Biosorption the Possible Alternative to Existing Conventional Technologies for Sequestering Heavy Metal Ions from Aqueous Streams: A Review

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Abstract:

Transition metal ions in industrial effluent discharge are of great threat to the environment. Several conventional treatment technologies viz., ion exchange, membrane separation, ultra-filtration, ion flotation, electro-coagulation, electrodialysis, sedimentation and reverse osmosis have been employed. However these methods involve high operating cost and produce large volume of toxic chemical sludge. In this context, biosorption process could be helpful and is emerging as a potential alternative to the existing technologies for the removal and recovery of metal ions from aqueous solutions. The major advantages of biosorption over conventional treatment methods include high efficiency, minimization of chemical sludge, low cost in regeneration of biosorbents and possibility of metal recovery. Agricultural waste materials being cellulosic are an excellent source for metal biosorption. They have different functional groups viz. hydroxyl, carboxyl, phenolic, amino, acetamido etc. having affinity for metal ions to form chelates and metal complexes. The mechanism of biosorption process includes chemisorption, complexation, diffusion, ion exchange, micro precipitation and surface adsorption. The aim of this review article is to provide the information on biosorption as a possible alternative to other conventional technologies and to highlight the chemical composition of agricultural waste material along with adsorption models and mechanism for metal biosorption.

1.0 Introduction:

Massive industrial pollution and uncontrolled population growth in India is a serious threat to the environment in one or the other way (Amirez et al., 2007; Gadd, 1990). The aqueous bodies viz., rivers, streams, ponds are rich with toxic metal ions such as mercury, lead, cadmium, zinc etc. above the prescribed limits, thus leading to various health hazards and environmental degradation (Table 1). The removal of the above mentioned metal contaminants from aqueous waste streams is currently one of the most important environmental issues being investigated. Environmentalists are primarily concerned with the presence of heavy metals due to their high toxicity, carcinogenic or mutagenic effects, bioaccumulation and subsequent magnification making them unavoidable even at very low concentrations (Barros et al., 2007; Preetha and Viruthagiri, 2007).

Several treatment technologies have been developed to remove heavy metal ions from industrial wastewaters and other effluents. These include membrane processing, evaporation, chemical precipitation, coagulation, ion exchange, electrolytic and adsorption (Gadd, 1990; Feng et al., 2004). However all these methods involve high operating cost and may produce large volume of sludge which creates further disposal problem. In this context, adsorption process could be helpful for the removal of toxic metal ions. The major advantages of adsorption over conventional treatment methods include: low-cost; high efficiency; minimization of chemical sludge; regeneration of biosorbent and possibility of metal recovery (Sud et al., 2008). However the high cost of activated carbon and its loss during regeneration restricts its application. Since 1990's adsorption of heavy metal ions by low cost renewable organic materials has gained momentum. The utilization of seaweeds, moulds, yeasts, dead microbial biomass and agricultural waste materials for removal of heavy metals has been explored (Bailey et al., 1999; Haung et al., 1996; Sudha and Abraham, 2003; Zhou

and Kiff, 1991). Recently, attention has been diverted towards the byproducts or the residues from agriculture and food industry.

Agricultural residues are usually composed of lignin and cellulose as the major constituents with other polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids and ethers that facilitate metal complexation resulting biosorption of heavy metal ions (Hashem et al., 2005b; Hashem, 2007) from wastewaters. Agricultural waste materials are economical, ecofriendly and have unique chemical composition. They being abundantly available, renewable, low in cost and more efficient seem to be viable option for heavy metal remediation. The removal of heavy metal ions using various agricultural wastes is shown in Table 2.

Table 1: Tolerable limits of different heavy metal ions present in industrial effluent discharge and their health hazards

