.7 ± 0.9	0.950	
			35	$5.3 \pm 0.8 \times 10^{-2}$	17.0 ± 0.6	0.950	
Baker's yeast	Ni(II)	6.75	27	0.2120	9.01	0.954	[82]
			40	0.1370	8.46	0.942	
			50	0.0940	7.73	0.915	
			60	0.0620	7.37	0.930	
Cedar sawdust	Cu(II)	5–6	25	3.584×10^{-3}	294.12	0.977	[83]
			35	6.290×10^{-3}	144.93	0.977	
			45	7.750×10^{-3}	106.38	0.980	
Crushed brick			25	5.274×10^{-3}	153.85	0.973	
			35	6.935×10^{-3}	104.17	0.977	
			45	10.243×10^{-3}	68.03	0.978	
<i>Caladium bicolor</i> (wild cocoyam)	Pb(II)	5	30	0.0393	37.17	0.999	[84]
			40	0.0380	52.63	0.994	
			50	0.0263	37.59	0.997	
			60	0.0260	20.45	0.999	
			70	0.0250	8.81	0.999	
	Cd(II)		30	0.0289	42.19	0.999	
			40	0.0253	59.02	0.998	
			50	0.0208	46.95	0.998	
			60	0.0141	22.47	0.998	
			70	0.0124	14.03	0.994	
Dried non-living biomass (NB) of different <i>Pseudomonas</i> strains	Co(II)	4	10	0.1884	24.75	0.970	[85]
			20	0.2393	22.39		
			30	0.3699	22.39		
			40	0.4123	22.98		
			50	0.5125	22.39		
	Zn(II)	4.4	10	0.3593	18.43	0.990	
			20	0.4327	18.43		
			30	0.5398	18.43		
			40	0.7141	18.43		
			50	0.8272	19.06		

Table 2 (Continued)

Biosorbent	Solute	Operational condition		Langmuir parameters			Ref.
		pH	Temperature (°C)	K_L (L/mg)	q_{max} (mg/g)	R^2	
<i>Sargassum wightii</i>	Pb(II)	3.6	10	0.2264	45.58	0.990	
			20	0.2639	43.51		
			30	0.3175	39.37		
			40	0.3778	37.29		
			50	0.4020	41.44		
	Hg(II)	4.7	10	0.0862	80.24	1.000	
			20	0.1176	76.22		
			30	0.1500	76.22		
			40	0.1949	78.23		
			50	0.2353	84.25		
	Ni(II)	3.0	30	0.0054	63.20	0.982	
				0.0055	76.10	0.989	
				0.0065	81.20	0.986	
				0.0057	79.10	0.991	
	Lyngbya putealis exopolysaccharides	Cr(VI)	2	45	0.1890	178.60	
Brown seaweed (<i>Turbinaria conoides</i>)	Pb(II)	4	30	0.0410	385.10	0.902	
			4.5	25	0.0440	420.10	0.733
			30	0.0480	439.40	0.842	
			35	0.0570	228.00	0.783	
			5	30	0.0470	401.40	0.854
<i>Chlorella vulgaris</i>	Cd(II)	4.0	25	28.3000	0.02	0.999	
				70.9000	0.03	0.999	
Treated sawdust	Cr(VI)	4.5 – 6	–	2.3600	3.60	–	
PVA-Sargassum Freely suspended <i>Sargassum</i>	Cu(II)	5	22 ± 1	28.0700	0.21	0.960	
				2.8600	0.96	0.980	
<i>Rhizopus oryzae</i> (viable) <i>Rhizopus oryzae</i> (NaOH treated)	Cu(II)	4 – 6	21	0.1290	19.40	0.999	
				0.0280	43.70	0.999	
<i>Gelidium</i>	Zn(II)	5.3	20	2.6 + 0.7	13. ± 1	0.900	
				2.1 + 0.4	18 ± 1	0.933	
Algal waste	Zn(II)			4.2 + 0.5	7.1 ± 0.2	0.973	
				3.3 + 0.5	11.8 ± 0.5	0.946	
Nopal (<i>Opuntia streptacantha</i>)	Pb(II)	2	–	2.868×10^{-4}	5.43	0.850	
				6.118×10^{-4}	11.29	0.990	
				20.41×10^{-4}	12.76	0.996	
				22.80×10^{-4}	13.39	0.998	
				9.894×10^{-4}	12.34	0.981	
Lignin	Pb(II)	5.5	20	0.2081	89.51	0.961	
				0.4309	22.87	0.978	
				0.1421	25.40	0.943	
				0.2046	11.25	0.988	
				0.2511	5.99	0.850	
Azadirachta indica bark	Zn(II)	6	30 ± 1	0.0572	33.49	0.998	
Water lily	Cr(III)	5 ± 0.5	30 °C	0.0310	6.11	0.979	
				0.0270	5.11	0.984	
Water hyacinth	Cr(III)			0.0500	6.61	0.957	
				0.9170	0.34	0.995	
Green taro	Cr(III)			0.0340	6.07	0.991	
				0.0420	1.42	1.000	
Mangrove leaves	Cr(III)			0.0320	6.54	0.926	
				0.0440	5.72	0.997	
Reed mat	Cr(III)			0.0420	7.18	0.989	
				0.0390	1.66	0.999	
<i>Agaricus bisporus</i>	Cr(VI)	1	20	0.0700	8.00	0.990	
			30	0.0500	11.28	0.990	
			40	0.0900	13.79	0.750	
Sugar beet pulp	Pb(II)	5.0 – 5.5	25 ± 1	0.4759	0.37	0.600	
				0.1237	0.13	0.740	
Non-living lichen biomass of <i>Cladonia rangiformis</i> hoffm	Cu(II)		15	0.1051	7.69	0.998	

Table 2 (Continued)

Biosorbent	Solute	Operational condition		Langmuir parameters			Ref.
		pH	Temperature (°C)	K_L (L/mg)	q_{max} (mg/g)	R^2	
Lignocellulosic substrate (Wheat bran extract)	Cu(II)	4.5		2.9600	12.58	0.980	[108]
				7.5700	10.61	0.990	
	Zn(II)	6.5		4.9500	16.02	0.990	
				5.4500	6.67	0.990	
Phosphorylated orange waste	In(III) Ga(III) Cu(II) Pb(II) Fe(III) Zr(IV) As(III) As(V)	2	30	0.1220	81.22	0.990	[109]
				0.2712	49.01	0.990	
				0.0452	67.35	0.990	
				0.0367	251.05	0.990	
				0.1201	173.14	0.990	
				0.0361	113.11	0.990	
				0.0174	91.40	0.980	
				0.0358	73.42	0.990	
<i>Ficus religiosa</i> leaves	Cr(VI) Pb(II)	1 4	40 25	0.0120	26.25	0.996	[110]
				0.0220	37.45	0.972	
Birch wood <i>Betula</i> sp.	Cu(II)	5.5	22 ± 1	0.2000	4.90	>0.997	[111]
Brown alga <i>Fucus vesiculosus</i>				1.1000	23.40	>0.997	
Terrestrial moss <i>Pleurozium schreberi</i>				1.1500	11.10	>0.997	
<i>Cupriavidus taiwanensis</i> TJ208	Pb(II) Cu(II) Cd(II)	5 5 6	37	0.0211	50.10	0.956	[112]
				0.0363	19.00	0.887	
				0.0167	19.60	0.956	
<i>Mimosa pudica</i> inoculated with TJ208	Pb(II) Cu(II) Cd(II)	5 5 6		0.0383	485.00	0.988	
				0.0990	25.40	0.966	
				0.0307	42.90	0.982	
<i>Mimosa pudica</i> without inoculation	Pb(II) Cu(II) Cd(II)	5 5 6		0.0413	26.10	0.977	
				0.0614	22.70	0.923	
				0.0392	25.30	0.927	
Reed	Pb(II)	4.5	–	1.49×10^{-3}	17.1552	>0.990	[113]
Marine algae DP95Ca (<i>Durvillaea potatorum</i>)	Pb(II)	1 2 3 4 5	21 ± 0.2	0	4.18		[114]
				0.1252	158.99		
				4.3258	269.88		
				11.8159	307.54		
				23.7369	324.28		
	Cu(II)	1 2 3 4 5			0	2.54	
					0.0031	11.44	
					1.1457	62.90	
					1.7485	76.88	
					2.6251	82.60	
Marine algae ER95Ca (<i>Ecklonia adiate</i>)	Pb(II)	1 2 3 4 5		0.0425	10.46		
				0.4421	87.87		
				1.2413	207.12		
				1.7155	244.78		
				1.8584	263.60		
	Cu(II)	1 2 3 4 5			0.0976	4.45	
					0.0630	28.59	
					0.6295	60.36	
					1.2890	67.35	
					2.0696	70.53	
Ca-alginate based ion exchange resin	Pb(II)	4	25	0.8730	670.20	0.980	[115]
Rice husk (<i>tartaric acid modified</i>)	Cu(II)	5.2	27 ± 2	0.1000	29.00		[116]
			50 ± 2	0.0500	22.00		
			70 ± 2	0.0300	18.00		
	Pb(II)	5.3		27 ± 2	0.0900	108.00	
				50 ± 2	0.0200	105.00	
				70 ± 2	0.0100	96.00	
<i>Fucus vesiculosus</i>	Cr(III) Cr(VI)	4.5 2	21 ± 1	0.0362	62.91	0.980	[117]
				0.0339	42.63	0.980	
<i>Fucus spiralis</i>	Cr(III) Cr(VI)	4.5 2		0.0340	60.83	0.990	
				0.0283	35.35	0.970	

Table 2 (Continued)

Biosorbent	Solute	Operational condition		Langmuir parameters			Ref.
		pH	Temperature (°C)	K_L (L/mg)	q_{max} (mg/g)	R^2	
<i>Ulva lactuca</i>	Cr(III)	4.5		0.0381	36.91	0.940	
	Cr(VI)	2		0.0379	27.55	0.990	
<i>Ulva</i> spp.	Cr(III)	4.5		0.0265	53.03	0.990	
	Cr(VI)	2		0.0231	30.15	0.970	
<i>Palmaria palmata</i>	Cr(III)	4.5		0.0950	29.63	0.980	
	Cr(VI)	2		0.1662	33.79	0.860	
<i>Polysiphonia lanosa</i>	Cr(III)	4.5		0.0258	33.79	0.990	
	Cr(VI)	2		0.0469	45.75	0.940	
<i>Termitomyces clypeatus</i>	Cr(VI)	3	30		54.05	0.998	[118]
Activated sludge	Cd(II)	4	–	0.3200	28.10	0.990	[119]
	Cu(II)	4		0.1201	19.06	0.950	
	Ni(II)	5		0.1697	7.78	0.940	
	Pb(II)	4		0.1000	142.96	0.940	
	Zn(II)	6		0.6098	15.69	0.990	
Grape bagasse	Cd(II)	7	25 ± 1 °C	0.0527	53.84	0.995	[120]
	Pb(II)	3		0.0074	42.27	0.979	
<i>Pinus sylvestris</i> Linn	Cr(VI)	1	25	0.0450	238.10	0.979	[121]
			35	0.1165	263.16	0.981	
			45	0.2166	256.41	0.975	
<i>Pseudomonas veronii</i> 2E	Cd(II)	7.5	32	0.0526	54.00	0.970	[122]

surface sites and as such, it should logically be independent of temperature. This is opposing the real condition as a small to modest increase [2,25,33,47,54,59,63,67,69,80,81] and decrease [20,82–85] in saturation capacity with temperature is generally observed as exposed in Table 2. It is the expected case indeed, if the saturation limit is associated with the surface functional groups rather than a set of identical surface sites. In biosorption process, saturation limit of certain biomass is affected by several factors such as the number of sites in the biosorbent material, the accessibility of the sites, the chemical state of the sites (i.e., availability) and the affinity between the site and the metal (i.e., binding strength). In covalent metal binding case, supposing that an occupied site is theoretically available, the extent to which the site is to be dwelled upon by a given metal depends further on its binding strength and concentration in opposition to the metals already occupying the site.

