

Heavy Metal Lead Removal by Biosorption – A Review

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Abstract— Biosorption technique is increasingly researched and used in the biosorption of various heavy metals from industrial effluents over the past decades. Factors such as temperature, pH, initial metal ion concentration, biomass concentration and the metal affinity to the biosorbent, affect the efficiency of the biosorption capacity. Biosorbents such as large scale industrial fermentation by-products, agricultural waste, seaweeds, etc are used for lead removal. This article reviews the various research on biosorbents reported from 2013 – 2016, for the biosorption capacity & the kinetics and equilibrium isotherm models that the sorbents follow for optimum process. The thermodynamics of the process of certain biosorbents have also been selectively overviewed.

Keywords— Lead; Biosorption; Biosorbent; Isotherm; Adsorption capacity.

I. INTRODUCTION

Heavy metal pollution is one of the major environmental problems prevalent today. Lead exists as Pb (II) and is toxic to living organisms in its concentrated forms. It is a metabolic poison which accumulates in the blood [1], mineralizing tissues (bones and teeth) [2] and soft tissues of human body (liver, kidneys, lungs, brain, spleen, muscles, and heart) [3]. It is an enzyme inhibitor which forms complexes with Oxo-groups in enzymes to affect virtually all steps in the synthesis of haemoglobin and porphyria metabolism [4]. It causes various health problems such as anaemia, Alzheimer's disease, nervous system deterioration, failure of kidneys, bone problems and nervous system deterioration [5]. It affects infants and small children as well [6, 7]. The World Health Organization considers lead to be in the top ten chemical of public concern. [8] The permissible limit of lead in drinking water and surface water intended for drinking, as set by EU, US-EPA and WHO are 0.010, 0.015 and 0.010mgL⁻¹ respectively [9, 10 and 11].

Industrial effluents containing high concentrations of lead are introduced in the water bodies from mining, manufacturing of batteries, paint, pigments, burning of coal, etc. Thus the removal and recovery of heavy metals from effluent streams are essential to the protection of the environment.

II. BIOSORPTION PROCESS

Biosorption is a property of certain types of inactive, dead, microbial biomass to bind and concentrate heavy metals from even dilute aqueous solutions. It is a metabolically passive process, meaning it does not require energy, and the amount of contaminants that a sorbent can remove is dependent on kinetic equilibrium and the composition of the sorbents cellular surface [12].

The biosorption process involves a solid phase (sorbent or biosorbents; biological material) and a liquid phase (solvent, normally water) containing the dissolved metal ions (adsorbate, heavy metal) to be sorbent. Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound by different mechanisms such as ion exchange, complexation, chelation, microprecipitation, etc. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases [13].

A. Advantages of Biosorption Process

Compared with the conventional heavy metal removal methods, the potential advantages of biosorption process includes [14]:

- High selectivity for recovery and removal of specific heavy metals
- High affinity thereby removing residual metals to < 1ppb
- Ability to treat large volumes of mixed wastes and wastewater with multiple heavy metals
- Use of naturally renewable biomaterial that are cheap and abundant, reducing the need for expensive reagents
- Wide range of physicochemical operational conditions including pH, temperature and also presence of other ions
- Relatively low investment and operational cost but with enhanced recovery of bound heavy metals ions
- The hazardous waste produces is greatly reduced in volume.

B. Factors Affecting Biosorption of Metals

Biosorption depends on many factors that are related to the biomass and metal; while some other factors are related to environmental conditions.

1) *Temperature*: For most biomass, the biosorption activity occurs at the room temperature. However in certain cases, the temperature plays a major role in determining the optimum conditions for the process. In the biosorption study using peanut shells, its capacity to adsorb Pb(II) decreased as the temperature increased. It was also observed that the process was exothermic and spontaneous [15].

2) *pH*: pH dependent experiments were advised not to be conducted at pH > 5 in order to avoid precipitation of Pb ions as hydroxides [16]. Since protons can be adsorbed or released in the biosorption process, the pH affects the metal ion solubility and the total charge of the biosorbent [17]. This behavior also depends on the functional groups present on the biomass' cell wall.