Metal Ions	Tolerable limits by International bodies (mg/L)		Tolerable limits by Indian Standards (mg/L) 2490 (1974)	Health Hazards
	WHO	USEPA		
Arsenic	0.01	0.05	0.20	Abdominal pain, diarrhea, excessive salivation, headache, vertigo, fatigue, paralysis, kidney failure, progressive blindness, and mental impairment.
Cadmium	0.003	0.005	2.00	Cadmium may promote skeletal demineralization, increase bone fragility and fracture risk, lung fibrosis, and weight loss.
Chromium	0.05	0.1	0.10	Causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems.
Copper	_	1.3	3.0	Long term exposure causes irritation of nose, mouth, eyes, headache, stomachache, dizziness and diarrhoea.
Lead	0.01	0.05	0.10	Gastrointestinal complaints, hypertension, fatigue, hemolytic anemia, abdominal pain, nausea, constipation, weight loss, peripheral neuropathy, cognitive dysfunction, loss of libido and depression.
Mercury	0.001	0.002	0.01	Excessive salivation, gingivitis, gum recession, tremors, stomach and kidney troubles, dermatitis, anorexia and severe muscle pain.
Nickel	_	_	3.0	Causes chronic bronchitis, reduced lung functions, cause of lung cancer and nasal sinus.
Zinc	_	_	5.0	Causes short-term illness called ''metal fume fever'' and restlessness.

Table 2: Different agricultural wastes as biosorbent for the removal of heavy metal ions from aqueous solutions

Adsorbent	Metal ion removed	References
Hazelnut shells	Co(II)	Demirbas (2003)
Peanut hull	Cu(II)	Johnson et al.(2002)
Red fir	Cu(II), Cr(VI)	Bryant et al. (1992)
Maple sawdusts	Cu(II), Pb(II)	Bin (1995)
Pinus bark	Cu(II)	Ajmal et al. (1998)
Different bark samples	Cd(II)	Freer et al. (1989), Vazquez et al. (1994), Al-Asheh and Duvnjak (1997), Aoyama et al. (1993)
Palm kernel husk	Pb(II), Zn(II)	Omgbu and Iweanya (1990)
Hazelnut shell activated carbon	Ni(II)	Demirbas et al. (2002)
Coconut husk	Zn(II), Cd(II)	Babarinde (2002)
Peanut skins	Cu(II)	Randall et al. (1975)
Modified cellulosic materials	Cu(II)	Acemıoglu and Alma. (2001)
Chemically modified cotton	Hg(II)	Roberts and Rowland (1973)
Corncobs	Cu(II)	Hawrhorne-Costa (1995)
Rice hulls	Cr(VI)	Low et al. (1999)
Waste tea leaves	Ni (II), Pb (II), Fe (II), Zn (II)	Ahluwalia and Goyal (2005a)
Bark	Hg(II)	Deshkar and Dara (1988)
Tea leaves	Pb(II), Cd(II), Zn(II)	Tee and Khan (1988)
Modified lignin	Cr(III), Cr(VI)	Demirbas (2004) and Demirbas (2005)
Modified sugar beet pulp	Ni(II), Cu(II)	Reddal et al. (2002)
Modified sunflower stalk	Hg(II)	Hashem et al. (2006)
Wheat bran Cd (II)	Cd(II)	Singh et al. (2005)

2.0 Various Technologies Used Till Date vs. Biosorption:

Different technologies as mentioned in the introduction have been used till date to remove polluting metal ions from aqueous streams. These processes have their own merits and demerits as mentioned in Table 3. The long list of demerits against each process leads to the search for new cost effective technology which directs towards biosorption process.

Biosorption is phenomenon in which the non living agricultural biomass binds and concentrate metals ions from even very dilute aqueous solutions. Biomass exhibits this property, acting just as chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of the biomass which was found responsible for the phenomenon. (Ravikumar et al., 2005; Allen et al., 2005; Mittal et al., 2005). Moreover the metal can

be desorbed readily and then recovered if the value and amount of metal recovered are significant and if the biomass is plentiful, metal-loaded biomass can be incinerated, thereby eliminating further treatment. The biosorption is easy to understand when it refers to a single metal solution however in a multi metal situation which is generally encountered in industrial effluents the assessment of sorption becomes complicated. Besides these plus points, biosorption has certain disadvantages such as (i) early saturation of the biosorbents i.e. when metal interactive sites are occupied, metal desorption is must prior to further use; (ii) the potential for biological process improvement (e.g. through genetic engineering of cells) is limited because cells are not metabolizing; and (iii) there is no potential for biologically altering the metal valency state (Das et al., 2008). Biosorption efficiency depends upon many factors, including the capacity, affinity and specificity of the biosorbents and their physical and chemical conditions in effluents.

