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REVIEW ARTICLE

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A REVIEW OF RECENT RESEARCH WORKS ON THE DESIGN OF BATCH ADSORPTION SYSTEMS FOR HEAVY METAL REMOVAL USING AGRICULTURAL BIOSORBENTS

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ABSTRACT
Water bodies are major sites of heavy metal deposits. Heavy metals are toxic to humans and animals. Due to rapid industrialization the rate at which heavy metal bearing effluents are discharged into the environment and water bodies has been on the increase. In this review agricultural biosorbents are discussed in detail. Low cost and high efficiency are the advantages in using adsorbents of bio origin. The present work represents a review of the recently published literature discussing the use of agricultural biosorbents for the removal of heavy metals from waste water. The potential health hazards of heavy metals and the factors affecting biosorption are discussed in detail. The kinetic and isothermal models usually assessed to fit the biosorption experimental data are also discussed. It can be concluded that Agricultural biosorbents show great scope for developing clear, cheap and highly effective process for heavy metal removal from waste water.
Keywords: biosorbents, heavy metals, operating parameters, kinetic models, isotherms.

INTRODUCTION

Today, heavy metals are a major group of substances of environmental concern. The toxicity to human and animal lives is the reason for this concern. There is a rapid increase in the discharge of these heavy metal bearing effluents into the environment and water bodies due to rapid industrialization[1]. Since streams and rivers flow through agriculture areas where pesticides and fungicides may have been used and through industrial areas where there may have been many metal waste deposits and direct discharge of effluents into waterbodies, water bodies are a major site for heavy metal deposits[1,2]. It is imperative to bring about applicable solutions to deal with this problem of toxic heavy metal pollution in the environment. Ion exchange, chemical precipitation, coagulation and bioremediation and sorption/adsorption are some treatment technologies known to date[3, 4, 5].Out of the available techniques adsorption is the technique that is widely accepted by all. Adsorption is preferred because of its handling ease, cost effectiveness and superior efficiency as well as availability of different adsorbents.

Recently, the focus is on the use of biosorbents which are derived from agricultural materials. Low cost and high efficiency are the advantages in using adsorbents of bio origin[6]. Table 1 shows some details of the metals, their sources and health hazards associated.

Table 1. Heavy metals, sources and health hazards.

Metal	Sources	Health Hazards
[11,12] Pb^{2+}	Manufacturing of batteries, pigments electroplating, ammunition	Anemia, brain damage, anorexia, malaise, loss of appetite.
[8,9,11,13] Cd^{2+}	Electroplating, smelting, alloy manufacturing, pigments, plastic and mining	Itai-Itai disease, carcinogenic, renal disturbances, lung insufficiency, bone lesions, cancers, hypertension, weight loss.
[14,19] Cu^{2+}	Electronics plating, paint manufacturing, wire drawing , copper polishing and printing operations	Reproductive and developmental toxicity, neurotoxicity and acute toxicity, dizziness, diarrhea.
[7,15] As^{3+}, As^{5+}	Smelting ,mining, energy production from fossil fuels, rock sediments	Bone marrow depression, haemolysis, liver tumors, gastrointestinal symptoms, cardiovascular and nervous system functions disturbances.
[15,16] Cr^{6+}, Cr^{3+}	Electroplating, paints and pigments , metal processing, steel fabrication and canning industry	Epigastric pain, nausea, vomiting severe diarrhea, lung tumors, carcinogenic, mutagenic, teratogenic.
[10,18] Hg^{2+}	Volcanic eruptions, forest fires, battery	Corrosive to skin, eyes, muscles, neurological and renal disturbances.
[17] Ni^{2+}	Copper sulphate manufacture, electroplating, non ferrous metal, mineral processing.	Reduced ling function, lung cancer, chronic bronchitis, dermatitis, chronic asthma.
[15,16,18] Zn^{2+}	Mining and manufacturing processes.	Causes short term "metal-fume fever", gastro intestinal distress, nausea and diarrhea.

Adsorption of heavy metals using biosorbents are reported to occur through the interaction of metals with some functional groups of the biosorbent. However, the efficiency of such interaction is dependent on the available binding sites and the binding strength[18].Agricultural materials are a good source of biosorbents as their efficiencies are good and they reduce the agro-wastes management problems[19].Agro-materials usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes aldehydes,alcohols, ketones, phenolic,carboxylic, and ether groups[19].