The decrease of K_L value with temperature rise signifies the exothermicity of the adsorption process (physical adsorption) [20,82–85], while the opposite trend indicates that the process needs thermal energy (endothermic), leading to chemisorption [2,25,33,47,54,59,63,67,69,80,81]. In physical adsorption, the bonding between heavy metals and active sites of the biosorbent weakens at higher temperature in contrast with chemisorption bonding which becomes stronger. The exothermicity or endothermicity of the biosorption process can be determined via heat of adsorption. This thermodynamic property is commonly obtained through integrated Van't Hoff equation, which relates the Langmuir constant, K_L to the temperature

$$K_L = K_0 \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

Heats of adsorptions for several heavy metal-biosorbent systems are tabulated in Table 3.

2.3. Other two parameters isotherms

A particular model might be invalid in a particular situation, and in most cases, more than one model can explain the

biosorption mechanism. Several models initially developed for gas phase adsorption can be implemented to correlate heavy metals biosorption processes. Some of these equations contain two fitting parameters (Temkin isotherm, Flory–Huggins and Dubinin–Raduskevich equations), whereas others can have more than two parameters (Redlich–Paterson and Sips isotherms). Table 3 lists numerous biosorption experiments correlated by these equations.

2.3.1. Temkin Isotherm

At first, Temkin equation was proposed to describe adsorption of hydrogen on platinum electrodes within acidic solutions. The derivation of the Temkin isotherm is based on the assumption that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic, as implied in the Freundlich equation

Table 3
Heat of adsorption obtained from Langmuir parameter (K_L)

Biosorbent	Heavy metal	E_a (kJ/mol)	Reference
<i>Aspergillus niger</i>	Cu(II)	28.90	[2]
	Pb(II)	38.30	
Coconut copra meal	Cd(II)	–13.70	[20]
	Ni(II)	17.07	[25]
	Zn(II)	23.93	[33]
<i>Cladophora fascicularis</i>	Cu(II)	39.00	[47]
	Pb(II)	29.60	
Trembling poplar forest	Cu(II)	25.18	[59]
Shells of lentil	Cu(II)	15.37	[63]
		18.79	
		10.05	
<i>Spyrogira</i> sp.	Pb(II)	4.00	[67]
	Pb(II)	–3.04	[69]
Baker's yeast	Ni(II)	30.72	[82]
Cedar sawdust	Cu(II)	–9.70	[83]
<i>Caladium bicolor</i>	Pb(II)	–16.14	[84]
	Cd(II)	–7.80	

[15,57]. Temkin isotherm has the form

$$q_e = \frac{RT}{b} \ln(aC_e) \quad (9)$$

Several experimental studies in chemisorption systems are correlated using this equation [15,57,59,86,87]. Basha et al. [15] conducted the biosorption of Hg(II) from aqueous solution onto *Carica papaya*. On the purpose of predicting the biosorption isotherms and determining the characteristic parameters for process design, they tried several models intended for gas phase use, of which Temkin isotherm was among them. They concluded that this model was not suitable for the prediction of their experimental data. For several systems such as biosorption of Ni(II) by ureolytic mixed culture [57] and *Sargassum wightii* [86], biosorption of Cu(II) using trembling poplar forest [59] and biosorption of Cr(VI) by *Lyngbya putealis* exopolysaccharides [87], Temkin isotherm are incapable to well-predict the biosorption equilibria.

It is apparent that Temkin equation is superior in the prediction of gas phase equilibria. Conversely, in liquid phase adsorption especially in heavy metals adsorption using biosorbent, this model fall-shorts in representing the equilibria data. Adsorption in the liquid phase is a more complex phenomenon than gas phase adsorption as the adsorbed molecules in here do not necessarily organized in a tightly packed structure with identical orientation. Further on, the presence of solvent molecules and formation of micelles from adsorbed molecules add to the complexity of liquid phase adsorption. Numerous factors including pH, solubility of adsorbate in the solvent, temperature and surface chemistry of the adsorbent influence the adsorption from liquid phase. Since the basis of derivation for Temkin equation are a simple assumption, the complex phenomenon involved in liquid phase adsorption are not taken into account by this equation. As a result, this equation is often not suitable for representation of experimental data in complex systems.

2.3.2. Dubinin–Radushkevich equation

Dubinin and his co-workers conceived this equation for sub-critical vapors in micropore solids where the adsorption process follows a pore filling mechanism onto energetically non-uniform surface. The Dubinin–Radushkevich (DR) equation is excellent for interpreting organic compounds sorption equilibria (in gas phase condition) in porous solids. DR equation is rarely applied onto liquid-phase adsorption due to the complexities associated with other factors such as pH and ionic equilibria inherent in these systems. Additionally, the solute-solvent interactions often render the bulk solution non-ideal. The mathematical expression for DR equation in the liquid phase system is

$$q_e = q_{\max} \exp \left(- \left(\frac{RT \ln(C_e/C_s)}{\beta E_0} \right)^2 \right) \quad (10)$$

By taking into account the energetically non-uniform surface, this equation is capable of describing the biosorption data well [73,75,86–88]. Still, an exceptional failure case happens for biosorption of Hg(II) from aqueous solution onto *C. papaya* [15]. Within DR equation, the characteristic energy can also be obtained as a parameter. As-summarized biosorption processes in this paper have mean characteristic energies (obtained from the DR model) in the range of 1–16 kJ/mol, signifying that a physical electrostatic force was potentially involved in the sorption process [73,75,86–88].

One of the best feature of the DR equation lies on the fact that it is temperature-dependent. If the adsorption data at different temperatures are plotted as the logarithm of the amount adsorbed versus the square of potential energy, all the suitable data shall in general lie on the same curve, called as the characteristic curve. This

curve can later be utilized as an initial “tool” to measure the applicability of the DR equation in expressing the adsorption equilibria data. In the case that the fitting procedure gives high correlation values but the characteristic curve obtained from analyzed data do not lie in the same curve, the validity of the ascertained parameters are still questionable. To that end, however the characteristic curve of biosorption systems cannot be examined since all of the experiments were conducted in one temperature [73,75,86–88].

2.3.3. Flory–Huggins isotherm

The Flory–Huggins (FH) isotherm is chosen on occasion to account for the surface coverage characteristic degree of the sorbate on the sorbent [86]. The FH isotherm has the form

$$\log \frac{\theta}{C_0} = \log K_{FH} + n_{FH} \log(1 - \theta) \quad (11)$$

$$\theta = 1 - \frac{C_e}{C_0} \quad (12)$$

Vijayaraghavan et al. [86] along with Kiran and Kaushik [87] used this isotherm to correlate their biosorption experimental data. In the biosorption of nickel(II) ion on *Sargassum wightii*, Vijayaraghavan et al. [86] observed that both FH constants (K_{FH} and n_{FH}) increased with pH rose and reached their corresponding maximum values at pH 4.0. They also made use of the obtained FH constant, K_{FH} to compute the Gibbs free energy of spontaneity, ΔG° . A negative value of ΔG° denotes the feasibility of the process and the spontaneous nature of nickel(II) biosorption onto *S. wightii*. Accordingly, Kiran and Kaushik [87] also reported a negative value of ΔG° as obtained from the biosorption of Cr(VI) onto exopolysaccharides (Table 2).

Although the FH isotherm is intended mainly for applications that require the accountability in the degree of surface coverage characteristic of the sorbate on the sorbent, these authors do not mention this aspect [86,87]. To complement the gap and highlight the surface coverage value, a study by Hanif et al. [6] can be referred upon which they related the surface coverage with Langmuir equation. In this study the fraction of biomass surface covered by metal ion was determined by plotting the surface coverage values (θ) against Ni(II) concentration. They perceived that the increase in initial metal ion concentration for *C. fistula* biomass enhances the surface coverage on the biomass until the surface is nearly full-covered with a monomolecular layer. Then again, at higher level of Ni(II) concentration, the surface coverage ceases to vary significantly with concentration as the reaction rate becomes independent of the Ni(II) concentration.

2.3.4. Halsey isotherm

Halsey proposed an expression for condensation of a multilayer at a relatively large distance from the surface

$$q_e = \left(\frac{K_H}{C_e} \right)^{1/n_H} \quad (13)$$

This equation is mainly employed for the adsorption of moisture in various kinds of polymers (natural or hydrocarbon base). Halsey isotherm is not too popular for the prediction of heavy metals adsorption equilibria in biosorbent. A report by Basha et al. [15] recommended the applicability of this model for correlating the biosorption of Hg(II) on *C. papaya*. Yet, further investigation is warranted before the multilayer sorption of Hg(II) on *C. papaya* can be confidently represented by this isotherm.

2.3.5. Brunauer–Emmer–Teller (BET) model

Previously, in the Langmuir model, it was assumed that adsorption only occurs on the unoccupied adsorption sites. In BET model, this restriction is removed. Supposing that the initial adsorbed layer

can act as a substrate for further adsorption; then the isotherm, instead of leveling off to some saturated value at high concentrations is able to rise indefinitely. The same kinetics concept proposed by Langmuir is applied to this multiple layering process, that is the rate of adsorption on any layer is equal to the rate of desorption from that layer. The simplified form of BET equation can be written in the following form

$$q_e = q_{\max} \frac{BC_e}{(C_e - C_s^*)[1 + (B - 1)(C_e/C_s^*)]} \quad (14)$$

Kiran and Kaushik [87] showed a superb applicability example of this model for Cr(VI) biosorption using *Lyngbya putealis* exopolysaccharides. They claimed that multilayer adsorption occurred in this system. However, to verify this case further investigations are necessary. A simple curve fitting procedure and high value of correlation is not valid enough to justify the occurrence of multilayer adsorption. As a note, other ideal assumptions within this model namely all sites are energetically identical along with no horizontal interaction between adsorbed molecules may be correct for heterogeneous material and simple non-polar gases but not for complex systems involving heterogeneous adsorbent such as biosorbents and metals. For that reason, this equation is unpopular in the interpretation of liquid phase adsorption data for complex solids.

2.4. Three parameters isotherms

Not much compensation is gained by using a more-complex model if a two-parameter model as described above can fit the data reasonably well. Still, in some cases, the available two parameters models are not competent enough to correlate the equilibria data; therefore more than two parameters models are still required. In here, several three parameters isotherms in-use for the prediction of biosorption experimental data are provided [2,7,15,20,68,69,82,86–89].

2.4.1. Sips isotherm

To circumvent the problem of continuing increase in the adsorbed amount with a rising concentration as observed for Freundlich model; an expression was proposed by Sips in 1948 which has a similar form to the Freundlich isotherm, differs only on the finite limit of adsorbed amount at sufficiently high concentration.

$$q_e = q_{\max} \frac{(K_S C_e)^\gamma}{1 + (K_S C_e)^\gamma} \quad (15)$$

Eq. (15) has similar form to Langmuir equation. The distinctive feature between Eqs. (15) and (3) is the presence of additional parameter, γ in Eq. (15). If this parameter is unity, Eq. (15) resembles Eq. (3). The parameter γ is regarded as the parameter characterizing the system's heterogeneity. Moreover, the heterogeneity could stem from the biosorbent or the heavy metal, or a combination of both.