3) *Initial metal ion and biosorbent concentrations*: The concentration of exchangeable sites on the cell wall of the biosorbents affects its removal capacity. At minute initial concentrations of metal ions, 1g (say) of biomass would be enough for complete removal by biosorption. But when the metal ion concentration increases, the exchangeable sites in the 1g of biomass will be not be sufficient for biosorption, resulting in obvious reduced removal capacity. The study by Hasan et al, 2016 [18], the gradual increase in equilibrium uptake of the biosorbent with the increase in initial metal ion concentration was reported. This was probably due to the higher interaction between the exchangeable sites of the biosorbent and the metal ions. Hence the metal ion to adsorbent ratio plays a critical role in the biosorption process. In contrast, the presence of NaCl reduced the sorption efficiency due to the competition for binding sites between the Na⁺ and divalent cations [19]. Hence the biosorption capacity could be determined by the temperature, pH, initial metal ion concentration, biomass concentration and the metal affinity to the biosorbent.

III. BIOSORBENTS

The first major challenge for the biosorption field was to choose the most promising types of biomass/ biosorbent from enormously available and inexpensive biomaterials. Even though several materials of biological origin bind heavy metals, biomaterials with sufficiently high metal-binding capacity and selectivity for heavy metals are appropriate for full-scale biosorption process [20].

A. Types of Biomass

The types of biomass used for biosorption process includes large scale industrial by-products of fermentation (e.g. mold *Rhizopus sp.* [21, 22] and bacterium *Bacillus sp.* [23]), agricultural waste (like husks of rice [24], coffee [25], etc), seaweeds (e.g. algae) [26], etc. These biomass types can accumulate in excess 25% of their dry weight in heavy metals. Moreover chemically modified biomass shows improved biosorption capacity. The functionalized *Saccharomyces cerevisiae* cell with biogenic intracellular CaCO₃ mineral scaffold was efficient for removing Pb(II) ions from aqueous solutions at the maximum removal capacity of 116.69 mg g⁻¹[27]. HNO₃ modified *Phytolacca americana* was found to have higher uptake capacity than the original *P. americana* [28]. The different lead removal capacities of several biosorbents under optimum conditions are summarized in table I.

For the biomass to be effective biosorbents, the vital evaluation elements for an adsorption process are the mechanism of biosorption and the reaction rate. Biosorbate uptake rate determines the time required for completing the adsorption reaction and can be described from the kinetic analysis.

IV. KINETICS OF ADSORPTION

To explain the solid/liquid biosorption processes, Lagergren first described the process and presented the first order rate equation. In order to differentiate the kinetic equations based on adsorption capacity from solution concentration, the Lagergren's first order rate equation is also known as the pseudo – first order kinetic equation [29, 30]. The pseudo – second order kinetic equation [31] and intra-particle diffusion model is also used to predict the sorption kinetics. The pseudo – first order and pseudo second order

define the metal interactions (physisorption or chemisorptions). The intraparticle diffusion model defines the internal diffusion that establishes the adsorption rate in most of the liquid systems [32]. The linear equations of these kinetic models are presented in table II

Lagergren's pseudo first order model describes the rate of adsorption reaction to be dependent on the available concentration of adsorbent. In previous studies, this model was not able to correlate with the experimental values, probably due to the time lag causing the presence of boundary layer that controls at the beginning of the biosorption process [37]. Pseudo second order model indicates chemisorptions to be the rate limiting step [42]. Biosorption of lead using corn husk [37], peanut shells [15], *C. interruptus* [38], Marula seed husk (*S. birrea*) [39], *P. americana* [28], maize stover [40], nanostructured cedar leaf ash [35], cashew nut shell (*A. occidentale* L.) [41], Casuarina Leaf Powder [16], *S. melongena* leaf powder [42], and Castor leaf (*R. communis*) [43] have been reported to follow pseudo second order model for adsorption.

TABLE I. LEAD REMOVAL CAPACITIES OF VARIOUS BIOSORBENTS

Biosorbent	Operation Conditions		Biosorption Capacity, q	Ref.
	pH	Biomass Concentration		
Peanut shells	5.5	2 g/L	33 mg/g	[15]
Coffee Husk	5	2 g	50 mg/g	[25]
<i>P. americana</i> L.	6	20 g/L	10.83 mg/g	[28]
HNO ₃ modified <i>P. americana</i> L.			12.66 mg/g	
Marula seed husk (<i>Sclerocarya birrea</i>)	5	0.8 g	20mg/g	[39]
Castor Leaf Powder	5	0.02 g	0.327 mmol/g	[44]
<i>Ulva lactuca</i>	5	0.8 g/L	68.9 mg/g	[50]
<i>Sargassum ilicifolium</i>	3.7	0.2 g/L	195 ± 3.3 mg/g	[51]
(live) <i>Spirulina (Arthospira) maxima</i> ,	7	0.24 (g/L)	27.25 mg/gdw	[52]
(live) <i>Spirulina (Arthospira) indica</i> ,			28.2 mg/gdw	
(live) <i>Spirulina (Arthospira) platensis</i>			28.25 mg/gdw	
<i>Curtobacterium sp. FM01</i>	6	1 mg	180.6 mg/g	[53]
<i>Streptomyces fradiae</i> biomass	5	1g dm ⁻³	138.88 mg/g	[54]
<i>Sophora japonica</i> pods	6.0 - 7.0	0.5 g/L	25.13 mg/g	[55]
<i>Otostegia persica</i>	5.5	1.06 g/L	17.3 mg/g	[56]