Table 3: Merits and demerits of different treatment technologies for the biosorption of heavy metals from aqueous systems

Technology	Merits	Demerits	Reference
Membrane Filtration	Low solid waste generation Low chemical consumption Small space requirement Metal selective method	Valid at room temperature. At elevated temperature membrane deterioration can be rapid Various types of polyamide TFM exhibit significant differences in stability at low pH High initial capital cost High maintenance and operation costs Membrane fouling and limited flow-rates	Madaeni and Mansourpanah, 2003
Electrochemical Treatment	Applicable for the treatment of very toxic wastes. Valid at room temperature and atmospheric pressure. Run by electricity and easy to operate.	High initial capital, maintenance and operation cost Needs continuous supply of electricity	Qin et al. 2002, Kongsricharoern and Polprasert, 1995
Flotation	Metal selective Low retention times Removal of small particles	High initial capital, maintenance and operation cost	Kongsricharoern, and Polprasert, 1996
Coagulation–Flocculation	Bacterial inactivation capability Good sludge settling and dewatering characteristics	Much chemical consumption Large volume sludge	Rubio et al., 2002
Chemical Precipitation	Process simplicity Applicable to different metals Low capital cost	Large volume sludge formation High sludge disposal and maintenance cost	Rubio et al., 2002
Ion exchange	Metal selective Limited pH tolerance High regeneration capacity	High initial capital and maintenance cost	Rubio et al., 2002
Adsorption	Wide variety of target pollutants High capacity and fast kinetics Possibly selective depending on adsorbent	Performance depends on type of adsorbent Needs chemical modification to improve its sorption capacity	Aderhold et al., 1996

3.0 Composition of Agricultural Residues:

Agricultural residues are usually composed of cellulose, and lignin as the main constituents. Other components are hemicellulose, lipids, proteins, simple sugars, starches, water, hydrocarbons, and many more compounds that contain a variety of functional groups present in the binding process. Agricultural residues particularly those containing cellulose and lignin show potential metal biosorption capacity. Cellulose is a polysaccharide made up of β-D-glucose molecules. The cellulose chain bristles with polar -OH groups. These groups form many hydrogen bonds with OH groups on adjacent chains, bundling the chains together. The chains also pack regularly in places to form hard, stable crystalline regions that give the bundled chains even more stability and strength. Lignin is an aromatic three-dimensional polymer with apparent infinite molecular weight and is covalently linked with xylans in the case of hardwoods and with galacto glucomannans in softwoods. Molecular weight of the polymeric lignin changes from 2000 to 15,000 g/mol (Mantanis, Young and Rowell, 1995) These properties of lignin and cellulose reveal that they have potential to be used as possible adsorption material to remove heavy metal ions from wastewaters. Unlike cellulose, hemicelluloses consist of different monosaccharide units. In addition, the polymer chains of hemicelluloses have short branches and are amorphous. Because of the

amorphous morphology, hemicelluloses are partially soluble in water. Hemicelluloses are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. Hemicelluloses are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micells and fiber (Theander et al., 1985).

4.0 Mechanism of Metal Biosorption Studies:

The biosorption process involves interaction between the biosorbent (solid phase) and a solvent (liquid phase) containing the dissolved species to be sorbed. This phenomenon can be explained by different mechanisms viz., complexation, chemisorption, adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces etc. (Sud et al., 2008). The biosorption continues till equilibrium is maintained between the amount of sorbed species and its portion remaining in the solution. The extent of biosorbent affinity for the dissolved species determines its distribution between the solid and liquid phase. Among the different species dissolved in the liquid phase, metal biosorption is a two-step process, where the first step involves a stoichiometric interaction between the metal ions and the reactive functional groups forming monolayer on the cell wall and the second step is an inorganic deposition of increased amounts of metals.

As mentioned above, agricultural residues possess cell walls made up of cellulose, hemicellulosic materials, lignin, and pectin with small amounts of protein. (Demirbas, 2008). Cellulose molecules collectively form microfibrils and water containing dissolved species can filter through the microfibrils along with hemicellulose and lignin. The dissolved species get entrapped into these microfibrils forming complexes and resulting the desalination of the liquid phase. Along with this entrapment, the several functional groups present in the biomass have the affinity for metal complexation. Some biosorbents are non-selective and bind to a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals depending upon their chemical composition (Demirbas, 2008).