Sips isotherm provides a reasonably accurate prediction of heavy metal biosorption experimental results with high value of coefficient correlation (R^2) [15,86,88,89]. As a rule, all of the Sips parameters q_{\max} , K_S and γ were governed by operating conditions such as pH, temperature, etc. In the adsorption of Cu(II), Cd(II), and Pb(II) on *Caulerpa lentillifera*, the parameter γ stays close to unity [88]. Within this system, the biosorption of heavy metal ions on *C. lentillifera* took place at the functional groups/binding sites on the surface of the alga, i.e., one mole of metal ion per mole of binding site. So, in this case the use of Langmuir isotherm is considered more appropriate.

Another example, the application of Sips model to the Pb(II) biosorption isotherm data leads to better correlation coefficients and the model suits the data well at all conditions examined [89].

Sips model constant, K_S was maximum at the optimum condition (4.0 and 30 °C), whereas the other two constants were lowest. Various thermodynamic parameters such as ΔG° , ΔH° and ΔS° were also obtained, of which their values indicate that the process was spontaneous and endothermic.

2.4.2. Toth equation

Freundlich and Sips equations have their limitations. Freundlich equation is inapplicable at low and high-end boundary of the concentration while the Sips equation is invalid at the low-end as both forms are not being reduced into the correct Henry law type in the low concentration limit. Another empirical equation that is popularly used and satisfies the two end limits is the Toth equation. This isotherm was derived from the potential theory. Toth equation has been proved as a valuable tool in describing sorption for heterogeneous systems. It assumes an asymmetrical quasi-Gaussian energy distribution with its left-hand side form widened, i.e., most sites have sorption energy less than the mean value [86].

$$q_e = q_{\max} \frac{b_T C_e}{(1 + (b_T C_e)^{1/n_T})^{1/n_T}} \quad (16)$$

Toth equation possesses the correct Henry law type limit besides a parameter to describe the heterogeneities of the system. However, this equation is still unable to predict the isotherm in a particular heterogeneous system as illustrated in the biosorption of Hg(II) into *C. papaya* [15]. On the other hand, in biosorption of nickel(II) ions onto *Sargassum wightii*, Toth equation offers the best model for nickel biosorption data at all pH conditions examined.

2.4.3. Redlich–Paterson isotherm

Redlich–Paterson is another empirical equation, designated as the “three parameter equation,” which is capable to represent adsorption equilibria over a wide concentration range. This equation has the following form

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta} \quad (17)$$

Eq. (17) reduces to a linear isotherm at low surface coverage and to the Langmuir isotherm when β is equal 1.

As shown in Table 4, this equation is quite popular for the prediction of heavy metals biosorption equilibria data [2,7,15,20,69,82,86]. This model fits the experimental data accurately in several systems, namely biosorption of chromium using suspended and immobilized cells of *Rhizopus arrhizus* [7], biosorption of cadmium on coconut copra meal [20], sorption of lead(II) onto peat [69] as well as biosorption of nickel(II) ions by baker's yeast [82].

Redlich and Paterson incorporated the characteristics of Langmuir and Freundlich isotherms into a single equation. Two limiting behaviors exist, i.e., Langmuir form for β equal 1 and Henry's law form for β equal 0. It is worth noting that the β values in most biosorption cases are close to unity as happening in biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger* [2], biosorption of Hg(II) from aqueous solutions onto *C. papaya* [15] and biosorption of nickel(II) ions onto *Sargassum wightii* [86]. This means that the data can preferably be fitted with the Langmuir model.

Table 5 sums up various isotherm equations utilized for correlation of heavy metals biosorption data. A particular model might be inapplicable in a certain situation, while in some cases more than one model can explain the biosorption mechanism.

2.4.4. Multicomponent heavy metals biosorption

Majority of the studies on biosorption of heavy metal ions by diverse kinds of biosorbents have focused on the single metal

Table 4
Other models for correlation of biosorption experimental data

Biosorbent	Solute	Others models	Reference
<i>Aspergillus niger</i>	Cu(II) Pb(II)	Redlich–Paterson model	[2]
<i>Rhizopus arrhizus</i>	Cr(VI)	Redlich–Paterson model	[7]
Palm Tree Leaves	Zn(II)	Gin Sips	[13]
<i>Carica papaya</i>	Hg(II)	Henry Dubinin–Radushkevich Temkin Halsey Gin Redlich–Paterson Sips Khan Radke–Prausnitz Toth Koble–Carrigan Fritz–Schluender	[15]
Coconut copra meal	Cd(II)	Redlich–Paterson model	[20]
Tea factory waste	Cr(VI)	Thomas model	[26]
Living and non-living ureolytic mixed culture	Ni(II)	Temkin	[57]
Litter of poplar forests	Cu(II)	Temkin	[59]
Marine brown algae <i>Laminaria japonica</i> (modified with epichlorohydrin potassium permanganate)	Pb(II)	Langmuir–Freundlich	[68]
Peat	Pb(II)	Redlich–Paterson	[69]
Maize husk (unmodified and EDTA modified)	Cd(II) Pb(II) Zn(II)	Dubinin–Radushkevich	[73]
Immobilized <i>Saccharomyces cerevisiae</i>	Pb(II)	Dubinin–Radushkevich	[75]
<i>Bacillus thuringiensis</i> (vegetative cell and spore-crystal mixture)	Ni(II)	Scatchard analysis	[78]
<i>Gelidium</i> Algal waste	Cu(II)	Langmuir–Freundlich	[81]
Baker's yeast	Ni(II)	Redlich–Paterson	[82]
<i>Sargassum wightii</i>	Ni(II)	Temkin Dubinin–Radushkevich Flory–Huggins Redlich–Paterson Sips Khan Radke–Prausnitz Toth	[86]
<i>Lyngbya putealis</i> exopolysaccharides	Cr(VI)	Temkin Flory–Huggins Dubinin–Radushkevich BET	[87]
<i>Caulerpa lentillifera</i>	Cu(II) Cd(II) Pb(II)	Sips Dubinin–Radushkevich	[88]
Brown seaweeds (<i>Turbinaria conoides</i>)	Pb(II)	Sips	[89]
<i>Gelidium</i> Algal waste	Cr(III) Ct(II)	Sips	[97]
<i>Azadirachta indica</i> bark	Zn(II)	Redlich–Paterson	[103]

uptake. In contrast to this ideal condition, various types of metals present in wastewater. Another discouraging fact, the equilibrium modeling of multi-metal biosorption, which is essential in the design of treatment systems, was often neglected. In the practice, examination of the effects of binary metal ions in various combinations is deemed to be more representative than the single-metal studies [12].

One of the major concerns arising from the adsorption of heavy metals from wastewater is the simultaneous presence of miscellaneous metals in wastewater. The interference and competition between different metals, metals and solvents as well as metals

and adsorption site are significant enough to be taken into account, leading to a more complex mathematical formulation of the equilibrium.

Given the adsorption of heavy metals in real system involving more than one component, adsorption equilibria engaging competition between molecules of different types is warranted for better understanding of the system and design purposes. In contrast, only a few isotherms were developed to describe equilibrium in such systems. These models range from simple equations associated with the individual isotherm parameters only (non-modified adsorption models) to more

Table 5
Summary of widely used isotherms for biosorption systems

Isotherm	Functional form	Advantages	Disadvantages
Freundlich	$q_e = K_F C_e^{1/n}$	Simple expression and has parameter for surface heterogeneity	Does not have Henry law and no saturation limit, not structured, not applicable over wide range of concentration
Langmuir	$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e}$	Has Henry law and finite saturation limit so valid over a wide range of concentration	Based on monolayer assumption
Temkin	$q_e = \frac{RT}{b} \ln(a C_e)$	Simple expression	Same as Freundlich. It does not have correct Henry law limit and finite saturation limit, not applicable over wide range of concentration
Dubinin–Radushkevich	$q_e = q_{\max} \exp \left(- \left(\frac{RT \ln(C_e/C_s)}{\beta E_0} \right)^2 \right)$	Temperature dependent	Violate thermodynamic principle at zero loading or very low concentration
Flory–Huggins	$\log \frac{\theta}{C_0} = \log K_{FH} + \eta_{FH} \log(1 - \theta)$	Based on thermodynamic approach, include non-ideality of system	-
Halsey	$q_e = \left(\frac{K_H}{C_e} \right)^{1/n_H}$	Calculate multisorption energy layer	-
Brunauer, Emmett and Teller (BET)	$q_e = q_{\max} \frac{B C_e}{(K_S C_e) [1 + (B-1)(C_e/C_s)]}$	Multilayer adsorption	Only valid at moderate concentration
Sips	$q_e = q_{\max} \frac{(K_S C_e)^B}{(1 + K_S C_e)^B}$	Has finite saturation limit	Does not have Henry law limit
Toth	$q_e = q_{\max} \frac{K_S C_e}{(1 + (b_T C_e)^{1/n_T})^{1/n_T}}$	Has Henry law limit and finite saturation capacity	-
Redlich–Paterson	$q_e = \frac{K_{SP} C_e}{1 + a_{SP} C_e^b}$	-	No significant advantage

complex models exploiting the individual isotherm parameters along with correction factors (modified adsorption models) [12].

In frequent use multi-component adsorption models are multicomponent Langmuir model including its modification as well as multicomponent Freundlich model. Multicomponent Langmuir model is expressed in the following form

$$q_{e,i} = q_{\max,i} \frac{K_{L,i} C_{e,i}}{1 + \sum_{j=1}^N K_{L,j} C_{e,j}} \quad (18)$$

If lateral interaction parameter, η_i which is a characteristic constant of each species (also depends on the concentrations of the other components) is introduced [12], Eq. (18) can be re-written as

$$q_{e,i} = q_{\max,i} \frac{K_{L,i} (C_{e,i}/\eta_i)}{1 + \sum_{j=1}^N K_{L,j} (C_{e,j}/\eta_j)} \quad (19)$$

And multicomponent Freundlich model [12] (only for binary component)

$$q_{e,1} = \frac{K_{F,1} C_{e,1}^{1/n_1+x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{x_2}} \quad (20)$$

$$q_{e,2} = \frac{K_{F,2} C_{e,2}^{1/n_2+x_2}}{C_{e,2}^{x_2} + y_1 C_{e,1}^{x_1}} \quad (21)$$

Aksu et al. [12] utilized Eqs. (18)–(21) to describe simultaneous biosorption of Cr(VI) and Ni(II) onto dried activated sludge. They noticed that the co-ion effect on the equilibrium uptake became more significant as their concentration in solution is increased along with the pH rise for Cr(VI) and (pH) reduction for Ni(II). In their study, multicomponent Freundlich model with parameters acquired through non-linear regression can well-fit the experimental results at different initial mixture concentration range and pH values [12].

Other studies of binary adsorption of heavy metals on biosorbents were carried out by Cay et al. [16] and Aksu and Donmez [90]. Cay et al. [16] examined single and binary component adsorption of Cu(II) and Cd(II) from aqueous solutions using tea-industry waste. Equilibrium uptake of cadmium(II) and nickel(II) is improved by incrementing its initial metal ion concentration up to 150 mg/L. In contrast, the presence of increasing concentrations of other metal ions brought about the deterioration in equilibrium uptake value [16]. In turn, binary biosorption of Cd(II) and Ni(II) onto dried *Chlorella vulgaris* was investigated by Aksu and Donmez [90]. Biosorption data in their binary systems showed that the adsorbed amount of one metal declines as the concentration of other competitive metal in the solution increases. The consequence is quite substantial for Ni(II) biosorption as the sorption process is strongly suppressed in the presence of higher Cd(II) concentration in solution.