TABLE II. KINETIC MODEL LINEAR EQUATION [33]

Kinetic Model	Linear Equation	Eqn. No.	Plot representation
Pseudo - first order	$\log (q_e - q_t) = \log (q_e) - \frac{k_1}{2.303} t$	(1)	$\log (q_e - q_t)$ vs t
Pseudo - second order	$\frac{t}{q_t} = \frac{k_2}{k_2 q_e^2} + \frac{t}{q_e}$	(2)	$\frac{t}{q_t}$ vs t
Intra - particle diffusion	$q_t = K_{id} t^{0.5} + C$	(3)	q_t vs $t^{0.5}$

Where the parameters are q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and time t (min), respectively; k_1 (1/min) and k_2 (g/ (mg min)) are the pseudo-first and pseudo-second order rate constants, respectively; K_{id} (mg/g min^{0.5}) is the intraparticle diffusion rate constant and C is the intercept.

The overall rate of adsorption can be described by the following three steps: (1) fluid transport, (2) film diffusion, (3) surface diffusion. If the nature of diffusion could not be identified by the first and second pseudo order model the intra-particle diffusion model is investigated. If the intraparticle diffusion is the sole rate-limiting step, intercept of the line, in the plot representation, should pass through the origin, i.e. $C=0$ [34]. The study on rapeseed [33] suggests that it underwent pseudo second order reaction and intra-particle diffusion.

V. EQUILIBRIUM MODELS OF ADSORPTION

In order to understand the relationship between the concentrations of lead adsorbed to its equilibrium concentration in the biosorbent solution, kinetic isotherms are applied. Isotherms define the adsorption efficiency. The different isotherm models along with its linear equation are given in table III.

TABLE III. BIOSORPTION ISOTHERM MODEL - LINEAR EQUATION [33]

Isotherm Model	Linear Equation	Eqn. No.	Plot representation
Freundlich [33]	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	(4)	$\log q_e$ vs $\log C_e$
Langmuir [33]	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$	(5)	C_e/q_e vs C_e
Temkin [58]	$q_e = \frac{RT}{b_t} \ln k_T + \frac{RT}{b_t} \ln C_e$	(6)	q_e vs $\ln C_e$
Dubinin – Radushkevich (D – R [59])	$\ln q_e = \ln q_m - \beta \epsilon^2$	(7)	$\ln q_e$ vs $\ln C_e$
	$\epsilon = RT \ln(1 + 1/C_e)$	(8)	
	$E_a = 1/\sqrt{2\beta}$	(9)	
Sips (Langmuir – Freundlich) [35]	$\ln \left(\frac{q_e}{q_m - q_e} \right) = n \ln C_e + \ln K_s^n$	(10)	$\ln \left(\frac{q_e}{q_m - q_e} \right)$ vs $\ln C_e^n$
Redlich–Peterson [35]	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right) = n \ln C_e + \ln b$	(11)	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right)$ vs $\ln C_e$

Where the q_e is the sorption capacity at equilibrium (mg/g); q_m is the maximum sorption capacity (mg/g); C_e (mg/L) is the equilibrium concentration of biosorbent; K_L is the Langmuir constant (L/mg); K_F is the Freundlich constants of the adsorption capacity and exponent n is the adsorption intensity which varies with heterogeneity of the material. K_s is the affinity constant for adsorption in Sips model (L/g); K_R (L/g) and b (L/mg) are the Redlich–Peterson constants of adsorption. K_T is the Temkin's equilibrium binding constant corresponding to the maximum binding energy (L/mg); b_t is

the Temkin isotherm constant (Jmol⁻¹); R is the gas constant (8.314JK⁻¹mol⁻¹); T is the temperature in Kelvin; ϵ is the Polanyi potential for adsorption; E_a is the change in free energy when 1 mol of ion is transported to the surface of the solid in solution. It is calculated from β , which is the D-R constant. If the magnitude of E_a is between 8 and 16 kJ/mol, then chemisorption process takes place and if the values of E_a is less than 8kJ/mol, then physisorption process occurs.