Bin, 1995 suggested ion-exchange mechanism for the removal of copper by adsorption on sawdust where divalent heavy metal ion (M^{2+}) attaches itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution. There are different parameters which govern the biosorption process such as pH, flow rate, adsorbent dose, and initial metal ion concentration. Among these mentioned parameters, pH is one of the most dominating parameter. pH of the liquid phase describes the fate of the dissolved species to be biosorbed on the solid phase. Every metal has a specific pH at which its adsorption is maximum. For example, Cr (VI) is adsorbed at pH around 2.0, Cu (II) around 4.0-5.0, Ni (II) between 6.0-7.0, Zn (II) 4-5, Hg (II) at nearly 6.0.

Further, Pehlivan and Altun, 2007 suggested electrostatic mechanism for Cr (VI) biosorption from aqueous solution using hazelnut, walnut and almond shell. They showed that there was increase of Cr (VI) sorption at acidic pH which was attributed to the electrostatic attraction between positively charged groups of biomaterial surface and the $HCrO_4^-$ anion which is dominant species at constant pH. Moreover, the decrease of sorption with increase of pH was due to decrease of electrostatic attraction and to the competitiveness between chromium anionic species ($HCrO_4^-$ and CrO_4^-) and OH^- ions in the bulk for the adsorption on active sites of the sorbent. For anions, electrostatic interaction plays an important role in allowing the approach of the ions to the sorbent surfaces. In this study $HCrO_4^-$ and $Cr_2O_7^{2-}$ anions account for about 80 and 20%, respectively. At pH 4, the sorbent surface is positively charged due to protonation, while the sorbate, dichromate ion, exists mostly as an anion leading to the electrostatic attraction between sorbent and sorbate. Park et al., 2008 suggested both direct and indirect reduction mechanisms for the removal of Cr (VI) from aqueous solutions by using banana skin. In direct reduction mechanism, Cr (VI) was directly reduced to Cr (III) in the aqueous phase by contact with electron-donor groups of banana skin, and the reduced Cr (III) remained in the aqueous phase or formed complexes with Cr-binding groups of it. Indirect reduction mechanism consisted of three steps; (i) the binding of anionic Cr(VI) to positively charged groups present on the surface of banana skin, (ii) the reduction of Cr(VI) into Cr(III) by adjacent electron donor groups, and (iii) the release of the reduced-Cr(III) into the aqueous phase due to electronic repulsion between the positively-charged groups and the Cr(III), or the complexation of the reduced-Cr(III) with adjacent groups, i.e., Cr-binding groups.

5.0 Kinetic Models:

Kinetics of metal sorption governs the rate that determines the residence time and it is one of the important characteristics defining the efficiency of an adsorbent. Sorption kinetics can be controlled by several independent processes that could act in parallel or in series such as external mass transfer (film diffusion), bulk diffusion, intraparticle diffusion and chemisorptions (chemical reaction). Film transport is the diffusion of heavy metals through boundary around biosorbent whereas bulk diffusion is transport of metal ions in solution. Chemisorption is the chemical reaction between active sites of biomass and heavy metal ions and intraparticle diffusion is the diffusion of metals from the surface to internal sites. Pseudo first order and pseudo second order, Elovich equation and intraparticle diffusion model have been extensively used by different authors to explain the kinetics of biosorption, and details of the models are mentioned Table 4.

Table 4: Different kinetic models used

Model	Equation	Parameters	Reference
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \dfrac{k_1}{2.303}t$	q_t (mg g^{-1}) = amount of adsorbate adsorbed at time t, k_1 (min^{-1}) = pseudo-first-order rate constant	Chowdhury and Saha, 2010
Pseudo-second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{1}{q_e}t$	k_2 (g mg^{-1} min^{-1}) = pseudo-second-order rate constant	Chowdhury and Saha, 2010
Elovich	$\dfrac{dq_t}{dt} = \alpha e^{-\beta q_t}$	α mg (g.min)$^{-1}$ = Initial adsorption rate β (g mg^{-1}): Desorption constant	Ho and McKay, 1998
Intraparticle-diffusion	$q_t = k_i t^{0.5}$	k_i (mg g^{-1} min) = intraparticle diffusion rate constant	Chowdhury and Saha, 2010

6.0 Adsorption Equilibrium Models:

The preliminary testing of solid liquid adsorption system is based on basically two types of investigation: i) equilibrium batch studies and ii) dynamic continuous flow sorption studies. Isotherm adsorption models have been used in waste stream treatment to predict the ability of a certain adsorbent to remove a pollutant down to a specific discharge value. When a mass of adsorbent and a waste stream are in contact for a sufficiently long time, equilibrium between the amount of pollutant adsorbed and the amount remaining in solution will develop. For any system under equilibrium conditions, the amount of material adsorbed onto the media can be calculated using the mass balance of Eq. (1):

$$\frac{X}{M} = (C_o - C_e)\frac{V}{M} \qquad (1)$$

where X/M (typically expressed as mg pollutant/g adsorbent) is the mass of pollutant per mass of adsorbent, C_o is the initial pollutant concentration in solution, C_e is the concentration of the pollutant in solution after equilibrium has been reached, V is the volume of the solution to which the adsorbent mass is exposed, and M is the mass of the adsorbent.