3. Kinetic studies in biosorption of heavy metals using various kinds of biosorbents

Adsorption equilibria studies are important to determine the efficacy of adsorption. In spite of this, it is also necessary to identify the adsorption mechanism type in a given system. On the purpose of investigating the mechanism of biosorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been exploited to test the experimental data. In addition, information on the kinetics of metal uptake is required to select the optimum condition for full-scale batch metal removal processes.

Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution

interface. In practice, kinetic studies were carried out in batch reactions using various initial sorbate concentrations, sorbent doses, particle sizes, agitation speeds, pH values and temperatures along with different sorbent and sorbate types. Then, linear regression was used to determine the best-fitting kinetic rate equation. As an additional step, linear least-squares method can also be applied to the linearly transformed kinetic rate equations for confirming the experimental data and kinetic rate equations using coefficients of determination [18].

Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. These include pseudo-first and -second-order rate model, Weber and Morris sorption kinetic model, Adam-Bohart-Thomas relation [83], first-order reversible reaction model [91], external mass transfer model [88], first-order equation of Bhattacharya and Venkobachar [92], Elovich's model and Ritchie's equation. The pseudo-first and -second-order kinetic models are the most well-liked model to study the biosorption kinetics of heavy metals and quantify the extent of uptake in biosorption kinetics. Table 6 encapsulates some kinetic studies of heavy metals biosorption using various kinds of biosorbents. As-acquired parameter values for pseudo-first and -second-order kinetics are also included in this table.

A comprehensive review about the employment of second-order models for adsorption system is available and can be referred upon by interested readers [93]. This summary report provides different second-order models for dissimilar type of adsorption systems. By acknowledging its presence, this section is thus focusing on the kinetic modeling of heavy metals biosorption system.

3.1. The pseudo-first-order kinetic

The Lagergren first-order rate expression based on solid capacity is generally expressed as follows

$$\frac{dq}{dt} = k_1(q_e - q) \quad (22)$$

Integration of Eq. (22) with the boundary conditions as follow: $t = 0$, $q = 0$, and at $t = t$, $q = q$, gives

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (23)$$

Eq. (23) can be written in the non-linear form

$$q = q_e(1 - \exp(-k_1 t)) \quad (24)$$

Hypothetically, to ascertain the rate constants and equilibrium metal uptake, the straight-line plots of $\log(q_e - q)$ against t of Eq. (23) were made at different initial metal concentrations [94]. The q_e value acquired by this method is then contrasted with the experimental value. If large discrepancies are posed, the reaction cannot be classified as first-order although this plot has high correlation coefficient from the fitting process. Non-linear procedure fitting of Eq. (24) is another way to achieve the predicted value of q_e and k_1 , although this is not a common exercise.

Kinetic adsorptions by numerous biological materials have been studied using Eqs. (22)–(24) [6,7,9,21,25,29,40,42,44,48,50–52,54,56,57,59,63,65,67,72,81–83,88,91,95–100]. As-fitted rate constants, predicted equilibrium uptakes along with the corresponding correlation coefficients for all as-summarized biosorption studies are listed in Table 6. Disagreement occurs for most systems, at which as-calculated q_e are not equal to the experimental q_e , further indicating the inability of pseudo-first-order model to fit the kinetic heavy metal biosorption data. The trend shows that the predicted q_e values seem to be lower than the experimental values. A time lag, probably caused by the presence of boundary layer or external resistance controlling at the beginning

of the sorption process was argued to be the responsible factor behind the discrepancy [9].

3.2. The pseudo-second-order kinetic

Predicting the rate of adsorption for a given system is among the most important factors in adsorption system design, as the system's kinetics determine adsorbate residence time and the reactor dimensions [93]. As previously noted that although various factors govern the adsorption capacity, i.e., initial heavy metals concentration, temperature, pH of solution, biosorbent particle size, heavy metals nature, a kinetic model is only concerned with the effect of observable parameters on the overall rate [18].

Pseudo-second order model is derived on the basis of the sorption capacity of the solid phase, expressed as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (25)$$

Integration of Eq. (25) with the boundary conditions $t = 0$, $q = 0$, and at $t = t$, $q = q$, results in

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \quad (26)$$

Eq. (26) can be stated in the linear form as

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (27)$$

The pseudo-second-order rate constants were determined experimentally by plotting t/q against t . Ho [18] conducted an evaluation using linear and non-linear methods to determine the pseudo-second-order kinetic parameters. He chose cadmium as the heavy metal and tree fern as the biosorbent. As-acquired kinetic parameters from four kinetic linear equations using linear method have discrepancies among themselves. Further, for linear method, pseudo-second-order model as written in Eq. (27) has the highest coefficient of determination. In contrast to linear model, the resulting kinetic parameters from non-linear model were almost identical among each other. To that end, the non-linear method is considered a better way to ascertain the desired parameters. Still, most of the biosorption studies in the literatures utilize Eq. (27).

A number of experiments fitted using pseudo-second-order model are given in Table 6. In most systems, the correlation coefficients were higher than 0.98. Moreover, the calculated q_e values agreed very well with the experimental data. As such, in comparison to pseudo-first-order kinetic this model is considered more appropriate to represent the kinetic data in biosorption systems. This tendency comes as an indication that the rate limiting step in biosorption of heavy metals are chemisorption involving valence forces through the sharing or exchange of electrons between sorbent and sorbate [10,11,21,27,47,50,56,59,64,66,79,96,98,100–102], complexation, coordination and/or chelation [23,40,66]. Yet, it is too early to arrive at the conclusion as a good fitting model does not necessarily illustrate the real nature of the rate-limiting step [52]. In other biosorption cases, diffusion as opposed to the chemical reaction can also be the rate-limiting step [43,72,95].

The variation of the rate controlling/limiting steps during biosorption process was identified by Djerebi and Hamdaoui [83]. In biosorption of copper(II) using cedar sawdust [83], two control mechanisms were observed. In their study, the film diffusion process controlled the early stage of biosorption process while in the later stage, chemical reaction become the limiting mechanism. The diffusion coefficient value of copper ions was $6.31 \times 10^{-11} \text{ cm}^2/\text{s}$. Similar mechanism was also observed by Villar et al. [97]. They found that both film diffusion and chemical reaction were the rate

Table 6
Kinetic studies on heavy metals biosorption

Biosorbent	Solute	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order			Pseudo-second order			Reference
				q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g/(mg min))	R ²	
<i>Cassia fistula</i> (Golden Shower)	Ni(II)	Leaves	145.29	34.64	6.51 × 10 ⁻⁴	0.916	135.13	4.29 × 10 ⁻⁴	0.999	[6]
		Stem bark	148.40	54.10	3.90 × 10 ⁻⁴	0.882	140.84	1.67 × 10 ⁻⁴	0.996	
		Pods bark	188.40	78.90	2.60 × 10 ⁻⁴	0.899	169.49	8.14 × 10 ⁻⁴	0.982	
<i>Rhizopus arrhizus</i>	Cr(VI)	50	9.60	5.38	0.0020	0.872	9.48	0.0020	0.989	[7]
		100	17.00	8.52	0.0020	0.821	16.81	0.0009	0.994	
		150	24.00	13.55	0.0030	0.942	24.45	0.0007	0.996	
		200	25.00	14.89	0.0040	0.980	25.97	0.0006	0.999	
Crab shell particles	Cu(II)	500	75.40	36.80	0.0340	0.920	75.80	0.0035	0.999	[9]
		1000	147.90	100.90	0.0380	0.958	149.30	0.0012	0.999	
		1500	181.40	130.90	0.0300	0.946	185.20	0.0006	0.999	
		2000	197.70	162.20	0.0310	0.991	200.00	0.0005	0.998	
	Co(II)	500	72.30	50.30	0.0330	0.895	72.90	0.0017	0.999	
		1000	131.70	93.40	0.0320	0.950	133.30	0.0009	0.999	
		1500	205.50	122.00	0.0330	0.935	208.30	0.0008	0.999	
		2000	259.40	162.50	0.0230	0.923	263.20	0.0004	0.999	
Dried activated sludge	Cd(II)	20	9.50			9.80	0.0157	0.995	[10]	
		50	25.90			26.40	0.0151	0.997		
		100	60.70			61.30	0.0053	0.983		
	Pb(II)	20	14.10			13.80	0.0113	0.994		
		50	38.90			39.40	0.0119	0.991		
		100	82.80			83.50	0.0062	0.993		
<i>Tamarindus indica</i> seeds	Cr(VI)	10		–	0.0767			[11]		
Palm Tree Leaves	Zn(II)	100	12.65			12.70	0.0460	0.999	[13]	
Tea waste	Cu(II)	200	18.00			19.00	0.0133	0.999	[14]	
		100	13.00			14.00	0.0170	1.000		
		50	8.00			8.00	0.0427	0.999		
		25	4.00			4.00	0.1268	0.999		
	Pb(II)	200	34.00			35.00	0.0091	0.999		
		100	19.00			19.00	0.0283	0.999		
		50	10.00			10.00	0.0586	0.999		
Wool	Cr(VI)	100			0.0396				[17]	
Olive cake				0.0090						
Sawdust				0.0090						
Pine needles				0.0001						
Almond				0.0088						
Coal				0.0074						
Cactus				0.0068						
Tree fern	Cd(II)					12.00	0.1070	0.934	[18]	
Palm kernel fiber	Pb(II)	120				23.80	0.4400	1.000	[19]	
<i>Rose (Rosa centifolia)</i> waste	Pb(II) at 303 K		47.77	72.26	0.3200	0.986	51.02	0.0080	0.999	[21]
		at 313 K	11.30	3.09	0.0700	0.830	13.75	0.0096	0.954	
		at 323 K	3.22	1.51	0.3200	0.925	3.97	0.0330	0.950	
		at 333 K	2.86	2.87	0.1900	0.859	3.35	0.0510	0.962	
	Co(II) at 303 K		36.37	64.46	0.9700	0.902	49.75	0.0008	0.941	
		at 313 K	6.79	4.95	0.0100	0.849	8.14	0.0056	0.940	
		at 323 K	5.37	2.87	0.0090	0.944	5.69	0.0170	0.952	
		at 333 K	4.50	1.50	0.1700	0.935	4.68	0.0391	0.990	

Table 6 (Continued)