Many research articles published in the recently reported the successful use of different kinds of agricultural materials in the removal of heavy metals.

2. Adsorbents of Bio-origin.

The use of Acacia leucocephala bark powder as an effective, low cost, and environmental friendly biosorbent for the removal of Cu (II), Cd (II), Pb(II) ions was reported by Munagapati et al.[20](2010), Reddy et al.,[21](2011) found that Moringa oleifera bark is very effective for the removal of Ni(II) from aqueous solutions. Ghodbane et al[22]., (2007) studied the effectiveness of eucalyptus bark as an inexpensive adsorbent for removing Cd (II) ions from aqueous solutions. The Triticum aestivum straw powdered has been examined by Farooq et al[23]., (2011) for Cd (II) removal. Han et al[24]., (2013) have investigated rice straw for Cd (II) removal from water.

Unmodified spent oil palm shell, a waste from palm oil industry has been examined for adsorption of Cu (II) and Pb (II) ions by Chong et al[25]., (2013). Antimony (III) was removed using green bean husk as an adsorbent. This study was done by Iqbal et al[26]., (2013).Montanher et al[27]., (2005) evaluated rice bran for its potential use as a biosorbent for Cd (II), Cu (II), Pb (II) and Zn (II). Low et al[11]., (2000) studied the use of spent grain, a byproduct of the brewing industry as an adsorbent to remove Cd(II) and Pb(II).

Saif et al[28]., (2012) investigated adsorption using Strychnos Potatorum seeds to remove Cd (II). Removal of Pb(II), Cu(II), Cd(II),Ni(II), As(II), Mn(II) and Zn(II) by Moringa oleifera seeds was examined by Obuseng et al[29]., (2012). Martins et al[30]., studied the effectiveness of castor leaf powder as adsorbent to remove Cd(II) and Pb(II) from contaminated water. The adsorptive ability of Ficus Carcia leaves for the removal of Cadmium (II) and Lead (II) ions from aqueous solutions was investigated by Farhen et al[31]., (2013). Recently, extensive studies on Cd (II) adsorption taking powdered leaves of a variety of trees have been carried out by Pandey et al[32]., (2008).

3. Factors affecting Biosorption:

The different operating parameters such as pH, biosorbent dosage, initial pollutant concentration, temperature, agitation speed, biosorbent size and their effects on the biosorption capacity are summarized in Table 2 [33](Chojnacka 2010).

Table 2.Effects of the major factors effecting biosorption of Heavy metals:

Factors	Effect
Solution pH	It enhances biosorptive removal of Cationic metals, but reduces that of anionic metals.
Biosorbent dosage	It decreases the quantity of biosorbed pollutant per unit weight of biosorbent, but increases its removal efficiency.
Initial pollutant concentration	It increases the quantity of biosorbed pollutant per unit weight of biosorbent, but decreases its removal efficiency.
Temperature	It usually enhances biosorptive removal of adsorptive pollutant by increasing surface activity and kinetic energy of the adsorbate, but may damage physical structure of biosorbent.
Agitation speed	It enhances biosorptive removal rate of adsorption pollutant by minimizing its mass transfer resistance, but may damage physical structure of biosorbent.
Ionic strength	It reduces biosorptive removal of adsorptive pollutant by competing with the adsorbate for binding sites of biosorbent.
Biosorbent size	It is favourable for batch process due to higher surface area of the biosorbent, but not for column process due to its low mechanical strength and clogging of its column.
Other pollutant concentration	If coexisting pollutant competes with a target pollutant for binding sites or forms any complex with it, higher concentration of other pollutants will reduce biosorptive removal of the target pollutant.

4. Biosorption Kinetics

Identifying optimum operating conditions is very important to conduct full scale batch processes and this is obtained by conducting the kinetic studies[34]. The sorption kinetics in the treatment of wastewater provides valuable insights into the mechanics and reaction pathways of sorption reactions[35]. The various kinetic models that are applied to fit the biosorption data of different heavy metals onto various biosorbents are Pseudo first order, Pseudo second order, Elovich, intraparticle diffusion etc.,

The two criterions that determine the suitability of a model to fit the experimental data are one, the correlation coefficient (R^2) and the other the calculated q_e value. If the model's R^2 approaches unity and its q_e calculated is equal to q_e experimental, then the model gives the best fit to the experimental data. The intraparticle diffusion model suggested by Weber and Morris suggests proportionality between the adsorption capacity and the square root of the time[36]. If the plot of f q_t versus $t^{0.5}$ gives a straight line, then the adsorption process is controlled by intraparticle diffusion only[37].