The Langmuir isotherm model assumes that there is finite number of active sites distributed homogeneously over the surface of the adsorbent. The affinity of these active sites for adsorption is same towards a mono molecular layer and the interaction between adsorbed molecules is nil [37]. The biosorbents that undergo the respective isotherm models are summarized in table IV.

TABLE IV. ISOTHERM PARAMETERS OF THE VARIOUS BIOSORBENTS

Biosorbent	Isotherm Model	Remarks	Ref.	
Peanut shells	Langmuir	$q_m = 39 \text{ mg g}^{-1}$	[15]	
Rice Husk Ash	Langmuir	$q_m = 0.0561 \text{ mmol/g}$	[24]	
<i>P. americana</i>	Freudlich	$K_f = 0.6006 \text{ (mg g}^{-1}) \text{ (L mg}^{-1})^{1/n}$ $1/n = 0.6742$	[28]	
	Langmuir	$q_m = 10.83 \text{ mg g}^{-1}$		
HNO ₃ modified <i>P. americana</i>	Freudlich	$K_f = 1.244 \text{ (mg g}^{-1}) \text{ (L mg}^{-1})^{1/n}$ $1/n = 0.5906$	[33]	
	Langmuir	$q_m = 12.66 \text{ mg g}^{-1}$		
Rapeseed biomass	Langmuir	$q_m = 18.35 \text{ mg/L at } 4^\circ\text{C}$	[33]	
	Langmuir	$q_m = 21.29 \text{ mg/L at } 20^\circ\text{C}$		
	Langmuir	$q_m = 22.7 \text{ mg/L at } 25^\circ\text{C}$		
Nanostructured cedar leaf	Langmuir	$q_m = 7.23 \text{ mg g}^{-1}$	[35]	
	Sips	$q_m = 8.045 \text{ mg g}^{-1}$		
Corn husk	Langmuir	$q_m = 3.034 \text{ mg g}^{-1}$	[37]	
<i>Cyclosorus interruptus</i>	Langmuir	$q_m = 46.25 \text{ mg g}^{-1}$	[38]	
Raw maize stover	Langmuir	$q_m = 19.65 \text{ mg g}^{-1}$	[40]	
Treated maize stover	Langmuir	$q_m = 27.1 \text{ mg g}^{-1}$		
Cashew nut	Langmuir	$q_m = 11.23 \text{ mg g}^{-1}$	[41]	
Olive stone	Langmuir	$q_m = 6.33 \text{ mg g}^{-1}$	[44]	
HNO ₃ modified Olive Stone	Langmuir	$q_m = 49.13 \text{ mg g}^{-1}$		
H ₂ SO ₄ modified Olive Stone	Langmuir	$q_m = 14.83 \text{ mg g}^{-1}$		
NaOH modified Olive Stone	Langmuir	$q_m = 38.93 \text{ mg g}^{-1}$		
Olive Tree Pruning	Langmuir	$q_m = 26.72 \text{ mg g}^{-1}$		
HNO ₃ modified Olive Tree Pruning	Langmuir	$q_m = 86.4 \text{ mg g}^{-1}$		
H ₂ SO ₄ modified Olive Tree Pruning	Langmuir	$q_m = 72.78 \text{ mg g}^{-1}$		
NaOH modified Olive Tree Pruning	Langmuir	$q_m = 123.8 \text{ mg g}^{-1}$		
<i>S. obliquus</i>	Langmuir	$q_m = 112 \text{ mg g}^{-1}$		[45]
	Freudlich	$K_f = 22.35 \text{ (mg g}^{-1}) \text{ (L mg}^{-1})^{1/n}$ $1/n = 0.768$		
	D – R	$\beta = -0.64 \times 10^{-8} \text{ mol}^2 \text{J}^{-2}$ $q_m = 31.6 \text{ mmol/g}$ $E_a = 8.84 \text{ kJ/mol}$		
Modified <i>S. obliquus</i>	Langmuir	$q_m = 207.2 \text{ mg g}^{-1}$	[46]	
	Freudlich	$K_f = 78.10 \text{ (mg g}^{-1}) \text{ (L mg}^{-1})^{1/n}$ $1/n = 0.6019$		
	D – R	$\beta = -0.46 \times 10^{-8} \text{ mol}^2 \text{J}^{-2}$ $q_m = 24.9 \text{ mmol/g}$ $E_a = 10.44 \text{ kJ/mol}$		
Lentil husk	Langmuir	$q_m = 81.43 \text{ mg g}^{-1}$	[46]	