Biosorbent	Solute	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order			Pseudo-second order			Reference
				q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g/(mg min))	R ²	
Spent-grain	Cu(II)	100	7.03	6.38	0.0230	0.928	7.38	0.0073	0.995	[23]
Coconut copra meal	Cd(II)	30					1.21	0.6300	1.000	[27]
		60					1.38	0.3890	1.000	
		90					1.62	0.3050	1.000	
		120					1.70	0.2590	1.000	
		140					1.84	0.1910	1.000	
Green coconut shell powder	Cd(II)	80	17.68	4.59	13.35 × 10 ⁻³	0.318	15.31	10.15 × 10 ⁻³	0.999	[29]
CTFS: crude tamarind fruit shells	Cr(VI)	50			0.0140					[30]
		100			0.0140					
		150			0.0140					
		200			0.0140					
H-TS: HCl treated shells		50			0.0310					
		100			0.0310					
		150			0.0310					
		200			0.0310					
O-TS: oxalic acid treated shells		50			0.0370					
		100			0.0370					
		150			0.0360					
		200			0.0370					
Rice bran	Zn(II)	–	–	–	45.4000	0.980	–	3.8300	0.998	[33]
Waste weed, <i>Salvinia cucullata</i>	Cr(VI)	400			0.0055	0.918		0.000496	0.996	[40]
		450			0.0074	0.954		0.000544	0.995	
		500			0.0053	0.894		0.000463	0.996	
		550			0.0053	0.912		0.000425	0.996	
		600			0.0048	0.919		0.000394	0.995	
		650			0.0050	0.933		0.000393	0.993	
		700			0.0055	0.936		0.000424	0.994	
Fresh and spent <i>Spirulina platensis</i> and <i>Chlorella vulgaris</i>	Cr(VI)				0.0004					[42]
Calcium alginate,(CA)	Ni(II)	100			0.0240	0.986		0.0012	0.988	[44]
		250			0.0400	0.987		0.0028	0.995	
		500			0.0520	0.991		0.0019	0.996	
Chitosan coated calcium alginate (CCCA)		100			0.0330	0.987		0.0004	0.999	
		250			0.0340	0.983		0.0005	0.997	
		500			0.0380	0.997		0.0004	0.997	
Chitosan coated silica (CCS)		100			0.0200	0.991		0.0002	0.997	
		250			0.0250	0.994		0.0003	0.996	
		500			0.0300	0.985		0.0002	0.996	
<i>Eichhornia crassipes</i>	Cr(VI)	10					2.53	5.7134		[46]
		20					4.74	1.2660		
		30					6.99	0.5500		
Non-living green algae <i>Cladophora fascicularis</i>	Cu(II),	63.54					35.58	0.0054	0.999	[47]
		127.08					67.35	0.0022	0.999	
		254.16					72.44	0.0013	0.998	
	Pb(II)	207.2					145.04	0.0012	0.999	
		414.4					190.62	0.0010	0.999	
		828.8					203.06	0.0009	0.998	

Table 6 (Continued)

Biosorbent	Solute	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order			Pseudo-second order			Reference	
				q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g/(mg min))	R ²		
The waste distillery sludge from sugar-cane industry											
Untreated	Pb(II)	100	37.76	4.29	0.0085	0.745	38.02	0.0073	0.999	[48]	
Autoclaved			40.23	4.15	0.0060	0.794	40.49	0.0065	0.999		
HCl			49.82	4.59	0.0069	0.688	50.25	0.0063	0.999		
NaOH			51.29	12.13	0.0014	0.963	52.35	0.0032	0.999		
HCHO			49.56	12.84	0.0018	0.957	50.76	0.0033	0.999		
SDS			40.87	8.92	0.0011	0.936	41.67	0.0036	0.999		
Sour orange residue (SOR)	Cu(II)	150					13.72	0.2520		[49]	
Loofa sponge immobilized biomass of <i>Chlorella sorokiniana</i> (LSIBCS),	Cr(III)	25	19.59	4.23	-0.0580	0.880	19.71	0.0660	1.000	[50]	
Free biomass of <i>C. sorokiniana</i> (FBCS)			23.15	2.47	-0.0550	0.950	23.17	0.1520	1.000		
Hydrophobic bacteria strain, <i>Rhodococcus opacus</i>	Cr(III)	10		14.27	0.0039	0.612	10.09	0.0128	0.993	[51]	
Pectin-rich fruit wastes (e.g. citrus peel)	Cd(II)	45	29.80	23.05	0.0430	0.950	33.17	0.0030	0.990	[52]	
Brown seaweed	Cu(II)		4.10	0.29	0.0209	0.989	0.03	0.1180	1.000	[54]	
Surfactant modified coconut coir pith	Cr(VI)	20	18.02	14.78	0.1720	0.994	20.24	0.0150	0.999	[56]	
		40	34.05	13.49	0.0550	0.969	34.97	0.0080	0.999		
		60	45.48	21.03	0.0440	0.963	46.08	0.0050	0.999		
		80	54.42	26.22	0.0440	0.925	55.25	0.0040	0.998		
		100	65.21	34.33	0.0450	0.971	67.57	0.0030	0.998		
Living ureolytic mixed culture	Ni(II)	83.20	16.81		0.0358	0.930		0.0300	0.031	[57]	
Non-living ureolytic mixed culture		86.50	13.50		0.0778	0.900	13.72	0.0730	0.984		
Vegetal biomass (olive pits)	Cd(II)		8.05	0.0078		^a				[58]	
Litter of poplar forest	Cu(II)	200		3.12	0.2750	0.886	25.91	0.2400	1.000	[59]	
			Live <i>Spirulina</i>		259.00			345.00	0.0004		
				435.00			435.00	0.0004			
		601.00				714.00	0.0002		[60]		
Dead <i>Spirulina</i>			35.00				26.00	0.0013			
			183.00				182.00	0.0006			
			313.00				333.00	0.0002			
Cystine-modified biomass	Cd(II)	5	4.98				4.99	51.4700	0.998	[61]	
		15	10.10				10.12	19.5200	0.997		
		20	11.26				11.43	16.7100	0.999		
	Pb(II)	30	29.95				30.21	126.5800	0.999		
		58	42.01				42.55	121.9500	0.998		
		80	43.48				43.86	123.4600	0.999		
Pretreated <i>Aspergillus niger</i>	Cu(II)						0.0210	0.999	[62]		
Lentil shell (LS)	Cu(II)	100		4.45	0.0160	0.993	7.96	0.0043	0.997	[63]	
Wheat shell (WS)				1.71	0.0180	0.834	3.93	0.0184	0.999		
Rice shell (RS)				1.75	0.0110	0.917	3.88	0.0032	0.933		
Green algae <i>Cladophora fascicularis</i>	Pb(II)	225.4					144.90	0.0004	0.999	[64]	
		426.0					192.30	0.0003	0.999		
		838.3					204.00	0.0003	0.998		
Protonated rice bran (using H ₃ PO ₄)	Ni(II)	100	25.04	3.38	0.0092	0.971	25.20	0.0088	1.000	[65]	
Baker's yeast	Cd(II)						6.40	0.999		[66]	
	Pb(II)						18.50	0.999			

Table 6 (Continued)

Biosorbent	Solute	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order			Pseudo-second order			Reference
				q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g/(mg min))	R ²	
Modified baker's yeast	Cd(II)						96.00		0.999	
	Pb(II)						210.50		0.999	
Green algae <i>Spirogyra</i> species	Pb(II)	100	52.00	43.00	0.0207	0.927	59.17	0.0005	0.997	[67]
		200	98.00	73.99	0.0205	0.932	111.11	0.0003	0.998	
Dead <i>Bacillus licheniformis</i>	Cr(VI)	300	–	–	0.0286	0.967	–	8.255 × 10 ⁻⁴	0.998	[70]
<i>Lyngbya putealis</i> (HH-15)	Cr(VI)	19.1	17.77				18.08	0.0104	0.999	[71]
		50.6	47.95				51.28	0.00157	0.9927	
Pre-treated arca shell	Pb(II)			18.63	0.0130	0.976				[72]
	Cu(II)			22.66	0.0120	0.978				
	Ni(II)			12.97	0.0110	0.957				
	Cs(I)			5.175	0.0170	0.986				
	Co(II)			11.36	0.0260	0.952				
Magnetically modified brewer's yeast	Hg(II)	25	38.50	32.30	0.0510	0.967	29.10	0.0025	0.996	[79]
		50	49.60	76.50	0.0610	0.876	54.00	0.0015	0.996	
		100	79.60	146.60	0.0560	0.933	91.70	0.0005	0.992	
		200	82.40	120.80	0.0620	0.866	90.10	0.0008	0.995	
Gelidium	Cu(II)	94	4.60	4.6 ± 0.1	0.20 ± 0.01	0.99	5.20 ± 0.3	5 ± 1	0.965	[81]
Algal waste			2.10	2.10 ± 0.02	0.183 ± 0.006	0.998	2.42 ± 0.06	9 ± 1	0.989	
Composite material			1.35	1.38 ± 0.03	0.14 ± 0.01	0.992	1.65 ± 0.08	9 ± 2	0.975	
Baker's yeast	Ni(II)	100	8.20	5.7	0.0021	0.836	8.1	0.0035	0.991	[82]
Cedar sawdust	Cu(II)				0.0352	0.997	31.348	0.00593	1.000	[83]
Crushed brick					0.0345	0.994	28.986	0.00460	0.999	
<i>Caulerpa lentillifera</i>	Cu(II)	10		5.86	2.2480	0.996	6.14	254.	0.999	[88]
	Cd(II)			3.85	1.3950	0.982	3.97	621	1.000	
	Pb(II)			2.56	2.1530	0.992	2.64	2036	1.000	
Treated sawdust	Cr(IV)	–	–	–	0.5622	0.977	–	0.1334	0.9997	[91]
Chitin	Cr(VI)	25						0.0118	0.99	[92]
		50						0.0074	0.962	
		100						0.0024	0.995	
		150						0.0011	0.979	
		200						0.0013	0.987	
		250						0.0003	0.922	
	Cu(II)	30							0.0165	0.979
		60							0.0042	0.974
		120							0.0010	0.964
		180							0.0009	0.912
		250							0.0012	0.976
300							0.0009	0.977		

Table 6 (Continued)

Biosorbent	Solute	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order			Pseudo-second order			Reference
				q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g/(mg min))	R ²	
Chitosan	Cr(VI)	25					0.0054	0.991		
		50					0.0024	0.998		
		100					0.0011	0.993		
		150					0.0005	0.987		
		200					0.0006	0.989		
	250					0.0005	0.989			
	Cu(II)	30						0.0014	0.946	
		60						0.0008	0.979	
		120						0.0004	0.961	
		180						0.0003	0.974	
250							0.0003	0.962		
300						0.0002	0.968			
Rhizopus arrhizus	Cr(VI)	25					0.0053	0.99		
		50					0.009	0.977		
		75					0.0019	0.97		
		100					0.0011	0.952		
		150					0.0014	0.976		
	Cu(II)	25						0.0033	0.949	
		50						0.0027	0.986	
		75						0.0024	0.999	
		100						0.0015	0.976	
		150						0.0014	0.984	
200						0.0009	0.945			
Immobilized marine algal biomass (<i>Sargassum</i>)	Cu(II)	31.773		9.83	0.0017	0.980	16.05	6.45 × 10 ⁻⁵	0.970	[95]
		63.546		10.87	0.0041	0.990	14.36	2.52 × 10 ⁻⁴	0.980	
		127.092		10.31	0.0042	0.990	13.88	0.0015	0.980	
<i>Rhizopus oryzae</i> (viable)	Cu(II)	50	–		0.0297	0.900		0.0081	0.999	[96]
<i>Rhizopus oryzae</i> (NaOH treated)					0.0052	0.905		0.0331	0.999	
Algae <i>Gelidium</i>	Cr(III)	85		8.80 ± 0.3	0.4800 ± 0.8	0.951	9.50 ± 0.3	7 ± 1 × 10 ⁻²	0.977	[97]
	Zn(II)	100		10.80 ± 0.3	0.3500 ± 0.05	0.960	11.90 ± 0.2	4.0 ± 0.4 × 10 ⁻²	0.990	
Agar extraction algal waste	Cr(III)	81		5.30 ± 0.1	0.7600 ± 0.08	0.980	5.60 ± 0.2	19 ± 5 × 10 ⁻²	0.951	
	Zn(II)	97		7.90 ± 0.1	0.9000 ± 0.08	0.983	8.30 ± 0.1	17 ± 1 × 10 ⁻²	0.998	
Composite material	Cr(III)	80		4.10 ± 0.1	0.5800 ± 0.08	0.961	4.39 ± 0.06	18 ± 2 × 10 ⁻²	0.991	
	Zn(II)	94		6.60 ± 0.1	0.097 ± 0.005	0.995	8.00 ± 0.2	1.3 ± 0.2 × 10 ⁻²	0.992	
Immobilized <i>Saccharomyces cerevisiae</i>	Pt(IV)	50			0.0670	0.410	44.25	0.0110	0.990	[98]
		100			0.1300	0.960	81.97	0.0036	0.990	
		200			0.0740	0.950	147.06	0.0021	0.990	
Powdered Waste Sludge (PWS)	Zn(II)	50			0.0125	0.870		0.00133	0.950	[99]
		100			0.0112	0.850		0.00043	0.970	
		150			0.0111	0.870		0.00035	0.910	
		200			0.0110	0.830		0.00033	0.950	
		250			0.0107	0.850		0.00025	0.970	
		300			0.0100	0.830		0.00022	0.940	
		350			0.0098	0.820		0.00020	0.950	