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Langmuir (Langmuir, 1916) or Freundlich (Freundlich, 1906) isotherms.

6.1 Langmuir and Freundlich Models:

The general Langmuir model can be defined by Eq. (2):

$$\frac{X}{M} = \frac{K_L C_e}{1 + a_L C_e} \qquad (2)$$

were K_L and a_L are the isotherm constants and their values can be determined using linear regression analysis. The Langmuir isotherm can be linearized to the following equation 3

$$\frac{1}{X/M} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} \qquad (3)$$

The Freundlich model can be defined by equation (4) as under:

$$\frac{X}{M} = K_F (C_e)^{1/n} \qquad (4)$$

The Freundlich isotherm can also be linearized by the following equation (5) :

$$In(\frac{X}{M}) = InK_F + \frac{I}{n}InC_e \qquad (5)$$

where K_F and n are adsorption capacity and affinity, respectively.

The Langmuir and Freundlich isotherm models are only applicable to batch studies where sufficient time is provided to allow equilibrium between the pollutant in solution and the pollutant adsorbed on the media to occur. During the flow through the adsorbent, many of the pollutants are expected to come into contact with active surface sites and thus be retained on the surface of the adsorbing media.

6.2 The Bed Depth-Service Time (BDST) Model:

This model is based on the Bohart and Adams quasi-chemical rate law. The assumption behind the equation (Bohart and Adams Equation, 1920) is that equilibrium is not instantaneous and therefore, the rate of the sorption reaction is proportional to the fraction of sorption capacity still remaining on the media. The linearized BDST model equation is as follows (McKay, 1996; Goel et al., 2005).

$$t_b = \frac{N_o}{1000\varepsilon v C_o}D - \frac{1}{kC_o}In\left(\frac{C_o}{C_b}-1\right) \qquad (6)$$

where t_b is the time until breakthrough (min), C_o is the initial concentration of pollutant (mg/L), C_b is breakthrough concentration of pollutant (mg/L), v is the fluid velocity or loading rate (m/min), ε is the porosity of the filter, k is quasi-chemical rate constant from Bohart and Adams theory (L/mg s), N_o is capacity of the media for each pollutant in a multi-component solution (mg pollutant per cubic meter of filter volume), and D is depth of the filter bed.

Several empirical models proposed in the literature (Bohart–Adams,Yoon, Nelson, Clark and Wolborska models) were investigated in order to obtain the best fit of column data, describing in a simple manner the breakthrough curves (Lodeiro et al., 2006)

6.3 Thomas Model:

It is one of the most general and widely used models to explain the column performance theory. The Thomas model (Thomas, 1944) assumes the Langmuir kinetics of sorption and desorption, with no axial dispersion. It assumes that the rate driving force in sorption obeys second order reversible reaction kinetics.

The expression by Thomas for an adsorption column is given as follows:

$$\frac{C_e}{C_o} = \frac{1}{1+\exp\left(\frac{k_{TH}q_e s}{R} - k_{TH}C_e t\right)} \qquad (7)$$

Where k_{TH} is the Thomas rate constant (mLmin^{-1}mg^{-1}), q_e the equilibrium metal uptake per gram of the adsorbent (mgg^{-1}), s the amount of adsorbent in gram in the column, C_o and C_e are the influent and the effluent concentrations (mgL^{-1}) of the metal, respectively at time t (min), $t=V_{eff}/R$ where V_{eff} is the effluent volume (mL) and R is the flow rate (mLmin^{-1}).