<i>Anabaena sphaerica</i>	Langmuir	$q_m = 121.95 \text{ mg g}^{-1}$	[47]
	Freundlich	$K_f = 28.28 \text{ (mg g}^{-1}) \text{ (L mg}^{-1})^{1/n}$ $1/n = 0.2631$	
	D – R	$\beta = - 0.2433 \times 10^{-8} \text{ mol}^2\text{J}^{-2}$ $q_m = 1.104 \text{ mmol g}^{-1}$ $E_a = 14.3 \text{ kJ/mol}$	
<i>Salvinia natans</i> (at temperature = 15°C)	Langmuir	$q_m = 0.614 \text{ mmol g}^{-1}$	[48]
	Freundlich	$K_f = 0.439 \text{ mmol g}^{-1}$ $n = 2.964$	
	D – R	$\beta = - 0.022 \times 10^{-5} \text{ mol}^2\text{J}^{-2}$ $q_m = 0.508 \text{ mmol/g}$ $E_a = 4.814 \text{ kJ/mol}$	
<i>Salvinia natans</i> (at temperature = 30°C)	Langmuir	$q_m = 0.295 \text{ mmol g}^{-1}$	[48]
	Freundlich	$K_f = 0.245 \text{ mmol g}^{-1}$ $n = 4.204$	
	D – R	$\beta = - 0.015 \times 10^{-5} \text{ mol}^2\text{J}^{-2}$ $q_m = 0.301 \text{ mmol/g}$ $E_a = 5.814 \text{ kJ/mol}$	
<i>Mimusops elengi</i> leaves	Langmuir	$q_m = 15.408 \text{ mg g}^{-1}$	[49]
	Freundlich	$K_f = 1.392 \text{ mg g}^{-1} \text{ (mg g}^{-1})^{1/n}$ $1/n =$	
	Redlich–Peterson	$A = 5.805 \text{ L/g};$ $B = 3.261 \text{ L/mg}$	
	Temkin	$A_T = 2.03 \text{ L/mg};$ $b_T = 865.71$	
<i>Jatropha curcas L.</i> seed husk ash	D – R	$\beta = 0.0099 \text{ mol}^2\text{kJ}^{-2}$ $q_m = 29.18 \text{ mg/g}$ $E_a = 7.106 \text{ kJ/mol}$	[49]
	Langmuir	$q_m = 263.1 \text{ mg g}^{-1}$	
<i>Jatropha curcas L.</i> seed husk ash	Langmuir	$q_m = 263.1 \text{ mg g}^{-1}$	[57]

VI. THERMODYNAMICS OF ADSORPTION

In order to assert the thermodynamic nature of lead biosorption, several basic parameters including change in free energy (ΔG^0), enthalpy (ΔH^0), entropy (ΔS^0) were found by researchers by the following formula.

$$\Delta G^0 = -RT \ln K \quad (12)$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (13)$$

Where T is the temperature (Kelvin, K); R is the ideal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and K is the thermodynamic equilibrium constant. According to the equation 12 and 13, ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the plot of $\ln(K)$ versus $1/T$ respectively. The thermodynamic equilibrium constant is the ratio of the amount of adsorbate (mg) adsorbed per litre to the equilibrium concentration of the adsorbate in mg/L.

Negative ΔG^0 indicates thermodynamic feasibility and spontaneity of the biosorption process. The magnitude of ΔH^0 indicates whether the biosorption is physical or chemical. The heat of adsorption for a physical reaction is around $2.1 - 20.9 \text{ kJmol}^{-1}$ and the energy of activation for chemical reaction (E_a) is in the range of $20.9 - 418.4 \text{ kJmol}^{-1}$ [37]. ΔS^0 indicates the randomness during biosorption.

C. interruptus [38] could biosorb lead chemically while peanut shells [15] and *M. elengi* leaves [49] manifested physical biosorption. Rice husk ash [24] and *P. americana* [28] were found to exhibit both physico-sorption and chemisorption process, exothermally and spontaneously, while the biosorption of lead by maize stover [40], *S. melongena* leaf powder [42], corn husk [37] and *S. ilicifolium* [51], was found to be spontaneous and endothermic.

CONCLUSION

The removal of lead by various biosorbents has been reviewed. The major demerits of conventional heavy metal removal techniques are high cost, low removal efficiency, increased chemical and biological effluent sludge, additional chemical requirements for regeneration of adsorption medium and difficulty in biosorbent recovery. Thus by using biosorbents, the problems caused by the conventional treatments can be minimized and the process can be performed in an environmental friendly way.

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