Table 6 (Continued)

Biosorbent	Solute	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order			Pseudo-second order			Reference
				q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g/(mg min))	R ²	
Pre-treated Powdered Waste Sludge (PWS)	Cu(II)	50			0.0137	0.950		0.00099	0.990	[100]
		100			0.0121	0.960		0.00039	0.930	
		150			0.0113	0.970		0.00023	0.940	
		200			0.0105	0.980		0.00019	0.910	
		250			0.0099	0.960		0.00018	0.920	
		300			0.0096	0.960		0.00018	0.930	
		400			0.0088	0.970		0.00017	0.990	
Nopal cladodes (<i>Opuntia streptacantha</i>)	Pb(II)	10	0.02				3.94	0.1518	0.999	[101]
		20	0.04				7.67	0.0354	1.000	
		30	0.05				11.40	0.0158	0.999	
		50	0.88				18.44	0.0058	0.999	
Lignin	Pb(II)						62.99	0.0409		[102]
	Cu(II)						17.53	0.0451		
	Cd(II)						18.21	0.0131		
	Zn(II)						8.96	0.0265		
	Ni(II)						6.46	0.0435		
<i>Azadirachta indica</i> bark	Zn(II)	20	5.18	2.08	0.0390	0.534	5.38	0.0494	0.999	[103]
Water lily	Cr(III)			1.11	0.1170	0.960	1.29	0.2716	0.999	[104]
	Cr(VI)			1.88	0.0364	0.959	2.43	0.0282	1.000	
Water hyacinth	Cr(III)			1.09	0.0701	0.952	1.44	0.3307	1.000	
	Cr(VI)			1.27	0.0032	0.873	1.91	0.0078	0.955	
Green taro	Cr(III)			1.42	0.1973	0.998	1.21	0.1966	0.999	
	Cr(VI)			1.43	0.0035	0.936	2.22	0.0075	0.984	
Mangrove leaves	Cr(III)			1.06	0.0958	0.992	1.15	0.3159	1.000	
	Cr(VI)			1.18	0.0078	0.901	2.50	0.0346	1.000	
Reed mat	Cr(III)			1.35	0.0242	0.843	1.57	0.1208	0.999	
	Cr(VI)			1.53	0.0035	0.995	2.00	0.0023	0.952	
Agaricus bisporus	Cr(VI)	50	4.62	0.94	0.0520	0.981	4.68	0.1600	0.999	[105]
		75	5.10	1.06	0.0950	0.865	5.18	0.2200	0.999	
		100	6.13	0.73	0.0280	0.608	6.22	0.1910	0.999	
		125	6.76	2.20	0.2530	0.923	6.83	0.3400	0.999	
Agro based waste materials	Cr(VI)	100	5.66 ± 0.43				5.86	0.0436	0.998	[110]
	Pb(II)		16.95 ± 0.75				17.54	0.0163	0.997	
Marine brown alga <i>Fucus vesiculosus</i>	Cu(II)	5					4.68	0.9500		[111]
		10					9.84	0.3400		
		20					16.83	0.1800		
Terrestrial moss <i>Pleurozium schreberi</i>		5					4.46	11.1700		
		10					7.14	4.2500		
		20					8.79	1.5000		
Birch wood <i>Betula</i> sp		5					0.92	9.7200		
		10					0.97	3.6900		
		20					1.44	1.4700		

Table 6 (Continued)

Biosorbent	Solute	C ₀ (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order		Pseudo-second order		Reference	
				q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)		k ₂ (g/(mg min))
<i>Pinus sylvestris</i> Linn	Cr(VI)	150	146	17.9	0.0281	0.9686	147.06	0.05081	[121]
	Cd(II) Ternary	25			0.5100 0.3700				[123]
<i>Moringa oleifera</i> seeds (SMOS)	Cr(III) Ternary				0.4000 0.3000				
	Ni(II) Ternary				0.3400 0.3400				
<i>Cassia fistula</i> (Golden Shower) biomass	Ni(II)		34.84	4.49	0.0007	0.894	34.24	0.0066	[124]

^a Not available.

determining steps in the biosorption of Cr(VI) and Zn(II) by algae *Gelidium* and algal waste.

3.3. The Weber and Morris sorption kinetic model

The Weber and Morris (WM) sorption kinetic model was initially employed by Pavasant et al. [43] to describe their biosorption experimental data. This model has the following form

$$q = K_{WM}\sqrt{t} \quad (28)$$

In their investigation, the sorption process by *C. lentillifera* biomass for Cu(II), Cd(II), Pb(II), and Zn(II) was regulated by two main mechanisms, i.e., intraparticle diffusion and external mass transfer. The intraparticle diffusion can be estimated with

$$D = \frac{\pi}{8640} \left(\frac{d_p K_{WM}}{q_e} \right)^2 \quad (29)$$

The external mass transfer process was determined by

$$\frac{dq}{dt} = K'_L A (C - C'_s) \quad (30)$$

They observed that the external mass transfer coefficients can be ordered from high to low values as Cu(II) > Pb(II) > Zn(II) > Cd(II) while the intraparticle diffusion coefficients (also in the decline sequence) as Cd(II) > Zn(II) > Cu(II) > Pb(II). Baral et al. [91] also utilized WM model to correlate biosorption data of Cr(VI) on treated sawdust.

3.4. First-order reversible reaction model

This model is not in common use for study of biosorption kinetics, albeit the fact that it can describe the adsorption and desorption phenomena simultaneously using rate constant parameters. To derive this model, the sorption of metal on biosorbent is assumed to be a first-order reversible reaction, as expressed by the following reaction mechanism [91].



In turn, the rate equation for the reaction is expressed as

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = k_1^o C_A - k_2^o C_B = k_1^o (C_{A0} - C_{A0} X_A) - k_2^o (C_{B0} - C_{A0}) \quad (32)$$

At equilibrium condition

$$K_C = \frac{C_{Be}}{C_{Ae}} = \frac{k_2^o}{k_1^o} \quad (33)$$

Integrating Eq. (32) and applying the equilibrium condition gives

$$\ln \left(\frac{-(C_{A0} + C_A)}{C_{A0} - C_{Ae}} \right) = -(k_1^o + k_2^o)t \quad (34)$$

Baral et al. [91] tried several equations to represent the Cr(VI) biosorption experimental data, and one among these equations was first-order reversible reaction model. This equation well-fit their experimental data. The reduced rate constants and increasing equilibrium constant with temperature rise signifies that the biosorption of Cr(VI) onto treated sawdust has exothermic nature (see Table 7). These observation, however suggesting a complication as a careful examination onto the rate constant parameters revealed an existing violation towards Le Chatelier's principle. Since adsorption process is exothermic as a rule, the rate constant value of k_1^o should decrease with increasing temperature. Based on Le Chatelier's principle, if the adsorption is exothermic, desorption would be endothermic. Therefore the rate constant value of k_2^o should be enhanced in parallel with temperature rise. As mentioned before, sorption of heavy metals on any biosorbents

Table 7

Parameters of first-order reversible reaction model for Cr(VI) biosorption onto treated sawdust (adapted from Ref. [91])

Temperature (K)	k_1^o (min ⁻¹)	k_2^o (min ⁻¹)	K_c	R^2
303	5.060	0.4769	0.0943	0.9609
308	2.833	0.4324	0.1527	0.9911
313	1.063	0.4208	0.2266	0.9978
318	0.542	0.2047	0.3776	0.9978

take place by either physical bonding, ion exchange, complexation, coordination/chelation or a combination of them. By restricted to reversible chemical reaction assumption, this model fails to capture any other possible complex mechanism involved.

4. Conclusion

Numerous empirical models for single solute systems have been employed to describe the biosorption equilibrium, namely Langmuir, Freundlich, Brunauer–Emmett–Teller (BET), Sips, Dubinin–Radushkevich, Temkin and Toth models. Langmuir and Freundlich equations are the most popular and widely used models in a large number of studies. Nonetheless, in many cases, these empirical models fall-short to represent the biosorption phenomena and its in-behind physical meaning. In addition, predictive conclusions are hardly drawn from systems operating at different conditions.

Pseudo-first and -second-order rate expressions have been and still in wide-use for studying the biosorption of heavy metals from aqueous solutions. In chemisorption process, the pseudo-second order is superior to pseudo-first order model as it takes into account the interaction of adsorbent-adsorbate through their valency forces.