6.4 Yoon and Nelson Model:

This is a relatively simple model based on the assumption that the rate of decrease in the probability of sorption for each sorbate molecule is proportional to the probability of sorbate sorption and sorbate breakthrough on the sorbent (Yoon and Nelson, 1984). The equation for the 50% breakthrough concentration from a fixed bed of sorbent is

$$In\left(\frac{C}{C_o - C}\right) = k_{YN}t - t_{0.5}k_{YN} \qquad (8)$$

where k_{YN} is the Yoon-Nelson rate constant (min^{-1}). The values of k_{YN} and $t_{0.5}$ can be obtained from the slope and intercept, respectively, of a liner plot of ln[$C/(C_0 - C)$] versus t.

6.5 Clark Model:

Clark used the mass-transfer coefficient in combination with the Freundlich isotherm (Clark, 1987) to define a new relation for the breakthrough curve as

$$\frac{C}{C_o} = \left(\frac{1}{1+Ae^{-n}}\right)^{1/n-1} \qquad (9)$$

with

$$A = \left(\frac{C_o^{n-1}}{C_b^{n-1}} - 1\right)e^{rt_b} \qquad (10)$$

and

$$r = \frac{\beta}{U}v_m(n-1) \qquad (11)$$

where n is the Freundlich constant, C_b is the concentration of sorbate at breakthrough time t_b (mg/dm^3), and v_m is the migration velocity of the

concentration front in the bed (cm/ min). v_m can be determined from the relationship shown in equation(12) as:

$$v_m = \frac{UC_o}{N_o + C_o}$$ (12)

Equation (12) can be rearranged to the following linear form

$$In\left[\left(\frac{C_o}{C}\right)^{n-1} - 1\right] = -rt + InA$$ (13)

For a particular sorption process in a fixed bed with a chosen treatment objective, the values of *A* and *r* can be determined by using the above equation, thereby enabling the prediction of the breakthrough curve.

6.6 Wolborska Model:

Wolborska deduced the following relationship (Wolborska, 1989) for describing the concentration distribution in a bed for the low-concentration range of the breakthrough curve by equation (14)

$$In\frac{C}{C_o} = \frac{\beta C_o}{N_0}t - \frac{\beta Z}{U}$$ (14)

where β is the kinetic coefficient of external mass transfer (min^{-1}) and the other symbols have their usual meanings. The values of β and N_0 can be determined from a plot of $\ln(C/C_0)$ versus *t* at a given *Z* and *Q*

7.0 Biosorption thermodynamics:

The spontaneity of the biosorption process can be decided by several thermodynamic parameters viz., Gibb's free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°). These thermodynamic parameters can be calculated using the following equations.

$$\Delta G^\circ = -RT \; In \; K_d$$ (15)

where *R* is the gas constant (8.314 Jmol^{-1} K^{-1}), *T* is the temperature (K), and K_d is the equilibrium constant. The value of K_d was calculated using equation (16).

$$K_d = \frac{q_e}{C_e}$$ (16)

where q_e and C_e are the equilibrium concentrations of metal ions on the adsorbent and in the solution, respectively. The enthalpy change (ΔH°) and entropy

change (ΔS°) of biosorption were calculated from the following equation (17).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$ (17)

The equations (15) and (17) can be combined together as:

$$InK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$ (18)

A plot between InK_d versus $1/T$ would give the values of the ΔH° and ΔS° from slope and intercept, respectively and the values of ΔG° were calculated from Equation (17). The negative values of ΔG° supports the spontaneity of the biosorption process while the positive value of ΔH° indicate that same process is endothermic in nature. The observed values of ΔH° could be used to predict the type of biosorption, viz., physical or chemical. The value of ΔH° < 4.2 kJmol^{-1} indicate the physical adsorption process while a value of ΔH° > 21 kJmol^{-1} for the same indicate the chemical adsorption process (Ucan, 2008). Further, the positive value of ΔS° supported that randomness at the solid/liquid interface increases during the biosorption of metal ions on the biosorbent.

8.0 Conclusion:

In this review, the importance of adsorption over other technologies have been studied and it has been concluded that adsorption using low cost natural and waste biomasses constitutes the basis for a new cost effective technology that can find its largest application in the bioremediation of heavy metals from industrial effluents. Application aspects of biosorption are being aimed at biosorption process optimization. Mathematical models are helpful in this regard to guide further experimental work and provide predictions of the biosorption process under different operating conditions. The process of biosorption requires further investigation in the direction of modeling, regeneration of biosorbent, recovery of metal ions, immobilization of the waste materials in order to make the process economic viable at industrial scale with focus for enhanced efficiency and recovery.

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