5. Equilibrium adsorption isotherms:

The sorption isotherms explain the adsorbent, adsorbate relationships well[38].The Langmuir isotherm model suggests that once a site is filled no further sorption can take place in that site[39]. The Langmuir equation is explained well by Langmuir et al.,(1918).The Freundlich isotherm model applies for adsorption on heterogeneous surfaces[40]. The Freundlich equation is discussed well by Freundlich et al.,(1906).As per Temkin isotherm model, the adsorption surface has an equal distribution of binding energies over a number of exchange sites.[41,42]The equation representing Temkin isotherm is elaborated well by Temkin[41] et al.,(1940).The adsorption follows a pore filling mechanism in the semi empirical equation, the D-R isotherm model . The Dubinin-Redushkevich (D-R isotherm) isotherm is discussed well by Hutson[43] et al.,(1997) and Cayllahua[44] et al., (2010).The empirical equation proposed by Sips is otherwise called as the Langmuir-Freundlich isotherm and is explained well by Sips[45] et al., (1948).The Redlich-Peterson isotherm is a three parameter model applied to homogeneous as well as heterogeneous systems and is explained well by Redlich[46] et al.,(1959).It is learnt from the tabular column given below (Table 3) that the adsorption using agricultural biosorbents as adsorbent fitted well with the Langmuir isotherm in majority of the cases.

Table 3: Equilibrium models fitted for biosorption of various heavy metal ions using agricultural biosorbents with references.

METAL ION	EQUILIBRIUM MODEL	BIOSORBENT	REFERENCE
Cd(II)	Langmuir	Straw from Triticum aesticum	[47]Tan and Xiao (2009)
Cd(II)	Langmuir	Straw from Triticum aesticum	[48]Dang et al., (2009)
Pb(II)	Freundlich	Straw from Triticum aesticum	[49]Farooq et al., (2007)
Cu(II)	Langmuir	Straw from Triticum aesticum	[48]Dang et al., (2009)
Cr(III)	Freundlich	Straw from Triticum aesticum	[50]Chojnacka et al., (2006)
Cu(II)	Langmuir	Groundnut shell	[51]Kiran et al., (2012)
Pb(II)	Langmuir	Rice husk	[52]Vieira et al., (2012)
Cu(II)	Langmuir	Rice husk	[52]Vieira et al., (2012)
Al(III)	Langmuir	Typha domingensis leaf powder	[53]Abdel Ghani et al., (2009)
Fe(III)	Langmuir	Typha domingensis leaf powder	[53]Abdel Ghani et al., (2009)
Zn(II)	Langmuir	Typha domingensis leaf powder	[53]Abdel Ghani et al., (2009)
Pb(II)	Langmuir	Typha domingensis leaf powder	[53]Abdel Ghani et al., (2009)
Cd(II)	Langmuir	Bran from Triticum aestivum	[54]Singh et al., (2006)
Cd(II)	Langmuir	Bran from Triticum aestivum	[55]Nouri et al., (2007)
Cd(II)	Langmuir	Bran from Triticum aestivum	[56]Nouri and Hamdaoui (2007)
Pb(II)	Langmuir	Bran from Triticum aestivum	[57]Bulut and Baysal (2006)
Cr(VI)	Langmuir	Bran from Triticum aestivum	[58]Singh et al., (2009)
Cr(VI)	Langmuir	Bran from Triticum aestivum	[59]Wang et al., (2008)

Cu(II)	Langmuir	Bran from Triticum aestivum	[60]Wang et al., (2009)
Cu(II)	Langmuir	Bran from Triticum aestivum	[61]Ozer et al., (2004)
Zn(II)	Langmuir	Bran from Triticum aestivum	[62]Dupont et al., (2005)

CONCLUSION

In this review work of recently published research works, we have understood the importance of biosorbents and their effectiveness in heavy metal removal from waste treatment. The recent works using agriculture materials as biosorbents were discussed above. The operating parameter, kinetic models and isotherms were discussed. Langmuir isotherm fitted well for majority of the adsorption studies using agricultural biosorbents.It can be concluded that Agricultural materials as biosorbents show great scope for developing clear, cheap and highly effective process for heavy metal removal from waste water.

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