References

- [1] D. Park, Y. Yun, J.H. Jo, J.M. Park, Biosorption process for treatment of electroplating wastewater containing Cr(VI): Laboratory-Scale Feasibility Test, *Industrial and Engineering Chemistry Research* 45 (2006) 5059–5065.
- [2] A.Y. Dursun, A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*, *Biochemical Engineering Journal* 28 (2006) 187–195.
- [3] S.M. Dal Bosco, R.S. Jimenez, C. Vignado, J. Fontana, B. Geraldo, F.C.A. Figueiredo, D. Mandelli, W.A. Carvalho, Removal of Mn(II) and Cd(II) from wastewaters by natural and modified clays, *Adsorption* 12 (2006) 133–146.
- [4] T.A. Kurniawan, G.Y.S. Chan, W. Lo, S. Babel, Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals, *Science of The Total Environment* 366 (2006) 409–426.
- [5] L. Deng, X. Zhu, X. Wang, Y. Su, H. Su, Biosorption of copper(II) from aqueous solutions by green alga *Cladophora fascicularis*, *Biodegradation* 18 (2007) 393–402.
- [6] M.A. Hanif, R. Nadeem, H.N. Bhatti, N.R. Ahmad, T.M. Ansari, Ni(II) biosorption by *Cassia fistula* (Golden Shower) biomass, *Journal of Hazardous Materials B139* (2007) 345–355.
- [7] B. Preetha, T. Viruthagiri, Batch and continuous biosorption of chromium(VI) by *Rhizopus arrhizus*, *Separation and Purification Technology* 57 (2007) 126–133.
- [8] D. Satapathy, G.S. Natarajan, Potassium bromate modification of the granular activated carbon and its effect on nickel adsorption, *Adsorption* 12 (2006) 147–154.
- [9] K. Vijayaraghavan, K. Palanivelu, M. Velan, Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles, *Bioresource Technology* 97 (2006) 1411–1419.
- [10] X. Wang, S. Xia, L. Chen, J. Zhao, J. Chovelon, J. Nicole, Biosorption of cadmium(II) and lead(II) ions from aqueous solutions onto dried activated sludge, *Journal of Environmental Sciences* 18 (2006) 840–844.
- [11] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium(VI) by *Tamarindus indica* seeds, *Bioresource Technology* 97 (2006) 949–956.
- [12] Z. Aksu, U. Acikel, E. Kabasakal, S. Tezer, Equilibrium modelling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge, *Water Research* 36 (2002) 3063–3073.
- [13] F.A.A. Al-Rub, Biosorption of zinc on palm tree leaves: equilibrium, kinetics, and thermodynamics studies, *Separation Science and Technology* 41 (2006) 3499–3515.
- [14] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, *Chemical Engineering Journal* 132 (2007) 299–309.
- [15] S. Basha, Z.V.P. Murthy, B. Jha, Sorption of Hg(II) from aqueous solutions onto *Carica papaya*: application of isotherms, *Industrial and Engineering Chemistry Research* 47 (2008) 980–986.
- [16] S. Cay, A. Uyanik, A. Ozasik, Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste, *Separation and Purification Technology* 38 (2004) 273–280.
- [17] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, *Advances in Environmental Research* 6 (2002) 533–540.
- [18] Y. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, *Water Research* 40 (2006) 119–125.
- [19] Y. Ho, A.E. Ofomaja, Pseudo-second order model for lead ion sorption from aqueous solutions onto palm kernel fiber, *Journal of Hazardous Materials B129* (2006) 137–142.
- [20] Y. Ho, A.E. Ofomaja, Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent, *Biochemical Engineering Journal* 30 (2006) 117–123.
- [21] M.A. Javed, H.N. Bhatti, M.A. Hanif, R. Nadeem, Kinetic, Equilibrium modeling of Pb(II) and Co(II) sorption onto rose waste biomass, *Separation Science and Technology* 42 (2007) 3641–3656.
- [22] R. Liu, W. Ma, C. Jia, L. Wang, H. Li, Effect of pH on biosorption of boron onto cotton cellulose, *Desalination* 207 (2007) 257–267.
- [23] S. Lu, S.W. Gibb, Copper removal from wastewater using spent-grain as biosorbent, *Bioresource Technology* 99 (2008) 1509–1517.
- [24] S. Luo, L. Yuan, L. Chai, X. Min, Y. Wang, Y. Fang, P. Wang, Biosorption behaviors of Cu²⁺, Zn²⁺, Cd²⁺ and mixture by waste activated sludge, *Transactions of Nonferrous Metals Society of China* 16 (2006) 1431–1435.
- [25] E. Malkoc, Y. Nuhoglu, Investigations of nickel (II) removal from aqueous solutions using tea factory waste, *Journal of Hazardous Materials B127* (2005) 120–128.
- [26] E. Malkoc, Y. Nuhoglu, Fixed bed studies for the sorption of chromium(VI) onto tea factory waste, *Chemical Engineering Science* 61 (2006) 4363–4372.
- [27] A.E. Ofomaja, Y. Ho, Effect of pH on cadmium biosorption by coconut copra meal, *Journal of Hazardous Materials B139* (2007) 356–362.
- [28] K. Parvathi, R. Nagendran, R. Nareshkumar, Lead biosorption onto waste yeast by-product, a means to decontaminate effluent generated from battery manufacturing industry, *Electronic Journal of Biotechnology* 10 (2007) 1–14.
- [29] G.H. Pino, L.M.S. Mesquita, M.L. Torem, G.A.S. Pinto, Biosorption of cadmium by green coconut shell powder, *Minerals Engineering* 19 (2006) 380–387.
- [30] S.R. Popuri, A. Jammala, K.V.N.S. Reddy, K. Abburi, Biosorption of hexavalent chromium using tamarind (*Tamarindus indica*) fruit shell—a comparative study, *Electronic Journal of Biotechnology* 10 (2007) 358–367.
- [31] M.F. Sawalha, J.R. Peralta-Videa, J. Romero-Gonzalez, M. Duarte-Gardea, J.L. Gardea-Torresdey, Thermodynamic and isotherm studies of the biosorption of Cu(II), Pb(II), and Zn(II) by leaves of saltbush (*Atriplex canescens*), *Journal of Chemical Thermodynamics* 39 (2007) 488–492.
- [32] S. Vinopal, T. Ruml, P. Kotrba, Biosorption of Cd²⁺ and Zn²⁺ by cell surface-engineered *Saccharomyces cerevisiae*, *International Biodeterioration and Biodegradation* 60 (2007) 96–102.
- [33] X. Wang, Y. Qin, Z. Li, Biosorption of zinc from aqueous solutions by rice bran: kinetics and equilibrium studies, *Separation Science and Technology* 41 (2006) 747–756.
- [34] B. Yuncu, F.D. Sanin, U. Yetis, An investigation of heavy metal biosorption in relation to C/N ratio of activated sludge, *Journal of Hazardous Materials B137* (2006) 990–997.
- [35] C.L. Mack, B. Wilhelm, J.R. Duncan, J.E. Burgess, Biosorption of precious metals, *Biotechnology Advances* 25 (2007) 264–271.
- [36] E. Romera, F. Gonzalez, A. Ballester, M.L. Blasquez, J.A. Munoz, Biosorption with algae: a statistical review, *Critical Reviews in Biotechnology* 26 (2006) 223–235.
- [37] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, *Separation and Purification Technology* 38 (2004) 43–74.
- [38] H.K. Alluri, S.R. Ronda, V.S. Settalluri, J.S. Bondili, V. Suryanarayana, P. Venkateshwar, Biosorption: an eco-friendly alternative for heavy metal removal, *African Journal of Biotechnology* 6 (2007) 2924–2931.
- [39] A. Delle Site, Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review, *Journal of Physical and Chemical Reference Data* 30 (2001) 187–439.
- [40] S.S. Baral, S.N. Das, P. Rath, G. Roy Chaudhury, Y.V. Swamy, Removal of Cr(VI) from aqueous solution using waste weed, *Salvinia cucullata*, *Chemistry and Ecology* 23 (2007) 105–117.
- [41] K. Parvathi, R. Nagendran, Biosorption of chromium from effluent generated in chrome-electroplating unit using *Saccharomyces cerevisiae*, *Separation, Science and Technology* 42 (2007) 625–638.
- [42] S.V. Gokhale, K.K. Jyoti, S.S. Lele, Kinetic and equilibrium modeling of chromium (VI) biosorption on fresh and spent *Spirulina platensis/Chlorella vulgaris* biomass, *Bioresource Technology* 99 (2008) 3600–3608.
- [43] P. Pasavant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu²⁺, Cd²⁺, Pb²⁺, and Zn²⁺ using dried marine green macroalga *Caulerpa lentillifera*, *Bioresource Technology* 97 (2006) 2321–2329.

- [44] Y. Vijaya, S.R. Popuri, V.M. Boddu, A. Krishnaiah, Modified chitosan and calcium, Carbohydrate polymers 72 (2008) 261–271.
- [45] W.S. Wan Ngah, A. Kamari, S. Fatinathan, P.W. Ng, Adsorption of chromium from aqueous solution using chitosan beads, Adsorption 12 (2006) 249–257.
- [46] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes*, Chemical Engineering Journal 117 (2006) 71–77.
- [47] L. Deng, Y. Su, H. Su, X. Wang, X. Zhu, Biosorption of copper (II) and lead (II) from aqueous solutions by nonliving green algae *Cladophora fascicularis*: equilibrium, kinetics and environmental effects, Adsorption 12 (2006) 267–277.
- [48] R. Nadeem, M.A. Hanif, F. Shaheen, S. Perveen, M.N. Zafar, T. Iqbal, Physical and chemical modification of distillery sludge for Pb(II) biosorption, Journal of Hazardous Materials 150 (2008) 335–342.
- [49] M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, Copper biosorption from aqueous solutions by sour orange residue, Journal of Hazardous Materials 149 (2007) 269–274.
- [50] K. Nasreen, I. Muhammad, Z.S. Iqbal, I. Javed, Biosorption characteristics of unicellular green alga *Chlorella sorokiniana* immobilized in loofa sponge for removal of Cr(III), Journal of Environmental Sciences 20 (2008) 231–239.
- [51] B.A. Calfa, M.L. Torem, On the fundamentals of Cr(III) removal from liquid streams by a bacterial strain, Minerals Engineering 21 (2008) 48–54.
- [52] S. Schiewer, S.B. Patil, Pectin-rich fruit wastes as biosorbents for heavy metal removal: equilibrium and kinetics, Bioresource Technology 99 (2008) 1896–1903.
- [53] R. Kumar, N.R. Bishnoi, K. Garima, Bishnoi, Biosorption of chromium(VI) from aqueous solution and electroplating wastewater using fungal biomass, Chemical Engineering Journal 135 (2008) 202–208.
- [54] W.M. Antunes, A.S. Luna, C.A. Henriques, A.C.A. Costa, An evaluation of copper biosorption by a brown seaweed under optimized conditions, Electronic Journal of Biotechnology 6 (2003) 174–184.
- [55] N. Ahalya, R.D. Kanamadi, T.V. Ramachandra, Biosorption of chromium(VI) from aqueous solutions by the husk of Bengal gram (*Cicer arietinum*), Electronic Journal of Biotechnology 8 (2005) 258–264.
- [56] C. Namasivayam, M.V. Sureshkumar, Removal of chromium(VI) from water and wastewater using surfactant modified coconut coirpith as biosorbent, Bioresource Technology 99 (2008) 2218–2225.
- [57] M. Isik, Biosorption of Ni(II) from aqueous solutions by living and non-living ureolytic mixed culture, Colloids and Surfaces B: Biointerfaces 62 (2008) 97–104.
- [58] Z. Salem, K. Allia, Cadmium biosorption on vegetal biomass, International Journal of Chemical Reactor Engineering 6 (2008) 1–9.
- [59] M. Dundar, C. Nuhoglu, Y. Nuhoglu, Biosorption of Cu(II) ions onto the litter of natural trembling poplar forest, Journal of Hazardous Materials 151 (2008) 86–95.
- [60] H. Doshi, A. Ray, I.L. Kothari, Biosorption of cadmium by live and dead *Spirulina*: IR spectroscopic, kinetics, and SEM studies, Current Microbiology 54 (2007) 213–218.
- [61] J. Yu, M. Tong, X. Sun, B. Li, Cystine-modified biomass for Cd(II) and Pb(II) biosorption, Journal of Hazardous Materials 143 (2007) 277–284.
- [62] M. Mukhopadhyay, S.B. Noronha, G.K. Suraiskumar, Kinetic modeling for the biosorption of copper by pretreated *Aspergillus niger* biomass, Bioresource Technology 98 (2007) 1781–1787.
- [63] H. Aydin, Y. Bulut, C. Yerlikaya, Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents, Journal of Environmental Management 87 (2008) 37–45.
- [64] L. Deng, Y. Su, H. Su, X. Wang, X. Zhu, Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*, Journal of Hazardous Materials 143 (2007) 220–225.
- [65] N.M. Zafar, R. Nadeem, M.A. Hanif, Biosorption of nickel from protonated rice bran, Journal of Hazardous Materials 143 (2007) 478–485.
- [66] J. Yu, M.S. Tong, X.B. Li, A simple method to prepare poly(amino acid)-modified biomass for enhancement of lead and cadmium adsorption, Biochemical Engineering Journal 33 (2007) 126–133.
- [67] V.K. Gupta, A. Rastogi, Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetics and equilibrium studies, Journal of Hazardous Material 152 (2008) 407–414.
- [68] F. Luo, Y. Liu, X. Li, Z. Xuan, J. Ma, Biosorption of lead ion by chemically-modified biomass of marine brown algae *Laminaria japonica*, Chemosphere 64 (2006) 1122–1127.
- [69] Y. Ho, Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods, Polish Journal of Environmental Studies 15 (2006) 81–86.
- [70] M. Zhou, Y. Liu, G. Zeng, X. Li, W. Xu, T. Fan, Kinetic and equilibrium studies of Cr(VI) biosorption by dead *Bacillus licheniformis* biomass, World Journal of Microbiology & Biotechnology 23 (2007) 43–48.
- [71] B. Kiran, A. Kaushik, C.P. Kaushik, Biosorption of Cr(VI) by native isolate of *Lyngbya putealis* (HH-15) in the presence of salts, Journal of Hazardous Materials 141 (2007) 662–667.
- [72] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of heavy metals and radionuclide from aqueous solutions by pre-treated arca shell biomass, Journal of Hazardous Materials 150 (2008) 376–386.
- [73] J.C. Igwe, A.A. Abia, Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk, Electronic Journal of Biotechnology 10 (2007) 536–548.
- [74] D.M. Vieira, A.C.A. da Costa, C.A. Henriques, V.L. Cardoso, F.P. de Franca, Biosorption of lead by the brown seaweed *Sargassum filipendula*—batch and continuous pilot studies, Electronic Journal of Biotechnology 10 (2007) 368–375.
- [75] A. Cabuk, T. Akar, S. Tunali, S. Gedikli, Biosorption of Pb(II) by industrial strain of *Saccharomyces cerevisiae* immobilized on the biomatrix of cone biomass of *Pinus nigra*: equilibrium and mechanism analysis, Chemical Engineering Journal 131 (2007) 293–300.
- [76] M.S. Rahaman, A. Basu, M.R. Islam, The removal of As(III) and As(V) from aqueous solutions by waste materials, Bioresource Technology 99 (2008) 2815–2823.
- [77] E. Lesage, C. Mundia, D.P.L. Rousseau, A.M.K. Van de Moortel, G. Du Laing, E. Meers, F.M.G. Tack, N. De Pauw, M.G. Verloo, Sorption of Co, Cu, Ni and Zn from industrial effluents by the submerged aquatic macrophyte *Myriophyllum spicatum* L., Ecological Engineering 30 (2007) 320–325.
- [78] A. Ozturk, Removal of nickel from aqueous solution by the bacterium *Bacillus thuringiensis*, Journal of Hazardous Materials 147 (2007) 518–523.
- [79] H. Yavuz, A. Denizli, H. Gungunes, M. Safarikova, I. Safarik, Biosorption of mercury on magnetically modified yeast cells, Separation and Purification Technology 52 (2006) 253–260.
- [80] C. Green-Ruiz, V. Rodriguez-Tirado, B. Gomez-Gil, Cadmium and zinc removal from aqueous solutions by *Bacillus jeotgali*: pH, salinity and temperature effects, Bioresource Technology 99 (2008) 3864–3870.
- [81] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Copper removal by algae *Gelidium*, agar extraction algal waste and granulated algal waste: kinetics and equilibrium, Bioresource Technology 99 (2008) 750–762.
- [82] V. Padmavathy, Biosorption of nickel(II) ions by baker's yeast: kinetic, thermodynamic and desorption studies, Bioresource Technology 99 (2008) 3100–3109.
- [83] R. Djeribi, O. Hamdaoui, Sorption of copper(II) from aqueous solutions by cedar sawdust and crushed brick, Desalination 225 (2008) 95–112.
- [84] M.H. Jnr, A.I. Spiff, Effects of temperature on the sorption of Pb²⁺ and Cd²⁺ from aqueous solution by *Caladium bicolor* (Wild Cocoyam) biomass, Electronic Journal of Biotechnology 8 (2005) 162–169.
- [85] M.A. Shaker, Thermodynamic profile of some heavy metal ions adsorption onto biomaterial surfaces, American Journal of Applied Sciences 4 (2007) 605–612.
- [86] K. Vijayaraghavan, T.V.N. Padmesh, K. Palanivelu, M. Velan, Biosorption of nickel(II) ions onto *Sargassum wightii*: application of two-parameter and three-parameter isotherm models, Journal of Hazardous Materials B133 (2006) 304–308.
- [87] B. Kiran, A. Kaushik, Chromium binding capacity of *Lyngbya putealis* exopolysaccharides, Biochemical Engineering Journal 38 (2008) 47–54.
- [88] R. Aparitukul, P. Pavaasant, Batch and column studies of biosorption of heavy metals by *Caulerpa lentillifera*, Bioresource Technology 99 (2008) 2766–2777.
- [89] R. Senthilkumar, K. Vijayaraghavan, M. Thilakavathi, P.V.R. Iyer, M. Velan, Application of seaweeds for the removal of lead from aqueous solution, Biochemical Engineering Journal 33 (2007) 211–216.
- [90] Z. Aksu, G. Donmez, Binary biosorption of cadmium(II) and nickel(II) onto dried *Chlorella vulgaris*: co-ion effect on mono-component isotherm parameters, Process Biochemistry 41 (2006) 860–868.
- [91] S.S. Baral, S.N. Das, P. Rath, Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust, Biochemical Engineering Journal 31 (2006) 216–222.
- [92] Y. Sag, Y. Aktay, Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan, and *Rhizopus arrhizus*, Biochemical Engineering Journal 12 (2002) 143–153.
- [93] Y. Ho, Review of second-order models for adsorption systems, Journal of Hazardous Materials B136 (2006) 681–689.
- [94] Y.S. Ho, G. McKay, Application of kinetic models to the sorption of copper(II) on to peat, Adsorption Sciences & Technology 20 (2002) 797–815.
- [95] P.X. Sheng, K.H. Wee, Y.P. Ting, J.P. Chen, Biosorption of copper by immobilized marine algal biomass, Chemical Engineering Journal 136 (2008) 156–163.
- [96] K.C. Bhainsa, S.F. D'Souza, Removal of copper ions by the filamentous fungus, *Rhizopus oryzae* from aqueous solution, Bioresource Technology 99 (2008) 3829–3835.
- [97] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Chromium and zinc uptake by algae *Gelidium* and agar extraction algal waste: kinetics and equilibrium, Journal of Hazardous Materials 149 (2007) 643–649.
- [98] C.L. Mack, B. Wilhelm, J.R. Duncan, J.E. Burgess, A kinetic study of the recovery of platinum ions from an artificial aqueous solution by immobilized *Saccharomyces cerevisiae* biomass, Minerals Engineering 21 (2008) 31–37.
- [99] F. Kargi, S. Cikla, Kinetics of zinc(II) ion biosorption onto powdered waste sludge (PWS) at different operating conditions, Environmental Engineering Science 24 (2007) 687–695.
- [100] M.Y. Pamukoglu, F. Kargi, Effects of operating parameters on kinetics of copper(II) ion biosorption onto pre-treated powdered waste sludge (PWS), Enzyme and Microbial Technology 42 (2007) 76–82.
- [101] P. Miretzky, C. Munoz, A. Carrillo-Chavez, Experimental binding of lead to a low cost on biosorbent: Nopal (*Opuntia streptacantha*), Bioresource Technology 99 (2008) 1211–1217.
- [102] X.Y. Guo, A.Z. Zhang, X.Q. Shan, Adsorption of metal ions on lignin, Journal of Hazardous Material 151 (2008) 134–142.
- [103] P. King, K. Anuradha, S.B. Lahari, Y.P. Kumar, V.S.R.K. Prasad, Biosorption of zinc from aqueous solution using *Azadirachta indica* bark: equilibrium and kinetic studies, Journal of Hazardous Materials 152 (2008) 324–329.

- [104] R. Elangovan, L. Philip, K. Chandraraj, Biosorption of chromium species by aquatic weeds: kinetics and mechanism studies, *Journal of Hazardous Materials* 152 (2008) 100–112.
- [105] N. Ertugay, Y.K. Bayhan, Biosorption of Cr (VI) from aqueous solutions by biomass of *Agaricus bisporus*, *Journal of Hazardous Materials* 154 (2008) 432–439.
- [106] E. Pehlivan, B.H. Yanik, G. Ahmetli, M. Pehlivan, Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp, *Bioresource Technology* 99 (2008) 3520–3527.
- [107] F. Ekmekyapar, A. Aslan, Y.K. Bayhan, A. Cakici, Biosorption of copper(II) by nonliving lichen biomass of *Cladonia rangiformis* hoffm, *Journal of Hazardous Materials* B137 (2006) 293–298.
- [108] L. Dupont, J. Bounanda, J. Dumonceau, M. Aplincourt, Biosorption of Cu(II) and Zn(II) onto a lignocellulosic substrate extracted from wheat bran, *Environment Chemistry Letters* 2 (2005) 165–168.
- [109] K.N. Ghimire, J. Inoue, K. Inoue, H. Kawakita, K. Ohto, Adsorptive separation of metal ions onto phosphorylated orange waste, *Separation Science and Technology* 43 (2008) 362–375.
- [110] S. Qaiser, A.R. Saleemi, M.M. Ahmad, Heavy metal uptake by agro based waste materials, *Electronic Journal of Biotechnology* 10 (2007) 409–416.
- [111] A. Grimm, R. Zanzi, E. Bjornbom, A.L. Cukierman, Comparison of different types of biomasses for copper biosorption, *Bioresource Technology* 99 (2008) 2559–2565.
- [112] W. Chen, C. Wu, E.K. James, J. Chang, Metal biosorption capability of *Cupriavidus taiwanensis* and its effects on heavy metal removal by nodulated *Mimosa pudica*, *Journal of Hazardous Materials* 151 (2008) 364–371.
- [113] B. Southichak, K. Nakano, M. Nomura, N. Chiba, O. Nishimura, Pb(II) biosorption on reed biosorbent derived from wetland: effect of pretreatment on functional groups, *Water Science & Technology* 154 (2006) 133–141.
- [114] J.T. Matheickal, Q. Yu, Biosorption of lead(II) and copper(II) from aqueous solutions by pre-treated biomass of Australian marine algae, *Bioresource Technology* 69 (1999) 223–229.
- [115] J.P. Chen, L. Wang, S. Zou, Determination of lead biosorption properties by experimental and modeling simulation study, *Chemical Engineering Journal* 131 (2007) 209–215.
- [116] K.K. Wong, C.K. Lee, K.S. Low, M.J. Haron, Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions, *Chemosphere* 50 (2003) 23–28.
- [117] V. Murphy, H. Hughes, P. McLoughlin, Comparative study of chromium biosorption by red, green and brown seaweed biomass, *Chemosphere* 70 (2008) 1128–1134.
- [118] S.K. Das, A.K. Guha, Biosorption of chromium by *Termitomyces clypeatus*, *Colloids and Surfaces B: Biointerfaces* 60 (2007) 46–54.
- [119] A. Hammami, F. Gonzalez, A. Ballester, M.L. Blazquez, J.A. Munoz, Biosorption of heavy metals by activated sludge and their desorption characteristics, *Journal of Environmental Management* 84 (2007) 419–426.
- [120] N.V. Farinella, G.D. Matos, M.A.Z. Arruda, Grape bagasse as a potential biosorbent of metals in effluent treatments, *Bioresource Technology* 98 (2007) 1940–1946.
- [121] H. Ucu, Y.K. Bayhan, Y. Kaya, Kinetic and thermodynamic studies of the biosorption of Cr(VI) by *Pinus sylvestris* Linn, *Journal of Hazardous Materials* 153 (2008) 52–59.
- [122] D.L. Vullo, H.M. Ceretti, M.A. Daniel, S.A.M. Ramirez, A. Zalts, Cadmium, zinc and copper biosorption mediated by *Pseudomonas veronii* 2E, *Bioresource Technology* 99 (2008) 5574–5581.
- [123] P. Sharma, P. Kumari, M.M. Srivastava, S. Srivastava, Ternary biosorption studies of Cd(II), Cr(III) and Ni(II) on shelled *Moringa oleifera* seeds, *Bioresource Technology* 98 (2007) 474–477.
- [124] M.A. Hanif, R. Nadeem, N.M. Zafar, K. Akhtar, H.N. Bhatti, Kinetic studies for Ni(II) biosorption from industrial wastewater by *Cassia fistula* (Golden Shower) biomass, *Journal of Hazardous Materials* 145 (2007) 501–505.